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PhD Programme in Chemical and Materials Sciences XXXVII cycle

Exploring innovative materials for carbon dioxide capture and valorization

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Torino, 2025

Table of Contents

Abstract	5
1. INTRODUCTION	6
1.1 Carbon dioxide emissions: risks and challenges	6
1.2 CO ₂ Capture Processes	10
1.2.1 CO ₂ capture and separation techniques	13
1.3 CO ₂ Utilization and Conversion processes	20
2. CONTENT OF THE THESIS	28
2.1 Materials for CO ₂ capture	28
2.2 Materials for CO ₂ conversion	31
3. MATERIALS AND METHODS.....	42
4. LTA ZEOLITE FOR CO ₂ CAPTURE: FROM POWDER TO 3D PRINTED MONOLITHS	51
4.1 Materials and Methods.....	52
4.2 From powder to beads LTA.....	55
4.3 Binderless 3D LTA monoliths	67
4.4 Concluding remarks and future perspectives.....	77
5. CO ₂ CAPTURE IN MOF: THE CASE OF F4 MIL-140A (Ce).....	82
5.1 Materials and methods	83
5.2 Unveil the mechanism of CO ₂ adsorption in F4 MIL-140A (Ce).....	85
5.3 Moving towards more realistic conditions: the effect of humidity.....	97
5.4 Moving towards more realistic conditions: the effect of shaping.....	105
5.5 Concluding remarks and future perspectives.....	110

6. LAYERED DOUBLE HYDROXIDES FOR CO ₂ CAPTURE AT MEDIUM-HIGH TEMPERATURE: FROM POWDER TO 3D MONOLITHS	118
6.1 Materials and methods.....	119
6.2 Evaluation of adsorption capacities of powder and 3D HTlc monolith.....	122
6.3 Concluding remarks and future perspectives.....	134
7. ELECTROCATALYSTS FOR CO ₂ REDUCTION REACTION.....	141
7.1 Materials and Methods.....	142
7.2 LDHs with different elemental composition: Zn-Al, Ni-Al, Ni-Fe LDH.....	143
7.3 Zn-Al LDH with different M ²⁺ /M ³⁺ molar ratio.....	152
7.4 The effect of Grinding.....	163
7.5 Toward operando conditions: Spectroelectrochemistry.....	168
8. DEHYDRATION OF ALCOHOLS INTO 1-ALKENES USING BIOMIMETIC CATALYST	178
8.1 Materials and methods.....	178
8.2 Catalytic tests and fundamental characterization.....	181
8.3 Advanced characterization.....	186
9. CONCLUSIONS.....	202
Appendix A, B.....	209

Abstract

This work aims to investigate and characterize different materials as potential candidates for Carbon Capture Storage and Utilisation (CCUS) processes, which are among the promising approaches currently being extensively investigated for the reduction of anthropogenic emissions.

Specifically, three different solid sorbents for CO₂ capture and various catalysts for the conversion of CO₂ into liquid jet fuels have been tested and/or fully characterised, in an attempt to study the different steps of the anthropogenic CO₂ cycle.

In the thesis section dedicated to the investigation of materials for CO₂ capture, a Zeolite, a MOF and a Hydrotalcite were selected, each offering distinct and unique properties as potential solid sorbents. For each class of adsorbents, a specific material (i.e. LTA, F4 MIL-140A(Ce) and Mg-Al 3:1 LDH) has been identified and thoroughly characterised in both powder and 3D monolith forms to highlight their possible potential strengths and weaknesses.

In the CO₂ utilization section, the work presented was performed as part of the European project “4AirCRAFT”. Among the various catalysts tested in the project, the attention was focused on the characterization of LDHs used as electrocatalysts in the CO₂ reduction reaction to CO and on the study of an acid-leached bentonite, FULCAT-22F, involved in the dehydration of 1-alkanols to produce 1-alkenes.

The thesis featured the use of various characterization techniques with a particular focus on IR spectroscopy. The results reported here are a combination of finalized, published data and new findings.

1. INTRODUCTION

1.1 Carbon dioxide emissions: risks and challenges

Since Svante Arrhenius published his pioneering work on the relationship between carbon dioxide concentrations and temperature rise in 1896, extensive research has focused on the causes, effects and solutions to global warming, which is one of the most debated challenges of XXI century.¹⁻⁴

It is widely recognized that the increase in anthropogenic emissions typically traced back to the onset of the Industrial Revolution, has significantly altered the composition of the atmospheric gases. The release of the so-called greenhouse gases (GHG) such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and fluorinated gases (F-gases) in the atmosphere has intensified the natural greenhouse effect. The sun radiation, which constantly strikes the Earth, is partially reflected by clouds or bright surfaces (e.g. ice), and mostly transmitted to the ground which is warmed up and the heat is then dissipated as Infra-Red (IR) radiation. This radiation is then re-absorbed (and re-emitted) by some gasses in the atmosphere, leading to naturally heating the mean surface temperature to about +15°C. However, when GHG concentration increases, a higher amount of IR is absorbed and consecutively the Earth's surface temperature further warms up.

A useful parameter to compare the effect of the different GHGs on the Earth's warming is the Global Warming Potential (GWP), first introduced by IPCC AR1 in 1990,⁵ which indicates how much infrared thermal radiation can be absorbed by the emission of 1 ton of gas over a given period of time, compared to 1 ton of CO₂.^{5,6} Such a parameter is calculated by integrating the radiative efficiency, which is the ability of a given gas to absorb energy, and the lifetime, which is the average time a molecule of gas spends in the atmosphere, over a selected time interval. This value is then compared to that of CO₂ which is considered as the reference gas with a GWP equal to 1.⁷ According to the GWP some GHGs seem to be potentially more pollutant than CO₂, as for example CH₄ and N₂O having a GWP of 84 and 264 in 20 years and of 28 and 265 in 100 years, respectively.⁸ However, even if the GWP of CO₂ is lower than that of many other gases, the longer lifetime of this molecule in the atmosphere and the huge level of emissions, which reached 36.8 Gt of CO₂ released worldwide in 2022, make it the main contributor to the greenhouse effect.^{9,10}

CO₂ is primarily generated as a result of using fossil fuels as an energy source to produce heat, fuel or electricity. Among the 36.8 Gt of CO₂, the 94% of the emissions comes from four sectors: power generation (14.65 Gt), industry (9.15 Gt), transportation (7.98 Gt), and building (2.97 Gt).¹⁰ Those anthropogenic emissions affects the natural carbon cycle, which regulates the amount of CO₂ through its transfer between the atmosphere, ocean and the land. For millions of years, these natural processes have maintained a constant balance of CO₂ in the atmosphere, but the increase of emissions has overwhelmed these mechanism, rendering them insufficient to maintain this balance. As a result, adopting mitigation strategies has become essential. A straightforward and mathematical way to visualise these processes is provided in Equation (1.1) and Figure 1.1:

$$\sum_{i=1,...,n} NEF + \sum_{i=1,...,n} AEF = \sum_{i=1,...,n} NMF + \sum_{i=1,...,n} AMF \quad (1.1)$$

Where NEF and NMF are the Natural Emission and Mitigation Factors and AEF and AMF are the Anthropogenic Emission and Mitigation Factors.¹¹

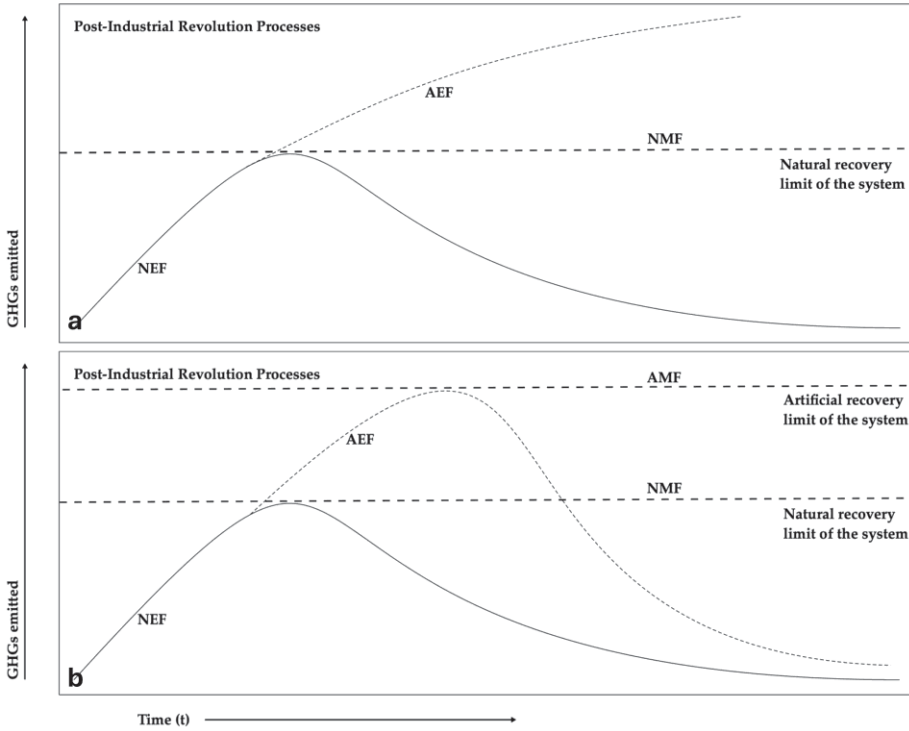


Figure 1.1. Representation of the NEF (Natural Emission Factor) and the AEF (Anthropogenic Emission Factor) balanced only by NMF (Natural Mitigation Factor) (a) or with the addition of AMF (Anthropogenic Mitigation Factor) (b). Adapted from reference 11.

Due to anthropogenic emissions (AEF) the natural regulation of the cycle is exceeded, leading to an alteration in our planet weather and climate system (Figure 1.1 a). Only through the application of some mitigation strategies (AMF) the natural safe limits can be reached (Figure 1.1 b). It is worth noting that such mitigation strategies are now expected to compensate not only for current emissions, but also for the whole period since the industrial revolution.

Different mitigation strategies have been investigated to counter CO₂ emissions with the final aim to meet the Paris requirements limiting the global temperature rise in this century within +2°C with respect to pre-industrial levels. Among them, much attention has been given to Industrial Carbon Removal (ICR) methods, in which CO₂ can be extracted directly from the air (Direct Air Capture, DAC), allowing for the removal of CO₂ already present in the atmosphere. Alternatively, CO₂ can be captured from some "point sources" as industries, where emissions are removed at their origin. Regardless of the origin of CO₂, Carbon Capture and Storage (CCS) and Carbon Capture Utilization and Storage (CCU/CCUS) technologies are expected to play a central role in reaching a decarbonized energy future. Although they are much debated, it is not always easy to make a clear distinction between the two technologies.¹² CCS technologies should be referred to processes in which CO₂ coming from air or separated from the flue gas of point sources, is permanently stored underground in some specific geological sites as saline aquifers or oceans. Additionally, CO₂ can then undergo a series of geochemical reactions with water, rocks and minerals (i.e. mineralization) which can sometimes even increase the storage capacity.^{13,14} On the other hand, the term "utilization", which started to be used around 2013¹⁵ to highlight the potential commercial values of CO₂, is related to the application of CO₂ as feedstock, for production of new chemical compounds and synthetic fuels. However, there are still some "borderline" cases in which a clear distinction is difficult to be made, such as Enhanced Oil Recovery (EOR) processes, in which captured CO₂ is pumped into geological formations to increase the amount of drilled oil. In this case CO₂ is injected underground not only for storing but with the final purpose to be used as a working fluid or solvent to enhance industrial production. A schematic representation of the above-mentioned strategies is represented in Figure 1.2.

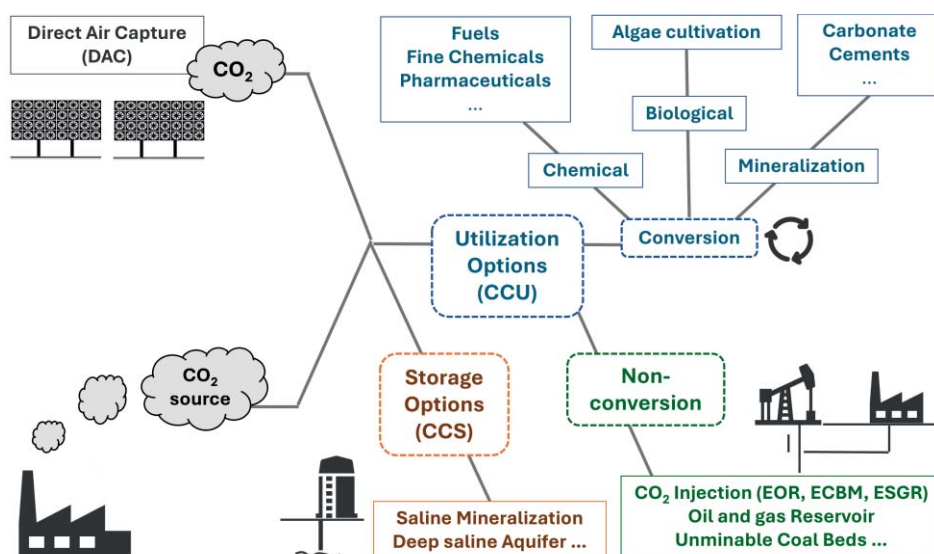


Figure 1.2. Schematic representation of the main CCS and CCU technologies. Adapted from reference 16.

The impact of CCS and/or CCU technologies on the achievement of net zero emissions may vary depending on the origin of the considered model. As a matter of fact, a variety of institutions ranging from intergovernmental, international, national, and private have provided models, data and strategic advice to meet the Paris requirements. The two most important organizations are the Intergovernmental Panel on Climate Change (IPCC) and the International Energy Agency (IEA) but some national (i.e. Dechema, Germany) or private bodies (i.e. Shell) cover similar topics. As a result, many factors can influence the vision presented in these roadmaps sometimes making it difficult to identify the most promising solution.³

Independently of the preferences between CCS and CCU, which vary significantly depending on the considered scenario, the two technologies together are expected to account for almost 15% of the cumulative emissions reduction compared to the 'Stated Policies' scenario, highlighting the importance of investigating these mitigation strategies.¹⁰

1.2 CO₂ Capture Processes

The first step to be investigated, regardless of whether CO₂ is eventually be permanently stored or reused as feedstock, is its capture. As power generation and industrial production are the primary sources of CO₂ emissions, the development of capture processes in these sectors has attracted significant attention.

The current technologies that have been developed for CO₂ capture are usually classified in three categories: oxyfuel combustion, pre-combustion and post-combustion. However, more recently a new division based on capture process with or without CO₂ separation have been proposed (see Figure 1.3 for a schematic representation).¹⁷

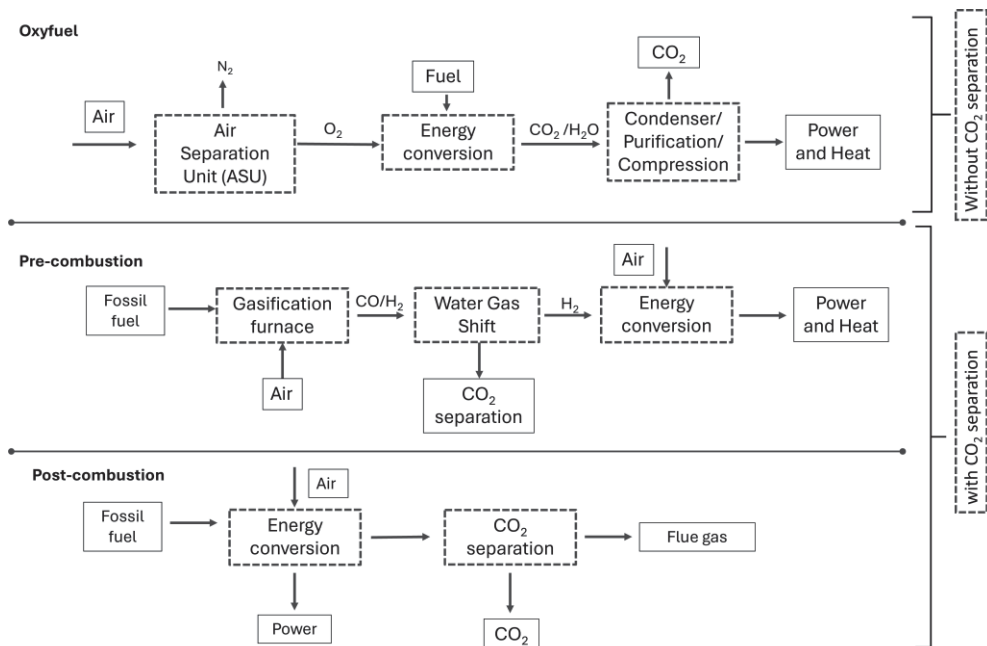
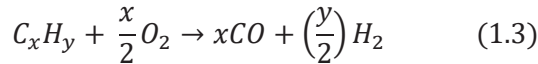
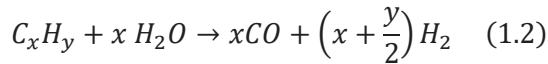


Figure 1.3. Schematic representation of oxyfuel, pre-combustion and post-combustion CO₂ capture processes. Adapted from references 18,19.

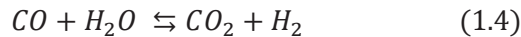
In **oxyfuel processes**, air first enters an air separation unit (ASU) where a cryogenic system is used to generate O₂ and remove N₂. Almost pure O₂ was then moved in the next chamber where fuel combustion takes place, obtaining high concentrations of CO₂ (75-80% vol) and H₂O. Water is then removed from the product by condensation and CO₂ is purified and compressed to supercritical conditions for

transport or reuse in the cycle. It is worth noting that, since CO₂ is obtained by condensing steam, no separation technologies need to be applied.¹⁷ The main advantage of this method is the low production of NO_x due to the absence of N₂ in the process. On the other hand, the production of O₂ in the ASU is energetically and economically demanding. However, oxyfuel combustion technology has been investigated in various demonstration projects and pilot plants around the world, and two plants, one in Spain and the other in South Korea, have currently a capture capacity exceeding 1000 MT day⁻¹.²⁰

In **pre-combustion** processes the CO₂ capture and separation is performed before the combustion of fuels. In a first step the fossil fuel (mainly coal) is gasified obtaining CO and H₂ (syngas) through steam reforming (equation 1.2) or partial oxidation reaction (equation 1.3).



The syngas is then transferred into a second unit in which Water Gas Shift reaction (WGSR) is carried out (equation 1.4) producing CO₂ and H₂.



Thanks to the high pressure (2-7 MPa) and concentration (15-60% by volume) of CO₂, it can be easily separated from H₂ by using a specific physisorbent. H₂ can be then used for both power generator or as feedstock.^{17,18,21} This technology is mainly used in Integrated Gasification Combined Cycle (IGCC) power plants and some of the most efficient already-existing implants are the one owned by the North West Redwater in Canada, having a capacity of 41100 MT day⁻¹, and the one of the Occidental Petroleum company in the USA (23000 MT day⁻¹).²⁰ The main advantage of pre-combustion is that it allows for easier CO₂ capture than other methods. However, the intensive energy demand of the gasification process and the cost of integrating it into an existing plant make this method not so feasible.

Post-combustion is the simplest process for CO₂ capture. In this case, the CO₂ is captured and separated from the flue gas after the combustion process. Compared to the other CO₂ capture methods, this technique is easier to adapt to existing implants, probably making it one of the most widely adopted. The two highest

performing plants are the China National Petroleum Company facility with a CO₂ capture capacity of 2750 MT day⁻¹ and the Korean Electric Power Corporation facility in South Korea with a capture capacity of 2740 MT day⁻¹, both based on amine-based chemical washing.²⁰ On the other hand, two major disadvantages of current CO₂ capture technologies are their high energy and cost demands, as well as the low concentration of CO₂ in the flue gas. The CO₂ content can vary a lot depending on the fossil fuel used but typically falls between 5-20% vol, with N₂ being the most abundant gas (75-76% vol).^{20,22} H₂O (8-10% vol) and O₂ (4-8%) are also present along with various types of contaminants such as SO_x, NO_x and fly ash, further complicating the separation process.¹⁸

Although each method has its own advantages and disadvantages (see table 1.1), post-combustion CO₂ capture is currently the most commercially developed option. It is the easiest method to integrate into existing infrastructure and a lot of research is underway to reduce the energy penalty associated with capturing CO₂ from point sources.²⁰ Ongoing advancements are expected to address the remaining challenges of these systems, leading to further advances in this technology and making a significant step forward in reducing CO₂ emissions.

Table 1.1. Main parameters, advantages and disadvantages of oxyfuel, pre-combustion and post-combustion processes. Adapted from reference 20.

	Oxyfuel	Pre-combustion	Post-combustion
CO₂ concentration (%vol)²⁰	75-80	15-40	5-20
Advantages^{17,18,20}	low production of NO _x , high CO ₂ purity	Efficient capture of CO ₂ , H ₂ production	Easy adaptability to existing implants
Disadvantages^{17,18,20}	energetically and economically demanding (ASU), difficult scale up	energy demanding (gasification process), difficult integration into an existing plant	Low CO ₂ concentration, energy demanding (compression),
Energy consumption (MJ kg⁻¹ of CO₂)²⁰	4.05	3.35	4.14
Cost (USD t⁻¹ of CO₂)²⁰	52	34-63	46-74

1.2.1 CO₂ capture and separation techniques

Research focused on CO₂ capture and separation technologies is a key step in increasing the efficiency of current processes, with particular attention, as previously mentioned, to post-combustion one. The main CO₂ capture and separation techniques are shown in figure 1.4 and briefly described below.

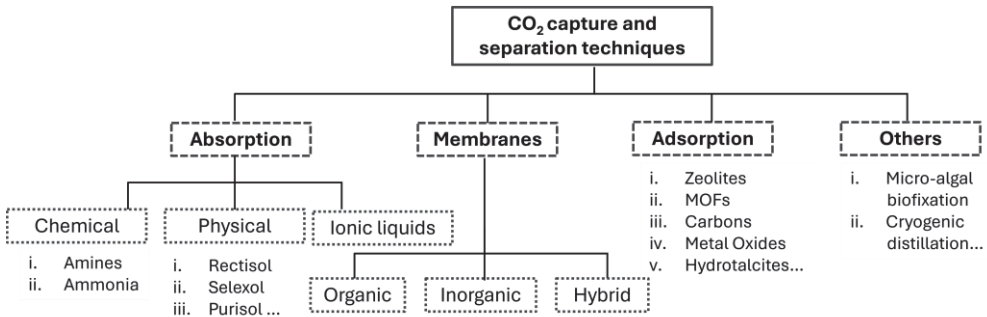


Figure 1.4. Schematic representation of the main CO₂ capture and separation techniques

Absorption is the most applied technique for CO₂ capture and separation. It is usually based on solvents or liquid absorbents capable of capturing and separating CO₂ from the flue gas in a first column (absorption section), which is then regenerated in a second section using various techniques, such as heating (Temperature Swing Adsorption (TSA)) or reducing pressure (Pressure Swing Adsorption (PSA)). Absorption processes are classically divided into chemical absorption and physical absorption. In addition, ionic liquids are also included as third class of absorption processes. Among the different classes, chemical absorption by aqueous amines solutions is the best known and most widely used method of CO₂ capture as well as the most employed in existing post-combustion plants. Three different classes of amines have been applied over the last 50 years: primary amines as monoethanolamine (MEA) (containing an -NH₂ group), secondary amines as diethanolamine (DEA) (containing and -NH) and tertiary amines as methyldiethanolamine (MDEA) (containing -N group). The first two kind of amines, MEA and DEA, are reacting with CO₂ through a zwitterion mechanism leading to the formation of carbamate species. Then, hydrogen carbonate is formed through hydrolysis. In the tertiary amine the carbamate cannot be formed leading to the formation of hydrogen carbonate through a base-catalysed hydration of CO₂. In the case of primary and secondary amines, where the carbamate has been formed, a fast absorption rate is ensured, but the strong C-N bond leads to high regeneration

energy. On the other hand, for tertiary amine a lower regeneration energy is required in face of a slower absorption rate. This balance between absorption rate and regeneration energy is the key challenge of this absorption process. Different solutions have been proposed to simultaneously address those two requirements such as blending primary/secondary amines with aqueous tertiary amines or with 2-amino-2-methyl-1-propanol (AMP).²³ Another possible strategy is provided by the use of ammonia based solutions. This process results to be more energy efficient compared to MEA scrubbing process reaching 60% less energy consumption.²⁴

While chemical absorption is based on an acid-base reaction between the solvent and CO₂, physical absorption processes are based on a simple dissolution of CO₂ into an organic solvent. Different commercial processes such as Rectisol, Selexol, Purisol and Fluor have been adopted using different solvent which physically absorb CO₂ together with other possible impurities (i.e. H₂S). However, even if the energy consumption is lower than for chemical absorption, the need to cool the flue gas temperature to improve CO₂ uptake is still an energy limiting factor. A promising class of absorbent materials are Ionic Liquids (ILs) which are made by an organic cation and a smaller inorganic anion. The potential combinations of anions and cations is giving rise to a vast range of structures that can be specifically tuned to increase CO₂ capture capacity, solubility, selectivity and other parameters.^{25,26} Even if they represent a promising sector, some further research should be performed in order to address their effective performance in large scale applications.²⁷

Despite absorption techniques are the most widely adopted CO₂ capture methods, different challenges should be addressed to make them more efficient. Some of the main drawbacks are the high energy demand of the regeneration of the amines solutions, equipment corruptions, high viscosity of ammonia-based solutions and low operational temperature of physical absorbents.²⁰

Membranes separation techniques are one promising process for CO₂ capture and separation for both pre and post combustion applications. The membranes are usually classified in organic, inorganic or hybrid depending on their composition. Organic membranes are mainly composed of polymers such as polyacetylene, polycarbonates, poly (ethylene oxide) and others. The principal separation mechanism in the membranes is the solution-diffusion process in which the gas molecules are adsorbed or absorbed in the voids of the matrix and diffuse through the channels between the polymer chains. The key challenge for this group of membranes is to find a compromise between selectivity and permeability, which in

general show an inverse relationship.²⁸ The selectivity issue become particularly relevant in case of separation between CO₂ and N₂ having very similar kinetic diameters (0.33 nm and 0.36 nm, respectively).²⁹ Additional problems could be generated from the swelling or plasticization generated by CO₂ adsorption.

The inorganic membranes which can be made of different materials such as zeolites, MOFs, carbons and others results to be more stable than the organic one especially under severe conditions.³⁰ The dominant separations method is the Knudsen diffusion. This mechanism, which occurs when the pore size and molecular diameters of the gas species are similar, is based on the different mean paths taken by gas molecules of different molecular weights when they collide with the pore walls.³¹ Other separation methods are surface diffusion based on the different surface diffusion coefficient of gasses, capillary condensation happening within the membranes pores and molecular sieving, where the separation is occurring only by differences in size.²⁰ Also in case of inorganic membranes selectivity and permeability still represent a challenge especially in presence of water vapour. To improve performance, recent research has also focused on hybrid membranes that can take advantage of both classes.³²

Adsorption of CO₂ by means of solid adsorbents is probably the most discussed and investigated technique in the recent years. Adsorption is a surface phenomenon regarding the interaction of gas molecules (adsorbate) with the surface of a solid material (adsorbent). Adsorption occurs *via* physisorption, which involves the formation of weak bonds (van der Waal forces) with a low isosteric heat of adsorption (Q_{st} ; a measurement of the heat released when an adsorptive binds to a surface) ($Q_{st} < 40 \text{ kJ/mol}$), or chemisorption, which involves the formation of stronger interactions ($Q_{st} > 40 \text{ kJ/mol}$).³³ The separation of the different gasses can happen through molecular sieving, quantum sieving, kinetic or equilibrium effect which relies on the different affinities of the gasses for the adsorbent surface. After CO₂ has been adsorbed, three main techniques are typically employed for the regeneration: PSA, TSA and Vacuum Swing Adsorption (VSA). As previously described for absorption the first two relies on a decrease of pressure and increase of temperature while in VSA the desorption is performed through the application of vacuum. Numerous adsorbent materials were studied for CO₂ capture and the most employed ones are briefly reported hereafter:

- **Zeolites** are crystalline aluminosilicate microporous materials. They are made by silicium or aluminium tetrahedral units connected through oxygen

atoms; the presence of the aluminium atoms gives an overall negative charge that needs to be balanced by the presence of extra-framework cations. The tetrahedral units can be linked together forming different structures giving rise to more than 230 different topologies. The CO₂ capture capacity is higher than other adsorbents such as carbons but, on the other hand, they have reduced adsorption efficiency in the presence of moisture and impurities (NO_x, SO_x).³⁴

- **Metal Organic Frameworks (MOFs)** are crystalline porous materials made by a metal ions or metal cluster connected to organic linkers through specific functional groups. By simply changing some synthesis parameters such as the ligands and the metal cluster the structure can be easily tuned to achieve specific characteristics. The tunability of the structure is the main strength of this class of materials while the cost and the stability under humid conditions are some of the main challenges that should be addressed.
- **Carbon based materials.** Being carbon one of the most earth abundant elements, it is the basis of a wide and cost-effective class of materials which includes activated carbons (ACs) and various carbon nanomaterials like carbon nanotubes (CNTs), fullerenes, graphene, nanofilms and others.³⁵ The main advantage of carbon-based materials is the ease of regeneration and the low cost, while the main disadvantage is the rather low CO₂ capture capacity compared to other adsorbents. A possible strategy to increase this is to modify the material with specific chemical groups able to enhance both capture and separation performances.³⁵
- **Metal Oxides** such as magnesium oxide (MgO), calcium oxide (CaO) and lithium oxides (Li₂ZrO₃ or Li₄SiO₄) have been studied for CO₂ captured and employed mainly in chemical looping processes. They are particularly suitable for CO₂ capture at high temperature (above 300°C) forming various carbonates species. On the other hand, the regeneration, taking place at high temperature (800°C-850°C), is particularly energy demanding.¹⁹
- **Hydrotalcites** also known as **Layered Double Hydroxides (LDH)** are anionic clays characterized by positive charged metal hydroxide layers balanced by anions and water molecules in the interstitial layer. Their structure is a modified Brucite structure in which a portion of M²⁺ ions in the octahedra have been replaced by M³⁺ generating the overall positive charge. They have some interesting properties such as swelling and memory effect. This last effect is the ability to fully recover, on contact with water, the structure

transformed during calcination into mixed oxides (Layered Double Oxide, LDO). These interesting properties together with the ability to capture CO₂ at high temperatures makes them particularly interesting for various applications. On the other hand, the adsorption is usually not completely reversible and the amount adsorbed is lower compared to other materials.

It is worth noting that these adsorbent materials are usually synthesised in powder form, whereas for industrial applications they need to be packed into a column. This has led to significant interest in developing composites or shaped adsorbent materials that can enhance adsorption kinetics, reduce attrition, minimize pressure drops and improve heat transfer compared to powdered materials. An example is represented by hollow-fiber composite in which some adsorbents such as zeolites are embedded into polymeric or cellulose matrices.³⁶ Another approach includes techniques as extrusion, additive manufacturing and 3D printed techniques. Notably, 3D Printing allows the creation of structures with precise control over wall thickness, cell density, and channel dimensions.³⁷ The modern 3D printing strategies require the presence of some specific components in addition to the adsorbent materials, such as additives and binders in order to achieve both a certain viscosity in the ink mixture and good mechanical properties of the printed monolith. The main challenge of this technique is to maintain the capture capacity, since the additional components can, in some cases, prevent access to specific adsorption sites of the active phase.

As it can be expected, with solid adsorbents it is difficult to generalise about advantages and disadvantages, as they are strictly dependent on the material analysed. However, the question may be: which characteristics should an ideal adsorbent have? There are at least nine specific properties that should be addressed:

- **CO₂ adsorption capacity:** it is defined as the ability to adsorb CO₂ under thermodynamic equilibrium.²⁰ However, for more practical applications, it is preferable to evaluate it in terms of working capacity, i.e. the amount of CO₂ that can be captured during a full adsorption/desorption cycle.³⁸ An ideal adsorbent should have a high CO₂ adsorption and working capacity (ideally higher than 2 mmol/g), possibly over a wide temperature range, since the flue gases from post-combustion are rarely at room temperature.³³

- **CO₂ selectivity:** an ideal adsorbent should preferentially adsorb CO₂ over other flue gases or vapours.
- **Fast kinetics:** the rate of CO₂ adsorption should be fast, since it can affect the overall cycle time and economics of the process. Ideally 80% of the total capacity should be reached in the first 2 minutes.³³
- **Easy regeneration:** after CO₂ adsorption, the material should be regenerated under mild conditions. The isosteric heat of adsorption (Q_{st}) should range between 35 kJ/mol and 50 kJ/mol.³³ Values below this range risk forming weak bonds, while, above, the energy needed for recyclability could be too high.
- **Stability over cyclability:** in order to be cost-effective, the material should maintain the same CO₂ capture capacity for multiple adsorption desorption cycles (more than 1000).³³
- **Mechanical and thermal stability:** the material should maintain constant mechanical and physico-chemical properties for all the adsorption cycles.
- **Low costs:** a crucial parameter for the feasibility of using a material as adsorbent is the cost. The target cost should be around 5-10\$/kg.³³
- **Tolerance to moisture and other impurities:** as previously mentioned, in post combustion process, 8-10 % vol of water is present together with some NO_x and/or SO_x contaminants. Ideally, CO₂ capture capacity should remain constant and unaffected by these impurities.
- **Possibility of shaping:** as previously explained especially for large scale applications, the use of shaped adsorbents instead of powdered ones is required. For this reason, an important parameter to consider is the possibility to shape the adsorbent material without losing all the previously mentioned properties, especially mechanical stability and capture capacity.

Even considering these properties, correctly classifying different adsorbents is challenging, as performance can vary significantly within the same class of materials. However, for some specific properties, such as CO₂ capture capacity, regenerability, thermal stability, cost and moisture tolerance, general trends have been observed, although exceptions that deviate from the average are possible (see Figure 1.5).³⁴

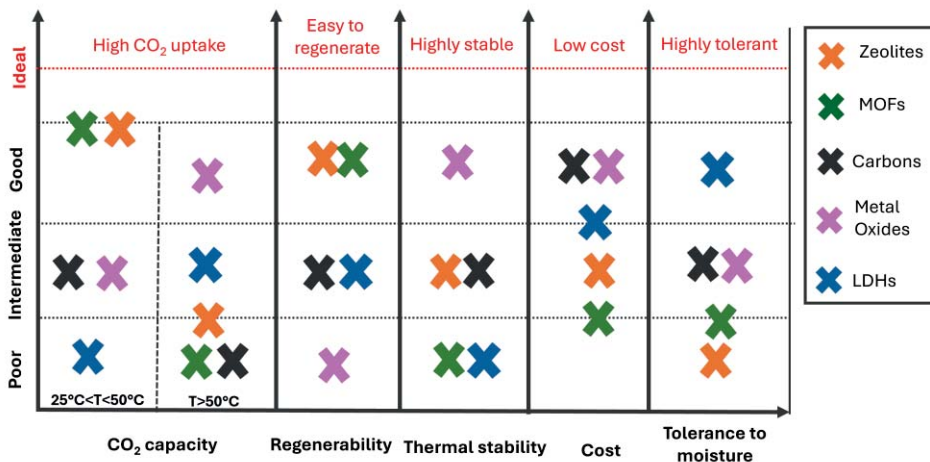


Figure 1.5. Schematic classification of some solid adsorbent (Zeolites, MOFs, Carbons, Metal Oxides and LDHs) according to CO₂ capacity, regenerability, thermal stability, cost and tolerance to moisture. The performance of the different materials is qualitatively classified as "poor", "intermediate", "good" and ideal (red dotted line). Adapted from references 34,39.

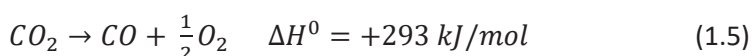
Rather than looking at the individual performance of each category, the overall behaviour should be considered: none of the adsorbents maintains good performances in all the properties analysed. Therefore, as expected, an ideal adsorbent, capable of excelling under all conditions, does not still exist. Researchers are actively studying and designing different adsorbents to improve their weaknesses as much as possible.

In this regard, three different adsorbent materials, each with unique strengths and weaknesses were chosen and characterized for CO₂ capture applications in the present thesis. A detail discussion is presented in Chapter 2.

1.3 CO₂ Utilization and Conversion processes

After the capture and separation of CO₂, different strategies could be applied for its utilization and conversion into valuable products. As previously discussed, some of them involved the direct utilization of CO₂ for a permanent storage or to recovery/enhance a specific industrial production (i.e. EOR and others). Among the various possible strategies to reach net zero carbon emission, one additional possibility is to transform the capture CO₂ into some new products such as fuels and chemicals. It is worth noting that this strategy does not aim to remove CO₂ directly from the air or from specific point sources, but rather to create a kind of parallel anthropogenic carbon cycle, in which CO₂ is converted into chemicals or fuels, which in turn are responsible for CO₂ emissions that are the starting point for a new cycle. This approach offers an interesting solution considering also: (i) the impossibility of achieving net-zero emissions using only direct CO₂ utilisation methods and (ii) the possibility of using renewable energy sources for CO₂ conversion, that are otherwise challenging to store.⁴⁰

The main challenge of CO₂ conversions into fuels and chemicals is the high thermodynamic stability of CO₂ molecule. As a matter of fact, the Gibbs free energy of formation (ΔG^0) for CO₂ is -394 kJ/mol, as both the enthalpic (ΔH^0) and the entropic (ΔS^0) variations are disadvantageous.⁴¹ This high stability of the molecule implies the necessity of substantial energy for the occurrence of chemical reactions as suggested by the CO₂ dissociation:



The high energy needed to run this reaction well explains why usually some additional co-reactants are introduced in the reaction: the addition of another substance with higher (i.e. less negative) Gibbs free energy, can reduce the enthalpies of reaction as shown for H₂.^{41,42}



Additionally, the use of solvents such as water also decreased the overall Gibbs free energy of the reaction as reported for the transformation of CO₂ into formic acid (CH₂O₂) which passes from $\Delta G^0_{298K} = 32.9$ kJ/mol in gaseous phase to $\Delta G^0_{298K} = -4$ kJ/mol with the addition of water.⁴²

However, even in the presence of those co-reactants most reactions still need a substantial quantity of energy and often require a catalyst to overcome the high activation barrier.

The additional energy required to carry out the reaction can finally be provided according to different approaches, starting from the more conventional thermal one to some more "novel" methodologies such as biochemical, photochemical, electrochemical ones and more. The main methodologies for CO₂ conversion are shown in figure 1.6 and briefly described below.

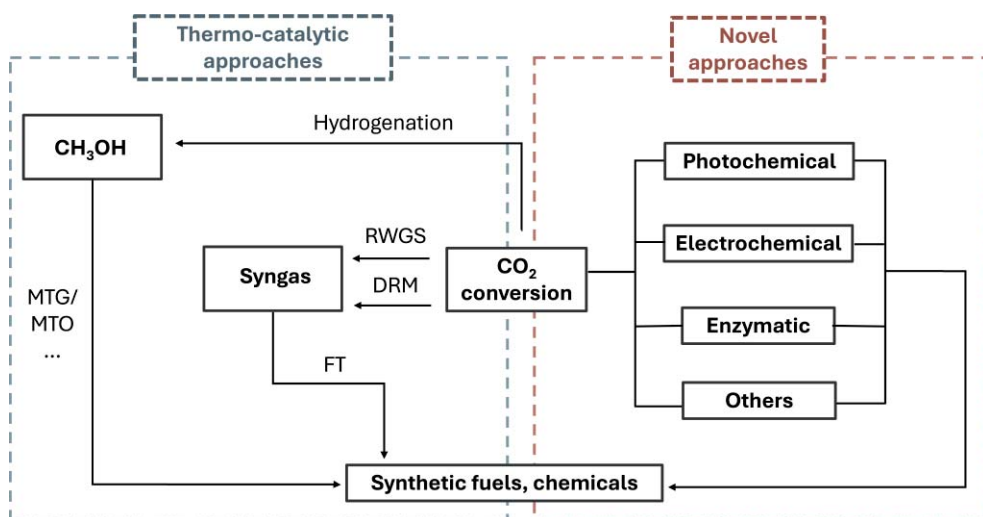


Figure 1.6. Schematic representation of the main CO₂ conversion approaches.

Thermo-catalytic approaches

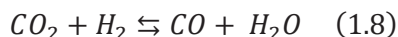
The most conventional thermal approaches to produce fuels and chemicals involve the formation of syngas (CO/H₂ mixture) and/or methanol.

The syngas, which is the primary feedstock for chemicals and fuels production, is mostly industrially produced by means of the steam reforming of methane (SMR) which has been employed for several decades also for hydrogen production.⁴³ In this process methane (CH₄) is reacting with water (H₂O) into a high endothermic reaction ($\Delta H_R = +251 \text{ MJ/kmol}_{\text{CH}_4}$) (eq. 1.7).⁴⁴ The produced CO can further react with H₂O through a water gas shift reaction (WGS) to produce CO₂ and H₂ (equation 1.4 previously reported in pre-combustion capture section).



However, the high temperatures (700-1000°C) and pressures (15-50 bar) involved in the process, as well as the use of CH₄ as the main source, have led to the search for alternative reactions.⁴⁴

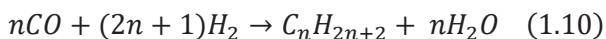
Two possible alternative ways for the syngas production are the Reverse Water Gas Shift (RWGS) and the Dry Reforming of Methane (DRM). In both reactions CO₂ is used as reactant, in the first case with H₂ (equation 1.8), in the second one with CH₄ (equation 1.9).



The RWGS reaction is favoured at high temperatures (550-750°C) due to its moderately endothermic character ($\Delta H^0 = +42$ kJ/mol), moderately low pressures (0-5 bar), high H₂ : CO ratios and low contact times.⁴⁵ The main side reactions are CO₂ methanation reactions or Sabatier reaction (CO₂+4H₂ → CH₄+2H₂O) and CO methanation reaction (CO+3H₂ → CH₄+H₂O). In order to run the reaction at milder temperature conditions, while maintaining high selectivity for the product and avoiding side reactions, different heterogeneous catalysts as well as changes in the concentration of different gases can be employed.⁴⁵ In this case, the catalysts require good CO₂ adsorption capacity and weak CO adsorption ability at the same time, to avoid further reactions. Those requirements are usually provided by systems based on noble and transition metals (i.e. Pt, Pd, Ru, Au) which could be dispersed onto some oxides surfaces (i.e. Al₂O₃). However, more recently some alternative catalysts based on more abundant and less expensive elements such as Cu, Fe, Ni and other have been studied.⁴⁵

The DRM reaction is another promising alternative to SMR, also considering the utilisation of CH₄, another greenhouse gas, in addition to CO₂. However, the high endothermicity ($\Delta H^0 = 247$ kJ/mol) of the reaction which implies the need of high temperatures (700–1000°C) and the possible coke formation, which leads to a deactivation of the catalyst, are the main two drawbacks. The most employed catalysts are usually Nickel and Ni/SiO₂, Ni/Al₂O₃ as well as Rhodium, or Iridium.⁴⁶

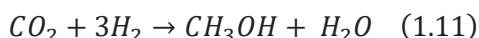
Once the syngas has been produced, it is usually converted into liquid hydrocarbons through the well-known Fischer-Tropsch (FT) process. The FT chemistry involves a series of complex reactions, which are usually reported as follows:



The process typically is carried out in the presence of catalyst at a pressure around 20–40 bar and at two different temperature range: 200–240 °C for the low Temperature FT (LTFT), or 300–350 °C in case of High Temperature FT (HTFT).⁴⁷ The catalyst involved in this reaction and its features are particularly important, not only for its development, but also to increase the final chain growth length of hydrocarbons which is otherwise limited according to Anderson-Schultz Flory distribution. The catalysts, in this case, are composed by different active metals (the most used are Co, Fe, Ni or Ru) supported on high-surface area materials (usually silica, alumina, titania or zeolites). The active metals adsorb the CO by forming metals carbides on catalyst surface, enabling the hydrogenation process. Among the possible metals, Ru is the most active one, but it is also the most expensive. The use of Ni is usually avoided due to the tendency to promote hydrogenation leading to methanol formation (methanation process). Fe and Co are eventually the most used one. The properties of the metal supported materials are also fundamental for the final products of the reaction. Support textural features, metal and support interaction strength and diffusion properties are some of the parameters that can play an important role in the final fuel produced.⁴⁸

Another possible route for the conversion of CO₂ into fuels and chemicals consists in the transformation of CO₂ in methanol (CH₃OH) and subsequently into liquid hydrocarbons.

The CO₂ is firstly hydrogenated to form CH₃OH following the reaction:



The produced methanol which could also be generated from syngas (CO + 2H₂ → CH₃OH) is then converted to an equilibrium mixture of methanol, dimethyl ether and water, which can be processed catalytically to either gasoline (methanol-to-gasoline, MTG) or olefins (methanol-to-olefin, MTO), depending on the catalyst and/or the process operation conditions.⁴⁹ In the first step of the reaction involving CO₂ hydrogenation to CH₃OH, a mixed metal/metal oxide heterogeneous catalyst is usually applied. The Cu/ZnO/Al₂O₃ (or CZA) based catalyst is the most used thanks to the synergical effect of adsorption of CO₂ on Cu and H₂ homogenous cleavage onto ZnO.⁵⁰

For these more conventional approaches, much research is now focused on the study and modification of different catalysts to reduce the thermal conditions required for the reactions and/or to increase selectivity towards specific processes,

which still remains the main challenges of those approaches. Intensive research is also being carried out to develop some advanced catalysts for converting CO₂ directly into hydrocarbons.⁴²

Photocatalytic CO₂ reduction

One emerging area for CO₂ conversion is represented by photocatalysis thanks to several advantages such as low costs, low temperature, low pressures and energy needed for the process.

The photocatalytic reduction of CO₂ is happening through several reaction steps and each of them has its own product and standard reduction potential. As a matter of fact, similarly to what previously explained for the direct thermal dissociation of CO₂, the reduction of CO₂ to CO^{•-} through a single-electron process is too energetically demanding (-1.9 V, vs NHE).⁵¹ To decrease the reduction potential needed, some multi-electron step reactions should be performed. For obtaining a specific CO₂ reduction product, a photocatalyst must have a sufficient reduction potential that is more negative than the potential required for that specific photocatalytic reaction.⁵²

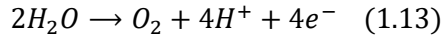
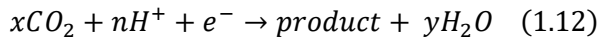
The main steps involved in a photocatalytic process can be divided into three main steps: (i) photoexcitation, (ii) charge separation, and (iii) charge transfer with the corresponding oxidation/reduction reactions.⁵¹ In the first step, a photon is absorbed generating an hole vacancy in the valence band due the excitation of an electron in the conduction band. In the second step, the electron-hole pares, whose recombination should be avoided, diffuse to the surface where they participate in the third step in oxidation and reduction reactions.

Different types of photocatalysts have been tested for photocatalytic conversion of CO₂ such as metal oxides (TiO₂, Cu₂O, Fe₂O₃), LDH (NiAl-LDH, MgAl-LDH etc.), non-metal semiconductors (SiC, graphene oxide etc.). Researchers are trying to increase the still low photocatalytic activity and selectivity of products focusing on improvement of band-gap, defect control, development of catalyst, surface sensitization and other parameters.⁵³

Electrochemical CO₂ reduction

Another promising alternative for CO₂ conversion is provided by the electrochemical route, due to some interesting properties such as low temperatures and pressures, use of water as a source of protons, great product selectivity and grate operational flexibility. However, there are still some limitations such as low CO₂ solubility, mass transfer limitations, low catalyst stability, and technology commercialization.⁵⁴

Usually, in the CO₂ Reduction Reaction (CO₂RR), CO₂ is reduced to different products at the cathode side, while H₂O is oxidized at the anode side, through the Oxygen Evolution Reaction (OER):



Different compounds can be obtained through the CO₂RR, depending on the number of electrons and protons transferred per molecule of CO₂, starting from carbon monoxide (CO) and formic acid (HCOOH) obtained for 2 electrons exchanged, up to propanol (C₃H₇OH) in case of 18 electrons.⁵⁴ The main parameters used to describe the electrochemical performance of a reactions are the current density, the Faradaic Efficiency (FE), the Energetic Efficiency (EE), and stability. The current density is the ratio between the current and the electrode area. On the other hand, FE is defined as the ratio between the charge used for the production of a given product and the total charge passed, while EF is the ratio between the energy stored in the desired product and the total energy input needed to synthesize it. Lastly the stability describes the variation of current density, FE and EE with time.⁵⁴ All those parameters can be influenced by different factors such as the materials of the electrode and catalysts, pressure and concentration of CO₂, pH, electrolyte solution and the design of the electrochemical cell. In this regard, the easiest cell and the most used for lab-scales applications is the H-type cell which is composed by two compartments, the anode and cathode, connected by an ion-exchange membrane. The Reference Electrode (RE) and Working Electrode (WE) are inserted in the cathode, while the Counter Electrode (CE) is placed at the anode. CO₂ is bubbled in the cathodic compartment through a capillary tube while, a gas chromatographer (GC) measures gas phase compositions at the outlet. Despite the large utilization there are some disadvantages of this reactor type such as: mass transport limitations, poor mixing, high cell electrical resistance, low CO₂ conversion and current density. These limitations can be overcome by flow cells reactors which

can be further divided into: basic flow, polymer electrolyte membrane (PEM), micro-fluid and solid oxide (SOE) electrolyser. The basic flow cell is characterized by the presence of three different compartments: one for the CO₂ gas flow, one for the catholyte and the other one for the anolyte which are separated by an ion-exchange membrane and filled with a liquid electrolyte. In PEM and SOE both the electrodes and electrolytes are in the solid phase and the cathodic and anodic compartments are separated by an ion-exchange membrane which can be polymeric (PEM) or made by a layer of solid oxides (SOE). Lastly, in case of micro-fluid reactors two (solid) electrodes are separated by a thin layer (< 1 mm) of a liquid electrolyte.⁵⁴ In general, these cells offer lower mass transport limitations, higher FE and easy scalability and industrial applicability, but require a significant cell design. For what concerns the catalysts, they strongly depend on the final product required. The most employed catalysts for CO₂RR to CO are noble metals such as gold (Au) and silver (Ag). Among the non-noble metals Cu and Zn have been tested also for other products such as ethylene, methane and alcohols.⁵⁴ Additionally also metal oxides, MOFs and LDHs have been recently tested as electrocatalysts.⁵⁴

Enzymatic conversion of CO₂

Lastly, a possible fascinating method for CO₂ conversion is through the utilization of enzymes which are naturally able to convert CO₂ into organic materials under specific conditions. In particular, CO₂ is converted in cells through six main pathways in which three particular enzymes (lyases, oxidoreductases, and synthases) are contributing significantly. One possible idea is to use those enzymes to catalyzed CO₂ reactions in vitro. To preserve the enzymes under reaction conditions, much research has focused on the possibility of supporting it on porous scaffolds that can protect the enzyme and act as catalytic sites themselves.⁵³

Finally, although it is difficult to compare the different CO₂ conversion processes, the main advantages and disadvantages are listed in Table 1.2. A common point in the development of all the techniques is the study of the catalyst and its characterisation, with particular emphasis on understanding the reaction mechanism, which helps to increase the efficiency and selectivity of the final products. In this regard, in the present thesis different catalysts employed in the European project 4AirCRAFT were deeply characterized using various techniques. Further details are reported in the following chapter.

Table 1.2. Main advantages, disadvantages and catalysts involved in thermos-catalytic, photochemical, electrochemical and enzymatic approaches for CO₂ conversion and utilization. Adapted from reference 55

	Advantages	Disadvantages	Most used catalysts
Thermo-catalytic	- High yield of production - Well established technologies	- Usually, high Temperature and/or Pressures required - Need to increase selectivity	Dependent on the process. Most used noble and transition metals (Pt, Pd, Ru, Au) dispersed onto oxides, zeolites...
Photochemical	- No additional energy required - Environmentally friendly	- Usually, low yield of production	metal oxides, LDH, non-metal semiconductors
Electrochemical	- Possible scale up	- Electric energy required - Need to increase catalysts stability	noble metals (Au, Ag...) non-noble metals (Cu, Zn...) Metal oxides, LDH, MOFs
Enzymatic	- No additional energy required - Environmentally friendly	- Still low stability of the enzyme	Supported enzymes (lyases, oxidoreductases, synthases...)

2. CONTENT OF THE THESIS

As the investigation of CO₂ capture, storage and utilization is a major research area and means of meeting Paris Agreement targets, some of the previously mentioned approaches will be discussed in the present thesis. In particular, three adsorbent materials for capturing CO₂ and various catalysts for converting CO₂ into liquid jet fuels were tested and deeply characterised, in an attempt to cover the overall anthropogenic CO₂ cycle.

For the sake of simplicity, the thesis is divided into two main parts that are closely interconnected: “Materials for CO₂ capture” and “Materials for CO₂ conversion”.

2.1 Materials for CO₂ capture

The CO₂ capture chapters will be focused on three materials: Zeolites, MOFs and LDHs. The study of these materials is not related to a specific project, but results from the collaboration of our group with the University of Pisa, the Advanced Ceramics and Glasses Group of the University of Padova, and the Politecnico of Torino. The first two partners were involved in the synthesis of the F4_MIL-140A(Ce) MOF and the various monoliths, respectively, the Politecnico of Torino helped to perform the dynamic breakthrough curves of the LTA beads, while my work was dedicated to the in-depth characterisation of the different materials.

As discussed in Chapter 1, solid adsorbents are a promising solution for CO₂ capture and separation, with properties that can vary considerably. Since no single adsorbent can effectively combine all the desired properties, these three materials have been selected because each of them offers unique features, while also having specific drawbacks.

Starting from Zeolites, they are well-known for their relatively high CO₂ uptake, as for example zeolite 13X. This material is usually considered as a reference for CO₂ capture in the zeolites world, exhibiting a CO₂ capture capacity of around 4.7 mmol/g at 298 K.⁵⁶ Additionally, zeolites are widely used commercial materials available on the market in different structures and shapes (e. g. powder, beads) with different price ranges, making some even economically viable. Also, their

regenerability, cyclability and thermal stability are suitable for industrial applications, as the adsorption process is completely reversible upon outgassing and the structures are usually stable at medium to high temperatures ($T \geq 400$). On the other hand, zeolites show a rapid decrease in CO_2 uptake as the temperature increases and they are particularly sensible to moisture and impurities. As a matter of fact, one of the commercial applications of zeolites is as industrial desiccants. Additionally, their selectivity is strictly dependent on their pores size and microporous structure.

For what concerns MOFs, probably their main quality is the tunability of their structure which can be employed in order to reach high selectivity and high working capacity in CO_2 adsorption. In this regard, a particular class of MOFs is attracting increasing attention due to the presence of a steep gas uptake when a threshold partial pressure of a given adsorbate is reached. This behaviour is ensuring the recovery of a large quantities of adsorbed gas by moving in the step between the adsorption and desorption pressures.⁵⁷ These materials are the so called “phase-change” or flexible MOFs. They have been classified in “breathing” and “swelling” frameworks characterized by a change in the unit cell volume and “subnetwork displacement” and “linker rotation” in which no change in the unit cell volume is observed.^{58,59} Usually, the framework flexibility is triggered by the interaction of the material with an adsorbate gas molecule, but it can also be caused by the temperature, the mechanical stress and the electromagnetic interactions.⁵⁹ While the tolerance to moisture can be tuned by inserting some specific functionalities, such as fluorinated groups in the structure of the MOFs, the main drawbacks still present in most of MOFs lie in the low thermal stability and in the difficulty in scaling up their synthesis, maintaining constant performances. This also affects their economic feasibility compared to other adsorbent materials.

Finally, in contrast to the first two classes of materials, LDHs generally show good adsorption performance in the presence of contaminants (i.e. H_2S) and water, with adsorption even being enhanced. In addition, while the other adsorbents tend to have modest adsorption capacities at medium to high temperatures, requiring gas pre-cooling and drying, LDHs are generally able to capture CO_2 at high temperatures. Selectivity, cyclability and mechanical stability results to be adequate for applications while the regeneration of the material, which is highly dependent on their chemical composition and synthesis, is usually completed when the sample is reheated at the pre-treatment temperature. The kinetics of adsorption usually displays a rapid initial CO_2 uptake, followed by a slow/intermediate adsorption in

the second stage. Lastly, the CO₂ uptake of Hydrotalcites, which is enhanced when the material is heated and transformed in a Layered Double Hydroxide (LDH), i.e. a mixed metal oxide, is still low in comparison with other solid sorbents, even at higher temperature, which is probably the main challenge for their practical applications.⁶⁰

Taking these different characteristics into account, a selection of materials for each class have been investigated and characterised in powder and in shaped form. In particular:

In **Chapter 4** Linde Type A zeolite (LTA) was deeply investigated and characterized to assess its potential application as solid adsorbents for CO₂ capture. An initial rapid screening of the capture capacity was carried out on the LTA in powder form, also evaluating the effect on the capture performances by changing the extra-framework cations of the zeolite following an ion exchange procedure. After that, the two most promising samples in form of commercial beads were deeply characterized and tested in both static and dynamic conditions. Lastly, in collaboration with the University of Padova, a binderless LTA monoliths with different geometries were synthesised by Direct Ink Writing. These new adsorbents were characterised and tested comparing their performances with the one shown by the commercial LTA beads.

In **Chapter 5** a flexible perfluorinated MOF, based on Ce^{IV} and tetrafluoroterephthalate (F4_MIL-140A(Ce)), showing a peculiar S-shaped CO₂ isotherm, was deeply characterized to understand the origin of its unusual adsorption behaviour and unveil the mechanism of CO₂ interaction. The CO₂ adsorption mechanism in the presence of H₂O was also investigated. Then, a first attempt of shaping was also performed, yielding promising results. These studies were carried out in close collaboration with the University of Pisa and the University of Padova.

In **Chapter 6** a Mg/Al Hydrotalcite (Mg Al LDH) was tested for CO₂ adsorption at high temperature (300°C), both as a powder and as a 3D monolith. The effect of the memory effect, i.e. the ability to completely recover the LDH structure, and consequently the CO₂ adsorption capacity, by rehydrating the material was also investigated. Also in this case the 3D monolith of LDH was synthesized by the University of Padova.

In the conclusions, the different materials were compared based on the key characteristics an ideal adsorbent should possess. The advantages and disadvantages of each material were highlighted, along with potential improvements that could enhance their effectiveness and broaden their applicability for CO₂ capture.

2.2 Materials for CO₂ conversion

The possible use of captured CO₂ for conversion into fuels was investigated following the approach proposed by the European project “Catalysts for Air Carbon Recycling in Aviation Fuel Technology - 4AirCRAFT” (Grant, Agreement Number JPMJSC2102) which founded my PhD. The four-year project, financed by the EU in the framework of H2020 under the Alternative Fuels and Mobile Energy Sources programme, started in May 2021 and involves three Spanish research centres (Aragon Hydrogen Foundation, BC Materials and Consejo Superior de Investigaciones Científicas (CSIC)), the University of Bielefeld, the University of Helsinki, the University of Antwerp, the University of Turin, as well as two international partners: Hokkaido University and the University of São Paulo. The main goal of 4AirCRAFT is the direct conversion of captured CO₂ into C₈-C₁₆ liquid jet fuels under low temperature and pressure conditions. To achieve this goal, the project aims to develop a single cascade reactor with a three-step reaction driven by the synergic combination of different catalysts, using some of the approaches previously introduced in Chapter 1. The three steps reactions include: (i) a first reduction of CO₂ into CO ($\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$) followed by (ii) hydrogenation of the produced CO to short chain hydrocarbons and (iii) a final transformation into C₈-C₁₆ products thanks to an oligomerization process.⁶¹ The first step was carried out by an electrocatalytic CO₂ reduction reaction (CO₂RR), while, for the second step, two possible different strategies were studied simultaneously. The first one involves a Fischer-Tropsch type reactions coupling metal/metal oxide systems to hierarchically structured highly acidic catalyst supports, while the second one involves the dehydration of 1-alkanols to 1-hexene through the application of Bio/Biomimetic catalysts. The final production of C₈-C₁₆ was finally achieved through some oligomerization reactions performed thanks to the application of some hierarchical acid catalysts. Among the different steps and catalysts involved in the project, we focused the attention especially on the electrochemical reduction of CO₂ to CO (step 1) and on the dehydration of primary alcohols (step 2 - strategy II). Figure 2.1 shows

a schematic of the different stages of the project, highlighting the one in which I was mainly involved.

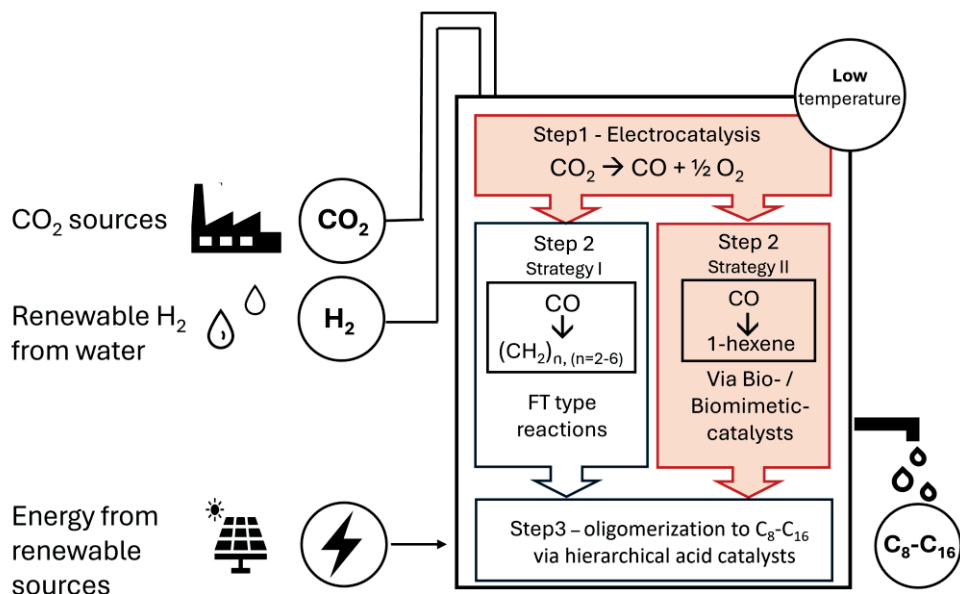


Figure 2.1 Schematic representation of the different steps involved in 4AirCRAFT project. the two steps investigated in the thesis and the ones in which I was mainly involved are highlighted in red. Adapted from reference 61.

For what concerns CO₂RR, as previously mentioned, the most active electrocatalysts for the selective reduction of CO₂ to CO are Au and Ag, but their high cost and scarcity are drawing attention to the study of lower-cost systems using earth-abundant elements. In the frame of 4AirCRAT project, a wide range of electrocatalyst materials have been investigated as potential alternatives for the electrochemical reduction reaction of CO₂ to CO. Among the different materials, LDHs, previously proposed as adsorbent materials and introduced in Section 1.2.1, have shown promising results as electrocatalysts, as well as interesting characteristics such as low cost, easy synthesis procedure, tunability of composition, good ionic conductivity, and high alkaline tolerance.^{62,63} A selection of the most promising LDHs, previously tested by our partners of Hokkaido University and CSIC-ICV center of Madrid, were characterized to explore the active sites present in the materials and to understand the reason of the different electrocatalytic performances.

In **Chapter 7** the characterization of LDHs for CO₂RR was reported. Initially the work was dedicated to three hydrotalcites having different elemental composition Zn-Al, Ni-Al, and Ni-Fe and equal stoichiometry (2:1). Since for Ni-Al and Ni-Fe samples, almost no carbon monoxide (CO) evolution was observed, the attention was then shift to Zn-Al LDH in which a higher FE occurred. Zn-Al LDHs having different stoichiometries (2:1, 1:1 and 1:2) were studied by means of ATR-IR spectroscopy. Lastly, the effect of mechanical grinding of the LDH on the electrochemical performance and on the physico-chemical properties of the original material was evaluated. Some preliminary results coming from the study of the most relevant electrocatalysts with a recently acquired spectro-electrochemical cell were also discussed at the end of this chapter.

The attention was then focused on the second step of the reaction involving the conversion of the electrochemically produced CO into C₈-C₁₆ compounds. To achieve this goal, we worked particularly on the second strategy which involves a first transformation of CO into 1-alkanols through a microbial transformation according to the process developed by Siemens and Evonik Industries and already available in the industry⁶⁴ and a subsequent dehydration to 1-alkenes, the desired final intermediates. These compounds are then further transformed via metathesis and hydrogenation into n-alkanes, serving as alternative air fuel. The main challenge of this step is the dehydration of the primary alcohol to alkenes due to the high difficulty of performing the reaction under mild conditions. Traditionally, very harsh conditions have been applied for dehydration of aliphatic primary alcohols, such as stoichiometric use of catalyst and reaction temperatures >300 °C.⁶⁵

In order to achieve this goal, our partners from Bielefeld tested different catalysts, ranging from biocatalysts to inorganic homogeneous and heterogeneous ones. Among the different one we particularly focused the attention on a bentonite, an heterogeneous catalyst which showed an alkene yield of 52% (at 180°C, 6 h, 2 mol% catalyst employed). In contrast, under the same reaction conditions the Triflic acid, a much more acidic homogeneous catalyst, reached only 8% alkene yield. The positive performances of this materials combined with the recycling and separation advantages of heterogeneous catalysis over homogeneous ones, led us to deeply investigate this catalyst.

In **Chapter 8** a deep characterization of this commercial bentonite was reported. A first fundamental characterization was performed to study its structure, thermal stability, porosity and morphology. IR spectroscopy was then carried out using

different molecular probes on the sample activated at different temperatures to understand the reason for the peculiar catalytic performances of this material.

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3. MATERIALS AND METHODS

This section explains the main techniques used in the thesis. In the case of specific conditions and/or different characterization techniques, these are specified in the individual chapters. In the case of characterizations carried out by other partners, this is indicated in the text when the data are presented. Otherwise, where not explicitly stated, characterizations were carried out by the author.

Fundamental characterization techniques

Thermogravimetric analysis (TGA) reported in Chapters 6 and 8 were performed by means of a TA Instruments Q600. The temperature ramp and measuring conditions were adapted to the individual sample requirements.

To check the morphology and the elemental composition of the samples, in Chapters 4 and 8 scanning transmission electron microscopy and energy dispersive X-ray analysis (FE-SEM) measurements were performed on a FESEM TESCAN S9000G equipped with Schottky-type EGF source. The voltage used for electron acceleration is 15kV and the probe current 300 pA. An OXFORD model Ultim Max Aztec software was used for the microanalysis.

In Chapters 4, 5 and 8 to study the textural properties of the samples N_2 adsorption/desorption isotherms were measured on a Micromeritics 3Flex at -196°C . Prior to the measurement the sample was outgassed according to the sample requirements. The textural properties were evaluated by using the Microactive software provided by Micromeritics. The Specific Surface Area (SSA) was determined by using the Brunauer–Emmett–Teller (BET) and/or Rouquerol consistency criteria. For each sample the method and the P/P_0 range will be reported while the linear BET fit is not reported for sake of brevity. If cumulative pore volume and pore size distribution have been evaluated, the method, geometry and model used are reported in each section. In Chapter 5, in addition to N_2 , also Ar and CO_2 isothermal physisorption measurements were performed on a Micromeritics ASAP 2020 at -186°C and 0°C , respectively.

Adsorption techniques

Volumetric measurements reported in Chapter 4, 5, 6 and 7 were performed by means of a Micromeritics ASAP2020 or Micromeritics 3Flex sorption analyser, by collecting adsorption/desorption isotherms. For CO_2 adsorption obtained in the

temperature range $0 \leq T \leq 90^\circ\text{C}$, the temperature was kept constant thanks to a special home-made patented apparatus coupled with the volumetric instrument, consisting of a glass cell inserted in a concentric jacket, in which a coolant or heating fluid circulates through a JULABO CD-200F.¹ The system ensures precise temperature control during the measurement in terms of homogeneity and stability over time, allowing isotherms collection with a very low temperature resolution. In case of CO_2 adsorption at $T > 90^\circ\text{C}$ the temperature was controlled by means of an external heater provided by Micromeritics for chemisorption measurement. Prior to measurement, the samples were activated in vacuum at different temperatures (specified in each chapter). In the desorption branch of the isotherm, no points were acquired at pressures below 200 mbar due to the slow kinetics.

The breakthrough CO_2 adsorption tests reported in Chapter 4 were carried out using two different setups, one for the beads and one for the monoliths.

In case of breakthrough curves performed on NaLTA and CaLTA in beads form, the measurements were carried out by Dr. M. Dosa under the supervision of Prof. M. Piumetti at Polytechnic University of Torino. The experimental set-up is characterized by the following equipment: a quartz-U reactor (inner diameter 1 cm, height 3 cm) with a fixed bed, a furnace and a paramagnetic gas analyzer (Emerson XStream X2GP). In this setup, the adsorbent material (300 mg) was placed into the quartz-U reactor. The reactor was positioned into the furnace and connected to the mass-flow controllers. A K-type thermocouple, placed in the quartz-U reactor chamber on the top of the adsorbent material (at around 1 mm distance), was used for the temperature control. The flow-out from the reactor was monitored by the gas analyzer every 10 s, monitoring the CO_2 volume fraction (ppm). Before the adsorption tests, a pretreatment was carried out to eliminate impurities on the adsorbent material (i.e., carbonates and humidity). The pretreatment was performed by using N_2 (total flow = 40 mL min^{-1}) at 400°C for 2 h. Then, the temperature was cooled down and the adsorption tests were performed: the total flow was 40 mL min^{-1} comprised by 10 vol% CO_2 volume balanced with N_2 . The temperatures chosen for the CO_2 adsorption tests were 25, 60 and 90°C , according to the volumetric measurements. In each adsorption test, the CO_2 volume fraction was recorded until the concentration reaches the initial value (10 vol%). The amount of CO_2 was evaluated by the integration of the breakthrough curves using the following equations:

$$CO_{2adsorbed} = \int_{t_0+\Delta t}^{t_f} (1 - \frac{C_{CO_{2out}}}{C_0}) d(Q_{out}t) \quad (3.1)$$

$$Q_{out} = Q_{in} \frac{1 - y_{CO_2}}{1 - y_{CO_2} \frac{C_{CO_{2out}}}{C_0}} \quad (3.2)$$

$$n_{CO_2(t)} = \frac{y_{CO_2}PV}{RT} \quad (3.3)$$

Where:

$C_{CO_{2out}}$ (ppm) is the CO₂ amount in the outlet recorded by the gas analyzer.

Q_{out} (m³ s⁻¹) is the volumetric flowrate.

y_{CO_2} is the CO₂ mole fraction in the inlet.

C_0 (ppm) is the initial CO₂ concentration.

Δt (s) is the presumed delay time.

Furthermore, the adsorption loading capacities of the adsorbent materials were evaluated by the following equation:

$$\alpha_{zeolite} = \frac{n_{CO_{2adsorbed}}}{m_{sor bent}} \quad (3.4)$$

Where:

$n_{CO_{2adsorbed}}$ is the total amount of CO₂ (moles) adsorbed by the material.

$m_{sor bent}$ is the total amount (mass - g) of adsorbent material used for the test.

For what concerns the breakthrough CO₂ adsorption of the monoliths, the measurements were performed in our department using a custom-made quartz reactor designed to accommodate the 3D printed monoliths. With respect to the previous setup, two major differences should be noted: (i) the measurement at 25°C was not performed in this case due to the difficulty of keeping the temperature constant for all measurements and (ii) the CO₂ pressure used in the breakthrough curves was 20 vol% CO₂/He and not 10% CO₂/N₂ due to setup limitations.

The quartz reactor has an internal diameter of 17 mm, which perfectly matches the dimensions/diameter of the monoliths. The monoliths were positioned correctly in the centre of the reactor by a narrowing of the reactor's diameter to 8 mm. This design eliminates the need for additional components, such as quartz wool or other supports, which could introduce contaminants. The reactor was positioned in the middle of a circular oven and the temperature was monitored by means of a K-type thermocouple. An electronic mass-flow controller system was used to flux the reactor using He as the inert and CO₂ tank for the adsorptive gas. The flow-out from the reactor was monitored by an Hiden Analytical HPR-20 mass spectrometer, monitoring CO₂ and He fragments over time.

Before the breakthrough test, a pretreatment was carried out to remove impurities (i.e., water and residual carbonates) from the monoliths. The pretreatment was conducted by using a total flow of 50 ml/min of the inert gas at 400°C for 4 hours. Then, the temperature was lowered to 60 or 90°C and the adsorption test was performed using a 20 vol% CO₂/He mixture maintaining the selected total flow. The amount of CO₂ adsorbed by the monoliths was evaluated integrating the breakthrough curves, as previously reported (Equation 4.1-4.3). In order to evaluate the “dead volume” of the system, a blank test was performed prior to the monoliths measurements. In this test, a comparable volume of sieved quartz, inert respect CO₂ adsorption, was put into the reactor to mime the presence of the adsorbent. The blank correction was carried out at the same flow rate and pressure (50 ml/min at 1 atm) for two times to cover both the two selected temperatures (60°C and 90°C). The blank response was then subtracted point-by-point from the monoliths response.

Prior to the analysis of the monoliths, the set-up was tested by performing the same measurements with commercial LTA beads, which were also used for comparative purposes.

A detailed scheme of the setup is show in Figure 3.1

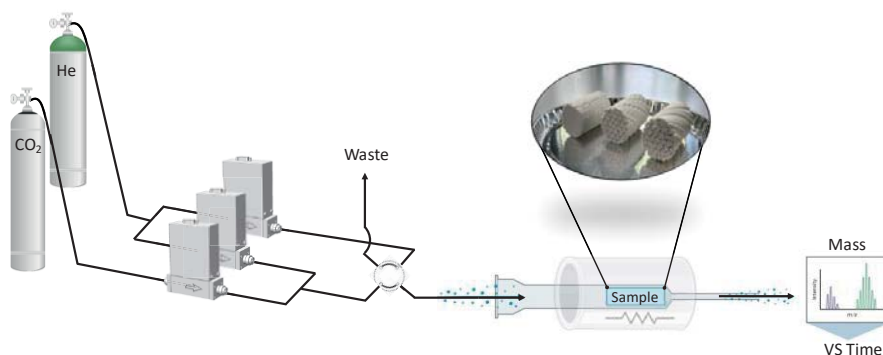


Figure 3.1. Detailed scheme of the experimental breakthrough setup used for the analysis of LTA monoliths.

Spectroscopic characterization

In Chapter 4, 5, 8 Fourier-transform infrared (FT-IR) spectroscopy was employed to the study of Lewis and Brønsted acidity present in the different samples. The spectra were performed by means of a Bruker Invenio or Bruker Vertex 70 spectrophotometer equipped with a MCT (mercury cadmium tellurium) cryo-detector. All the spectra were collected in the $4000\text{--}650\text{ cm}^{-1}$ spectral range with a resolution of 2 cm^{-1} and an average of 32 scans. Before the analysis all the samples, in form of self-supported pellets protected by a gold envelope, were inserted in a special home-made quartz cell and activated in vacuum at various temperatures (data reported in each section). Then, they were cooled down to Room Temperature (RT) and different gaseous probe molecules such as carbon monoxide (CO), deuterated acetonitrile (CD_3CN), nitrogen (N_2), pyridine (Py), ammonia (NH_3) and heptannitrile ($\text{C}_7\text{H}_{13}\text{N}$) were dosed to the sample. In the case of CO and N_2 , the experiment was then performed by cooling the cell with liquid nitrogen at -196°C (i.e. nominal temperature $\sim 100\text{ K}$). The specific experiments were reported elsewhere.^{2–4}

In-situ ATR-IR measurements reported in Chapter 7 were performed with a Bruker Invenio Fourier transform spectrometer to investigate the effect of the interaction of CO_2 with the samples. The spectrometer is equipped with a MCT cryo-detector (Mercury Cadmium Telluride) which operates at liquid nitrogen temperature (-196°C). During the test, each collected spectrum consists of an average of 32 scans (64 for the background spectrum). The ATR-IR measurements were carried out using a commercial horizontal ATR mirror unit and cell (HATR, Horizontal ATR accessory

provided by Pike Technologies) equipped with an AMTIR single crystal (internal reflection element 80×10×4 mm, 45°, Specac). Prior to each measurement, the samples were suspended in deionized H₂O (~10 mg per 0.5 ml), deposited on the crystal and dried overnight at room temperature. The ATR-IR spectra of the dried samples were collected before each experiment. The structural interlayer carbonates were identified, and the underlying area was used to normalize the following LDH spectra. The ATR cell was then flushed with liquid H₂O saturated with N₂ which was supplied through a mass flow controller with a flow rate of 15 mL min⁻¹. H₂O and N₂ were circulated over the deposited samples at room temperature for 30 minutes to verify the stability of the deposition. The circulation was controlled through a peristaltic pump operated at 2.0 mL min⁻¹. The inlet gas was then switched to CO₂ and a CO₂-saturated liquid H₂O flow was circulated over the sample for another 30 minutes (a schematic representation of the setup is reported in Figure 3.2).

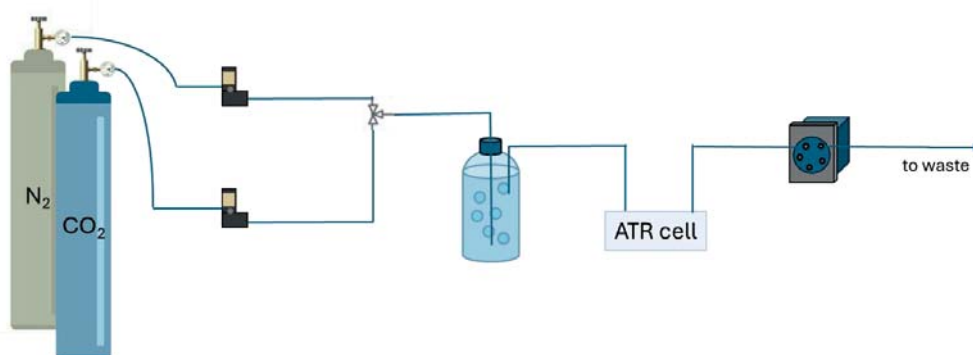


Figure 3.2. Schematic representation of the set-up used during the in-situ ATR-IR measurement.

In some cases the same experiment was repeated with cyclohexane instead of H₂O to further characterize the sample.

The band fitting of the carbonates-like species formed on the LDH structure was performed by means of the FIT routine by Bruker, which allows the interactive search for the best fit to the examined experimental spectral segment based on several spectral components imposed by the operator. Once the spectral position and all the major spectral parameters (half-bandwidth, percent of Gaussian profile) have been fixed, the remaining ones were allowed to float freely. The carbonates evolution in time was studied by making a fitting of the carbonates originated from

the CO₂-saturated H₂O flow at 0,7.5,15, 22.5, 30 minutes and the underlying area of each couple of carbonates was calculated and reported in histograms.

Electrochemical characterization

The electrocatalytic CO₂RR experiment reported in Chapter 7 were carried out by Dr. R. Nakazato under the supervision of Prof. K. Tadanaga at Hokkaido University by means of a custom-made three-electrode setup composed of three-compartment cell (Figure 3.3)

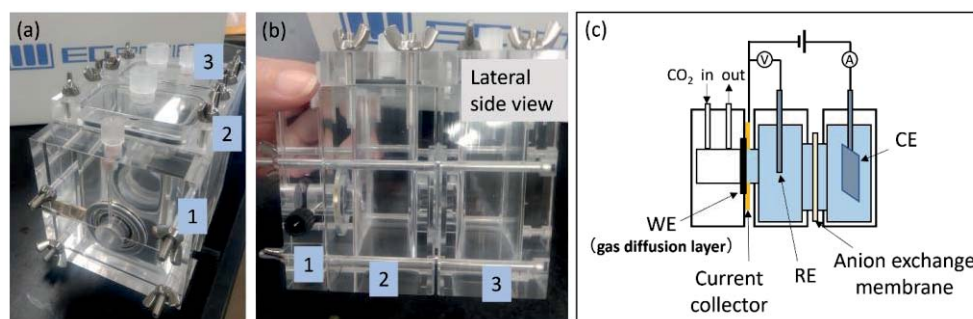


Figure 3.3. Custom-made three-electrode setup composed of a three-compartment cell from front view (a), lateral view (b) and in a schematic representation (c).

The cathodic and anodic compartments were separated by a piece of the anion exchange membrane to avoid the unexpected influence of the oxidation reaction taking place on the counter electrode. The LDH-loaded gas-diffusion electrode (GDE) and a platinum mesh electrode (35 × 25 mm, LAKE SHORE CRVOTRONICS Inc.) were used as working and counter electrodes, respectively. The LDH-loaded GDE was prepared by simple drop-casting of the catalyst ink on a gas-diffusion layer (GDL: Sigracet 36BB, SGL CARBON JAPAN Ltd.). The catalyst inks were prepared by mixing 4 mg of LDH ground for 5 min with 1 mg of the conductive aid (carbon black: Vulcan XC72, CABOT Corp.) and 30 μL of the binder (Nafion solution, SIGMA-ALDRICH Co. LLC) in 570 μL of ethanol and sonicating for 10 min. The catalyst ink was drop-casted to the GDL on a hot plate pre-heated at 80°C. The ink coating area was 1.89 cm², whose shape was a 1.55 cm diameter circle and the loading level of the LDH was 2.1 mg cm⁻². The LDH-loaded GDE was further dried at 80°C for at least 30 min to remove the solvents. Ag/AgCl (3.0 M KCl, BAS Inc.) electrode was used as a reference. An aqueous solution (0.10 M) of KHCO₃ was used as an electrolyte. The CO₂ gas flowed with a 50 mL min⁻¹ flow rate and 0.10 MPa inlet pressure to the cathodic compartment, while the solution in the reference electrode compartment

was stirred at 600 rpm with a PTFE stirring bar. Under the above conditions, CO₂ electrolysis for 10 min was performed by applying a voltage with an electrochemical analyser (IviumStat, IVIUM TECHNOLOGIES B.V.). Gas-phase products were detected by gas chromatography techniques (GC-2014, SHIMADZU Corp.; carrier gas: nitrogen, flow rate: 10 mL min⁻¹, pressure: 53.2 kPa, vaporization chamber temperature: 393 K). For the detection of hydrogen (H₂), Molecular Sieve 5 A (GL SCIENCES Inc.; column temperature: 50°C, injected sample volume: 1 mL) and a thermal conductivity detector (TCD, SHIMADZU Corp.; detector temperature: 120°C) were used. For the detection of CO and gaseous hydrocarbons, PoraPak N (GL SCIENCES Inc.; column temperature: 50°C, injected sample volume: 1 mL) for a flame ionization detector (FID, SHIMADZU Corp.; detector temperature: 120°C) were used. Electrode potentials in the study were converted to the reversible hydrogen electrode (RHE) according to the following equation (Eq.3.5):

$$E_{RHE} = E_{Ag/AgCl} + 0.222V + 0.059 \cdot pH \quad (3.5)$$

All potentials and voltages in this work were evaluated without IR calibration. The Faradaic efficiency (*FE*) for CO and H₂ was calculated based on the Equation 3.6:

$$FE = \frac{2Vp rF}{IRT} \quad (3.6)$$

Where *V* was the volume concentration of CO or H₂ in the produced gas from the reaction cell. *I* (mA) was the average current during the reaction, and *r* was the CO₂ flow rate (m³/s) at ambient temperature and pressure. For the other constants in the formula, *p* was 1.013 × 10⁵ Pa, *F* was 96485 C mol⁻¹, *R* was 8.3145 J mol⁻¹ K⁻¹, and *T* was 25°C.

References:

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4. LTA ZEOLITE FOR CO₂ CAPTURE: FROM POWDER TO 3D PRINTED MONOLITHS

As previously mentioned in chapter 1 there are some specific properties that an ideal adsorbent should address such as adsorption capacity, selectivity, fast kinetics, easy of regeneration, stability over cyclability, mechanical and thermal stability, low costs, tolerance to moisture and to other impurities and possibility of shaping. However, given the impossibility of satisfying all these requirements at the same time, three different classes of materials (i.e. Zeolites, MOFs and Hydrotalcites) have been selected, considering their specific benefits and drawbacks (see Chapter 2).

In this chapter, a specific zeolite framework was investigated to assess its possible application as adsorbent for CO₂ (especially in post-combustion processes). Among the different zeolites, Linde Type A (LTA) was chosen based on the quite high CO₂ capture capacity displayed in the literature, the easy regenerability and its competitive price compared to other commercially used adsorbents.¹⁻³ Indeed, an evaluation of the average selling price of this commercial zeolite and zeolite 13X, which is commonly used as a reference material for CO₂ capture applications, showed that the average price per tonne of LTA is only 1300 \$, definitely cheaper than 13X (2500 \$ for Ton).⁴ The material was therefore investigated and tested as CO₂ adsorbent, to check if other 'ideal' requirements could also be fulfilled, in addition to its low cost on the market.

In the following pages, the LTA zeolite and its adsorption properties towards CO₂ were initially investigated on the commercial material in powder form and then analysed using a commercially available LTA sample in spherical beads. Finally, the possibility of synthesising pure LTA zeolite monoliths of different shapes was explored.

The study of LTA in beads form reported in paragraph 4.2 is based on the publication: “Cavallo, M.; Dosa, M.; Porcaro, N. G.; Bonino, F.; Piumetti, M.; Crocellà, V. Shaped Natural and Synthetic Zeolites for CO₂ Capture in a Wide Temperature Range. *J. CO₂ Util.* 2023, 67, 102335”. On the other hand, the synthesis of LTA monoliths characterised in paragraph 4.3 is the subject of an Italian patent application “Franchin, G.; D’Agostini, M.; Colombo, P.; Conte, A.;

Crocellà, V.; Bonino, F. C.; Porcaro, N. G.; Cavallo, M. Metodo per La Preparazione Di Monoliti Di Zeolite LTA. 102023000013929, 2023” and a paper is in preparation.

4.1 Materials and Methods

The synthetic LTA zeolite was purchased in sodic form (NaLTA) from Sigma Aldrich in both powder (provided by Saes Getters) and spherical beads form ($\varnothing$ 3–5 mm), (Molecular sieves 4A Lot. MKCH5817). Zeolite 13X, used as a reference for CO₂ capture was purchased in powder form from Sigma Aldrich. The general formula of this type of synthetic Zeolite is: $[\text{Na}^+_{12} (\text{H}_2\text{O})_{27}]_8 \mid [\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]_8$. As all the other zeolites, LTA is made by tetrahedral units where the central atom can be Si or Al. LTA is characterized by a full alternation of Al and Si leading to a Si/Al ratio equal to 1. Na⁺ extra-framework cations balance the negative charge induced by the presence of aluminium cations. This ratio is the minimum possible according to Loewenstein’s law and leads to an increase in density of acid sites and cations exchange capacity due to abundance of Al³⁺ and its exchangeable cations⁵. In LTA, tetrahedra are organized to form a structure composed by 8 beta cages (sodalite cages) connected each other with cubic structures (d4r) creating a central alpha cage (made by 48 T structures) (Figure 4.1). The dimension of the diameter of the central alpha cage is 11.05 Å, while the external 8-member ring aperture is about 4.20 Å.⁶

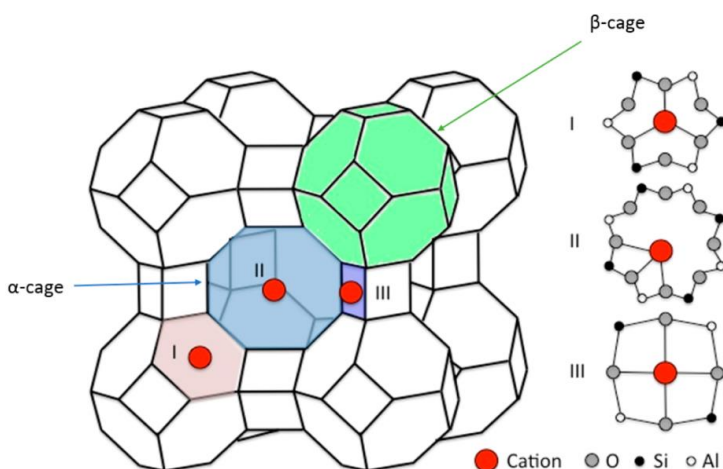


Figure 4.1. Pictorial representation of framework structure of LTA Zeolite. From reference 7.

An ion-exchange procedure was performed on the commercial sodium LTA (NaLTA) in both powder and beads in order to prepare CaLTA and MgLTA samples. A solution 0.5 M of $\text{Ca}(\text{NO}_3)_2$ or $\text{Mg}(\text{NO}_3)_2$ was prepared. The starting LTA zeolite was inserted into the nitrate solutions (1 g of LTA into 20 mL of solution) and left under continuous stirring on a heated plate at 60°C for about 18 hours. A second exchange cycle was repeated using the same procedure after removing the previous solution by centrifugation. Finally, the solution was removed by centrifugation, and the exchanged LTA were washed 3 times with deionized water by stirring them with Vortex. The exchanged samples were dried at 100°C for one night in static oven.

The LTA monoliths were synthesised by M. D'Agostini under the supervision of Prof. G. Franchin and Prof. P. Colombo at University of Padova. This synthesis has been the subject of a joint Italian patent application by the University of Turin and the University of Padova.⁸ The synthesis protocol consists essentially in a two-step procedure, first involving production of LTA powder as filler and then its dispersion into a second LTA synthesis gel acting as liquid-phase binder for shaping. The initial LTA precursor gel with molar composition $[2\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{Na}_2\text{O} : 25\text{H}_2\text{O}]$ was prepared by dropwise addition of colloidal silica (LUDOX® TM-50, Sigma Aldrich, USA) into a NaAlO_2 solution under vigorous mixing. The gel was allowed homogenising at high shear for 60 min through the use of a mechanical mixer (ArgoLab), then transferred to a sealed polyethylene mould and crystallised for 48 h at 75°C. The resulting monolith was dried at 75°C for 24 h, after which it was milled and sieved below 63 μm to obtain zeolite LTA in powder form. After that, a second batch of gel with identical composition and synthesis protocol was prepared. After the homogenisation step, 40wt% of the previously obtained LTA powder and 2wt% of carboxymethylcellulose (CMC Na-salt, Sigma Aldrich, USA) were added to the gel and homogeneous dispersion of the solids was ensured by subjecting the resulting slurry to five 5-minute cycles of high-energy mixing (ARE-250, Thinky Corporation, Japan) alternated by four 5-minute cycles of sonication. The slurry was then defoamed on the same high-energy mixer for 5 minutes and transferred to a syringe (Vieweg, Germany). The Direct Ink Writing process was carried out with a Delta-type 3D printer (Delta Turbo 2040, WASP, Italy). A pneumatic system pushes the slurry from the syringe into the barrel of an auger-type extruder (LDM module, WASP, Italy), by which it is then dispensed at room temperature through a tapered 580 μm nozzle (Vieweg, Germany) to shape the desired object from a CAD model layer by layer.

After printing, the monoliths were placed into a sealed container and crystallised for 48 h at 75°C, then dried for further 24 h at the same temperature. Water was added into the container during the crystallisation step to maintain 100% Relative Humidity and prevent the premature evaporation of water from the monoliths before crystallisation was complete. The monoliths were then subjected to a washing procedure with deionized (DI) water followed by a heat treatment at 400°C for 10 h in air to remove the CMC additive. Such treatment protocol had been designed to ensure good removal of CMC without damaging the LTA phase.

It should be noted that the two steps are carried out with the same reagents and composition, largely using the same equipment. This synthesis process is suitable for the production of large batches.

The powder X-ray diffractograms of the LTA beads were collected on a PANalytical X' Pert diffractometer using Cu K α radiation and a power of 45 kV 40 mA in Capillary configuration (2 θ range = 5–65°). Diffraction patterns of the synthesised monoliths were performed by University of Padova and were collected from the samples in powder form on an X-ray diffractometer (D8 Advance, Bruker, USA) with 0.01° resolution and 100 s deg⁻¹ scan-speed. Phase identification was carried out through the “QualX2.0” software.

The specific surface area was determined by both N₂ and CO₂ adsorption isotherms at -196°C and 0°C respectively, applying the Brunauer–Emmett–Teller (BET) equation in the 0.05 < p/p⁰ < 0.3 and 0.003 < p/p⁰ < 0.03 range respectively. The linear BET fit is not reported for sake of brevity but the R² values were around 0.99 for all plots.

The characterization by means of EDX, IR spectroscopy, volumetry and breakthrough curves was performed following the procedures described in Chapter 3, the activation protocol for all the LTA samples consisted of heating at 400°C for 4 hours in vacuum.

An evaluation of the isosteric heat of adsorption was also performed by applying the Clausius-Clapeyron equation to the isotherms measured at 25°C, 60°C and 90°C:

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \quad (\text{Equation 4.1})^9$$

Different isosteric curves can be obtained plotting the natural logarithm of the pressure at constant loading as a function of $1/T$. Multiplying the slope of this curve by the gas constant the isosteric heat for different quantities adsorbed was obtained.¹⁰ Data elaboration was performed by using the Micromeritics' data analysis software (MicroActive version 5.02.01).

Lastly, it is worth noting that in the following sections the last letter in the name of the samples refers to the shape (i.e. LTA-P for powder, LTA-B for beads and LTA-3D for monoliths).

4.2 From powder to beads LTA

An initial rapid evaluation of the pure CO_2 adsorption performance of LTA zeolite in powder form was carried out. The zeolite in its original raw form (NaLTA) was studied together with the ion-exchanged CaLTA and MgLTA samples to investigate the possibility of increasing the adsorption capacities of the materials by means of a simple exchange procedure. The uptake capacities of NaLTA, CaLTA and MgLTA were evaluated in comparison to that of Zeolite 13X, used as a reference for CO_2 capture. The pure CO_2 adsorption capacity was evaluated by collecting adsorption/desorption isotherms at different temperatures (25°C, 60°C and 90°C), until 1100 mbar, as reported in Figure 4.2 a, c and e. Their adsorption capacities at 1000 mbar were reported in the respective histograms (Figure 4.2 b, d and f) to better highlight the adsorption trend at atmospheric pressure at the different temperatures.

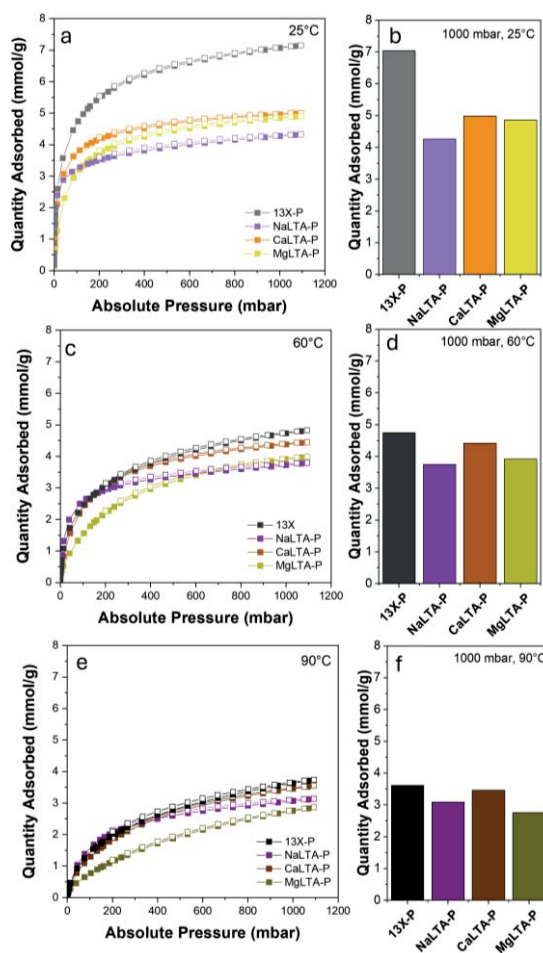


Figure 4.2. CO₂ adsorption/desorption isotherms of zeolites 13X, NaLTA, CaLTA and MgLTA in powder form at: 25°C (a), 60°C (c) and 90°C (e) and quantity adsorbed in mmol_{CO₂}/g_{adsorbent} at 1 bar absolute pressure and 25°C (b), 60°C (d) and 90°C (f).

For all samples, the isotherms and histograms show a general predictable decrease in CO₂ uptake with increasing temperature. As can be gathered by the histograms, the CO₂ uptake capacity of the samples at 25°C and 60°C has the same trend, with the 13X zeolite dominating over the CaLTA, followed by the MgLTA and NaLTA. On the other hand, a different adsorption trend can be observed at 90°C, where at 1 bar the adsorption capacity of 13X almost coincides with that of CaLTA, followed at a slight distance by NaLTA and MgLTA. Additionally, by considering the isotherms of zeolites 13X, NaLTA and CaLTA at 60°C and 90°C in a lower pressure range (absolute pressure < 300 mbar) they almost coincide. Based on the CO₂ isotherms and the uptake at 25°C, 13X appears to be the most efficient material, but when

we consider the performance as the temperature rises from 25 to 90°C, it shows the highest reduction in CO₂ adsorption which is almost halved. On the other hand, NaLTA shows the smallest decrease in performance upon heating passing from 4.26 mmol/g at 25°C and 1 bar to 3.09 mmol/g at 90°C and 1 bar (-27.5%). A slightly higher reduction is observed in CaLTA passing from 25°C to 90°C (-30.5%) while, for MgLTA, the 43% of uptake capacity is lost in the same temperature range. Based on these results for MgLTA, it appears that the ion exchange with Mg²⁺ did not result in any particular increase of CO₂ capture capacity with respect to the raw NaLTA, in contrast to what was observed for the CaLTA sample. Additionally, the acquisition time for MgLTA was much longer than for other samples suggesting a much slower adsorption kinetics. For this reason, the MgLTA was not taken into consideration in the following paragraphs.

Based on the good adsorption capacity, especially at high temperatures, and the lower price compared to 13X zeolite,⁴ NaLTA and CaLTA could be interesting samples for CO₂ capture and a more detailed investigation of their properties and capture performance was carried out. In order to get closer to more practical and industrial applications, the following characterization was carried out using LTA beads rather than powder samples.

The raw commercial NaLTA beads and the ion-exchanged CaLTA were therefore firstly characterized. XRD patterns were collected to prove that the crystalline structure of the zeolites was not affected by the ion-exchange procedure. As reported in Figure 4.3, NaLTA and CaLTA samples show the characteristic diffraction pattern of the LTA topology.¹¹ The CaLTA displays no changes in the position of the main peaks, confirming that the zeolite structure has been preserved after the ion-exchange process. The elemental composition of the zeolite was checked by means of EDX analysis (Table 4.1). As expected for a synthetic zeolite, in the starting NaLTA sample the main cation present in the zeolite framework is Na⁺, with some Ca²⁺ and Mg²⁺ impurities. Na⁺ ions are largely replaced by Ca²⁺ in the CaLTA sample, demonstrating that the ion exchange process has successfully replaced the cations of the LTA zeolite beads. Interestingly, the Mg²⁺ impurities present in NaLTA are also slightly reduced in the CaLTA sample, probably partially replaced by Ca²⁺. Both NaLTA and CaLTA exhibit a Si/Al ratio around the theoretical value (~1), proving that the exchange procedure does not modify the Al content of the sample.

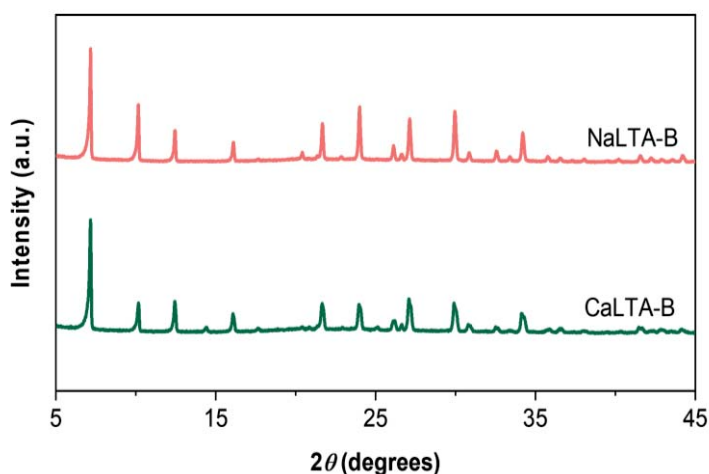


Figure 4.3. X-ray diffraction patterns of the NaLTA and ion-exchanged CaLTA samples in beads form. The figure is adapted from reference 4.

Table 4.1. Elemental composition of the samples obtained by EDX analysis. The table is adapted from reference 4.

Sample	Atomic (%)			Si/Al atomic ratio
	Na	Ca	Mg	
NaLTA-B	10.99	0.29	1.75	1.28
CaLTA-B	1.26	6.92	1.36	1.29

The semi-quantitative information about the composition of the samples obtained by the elemental analysis can be further improved by performing *in situ* IR spectroscopy using carbon monoxide (CO) as a molecular probe. CO is commonly used in zeolites characterization, for studying the presence of isolated ions located in the structure thanks to its ability to discriminate between sites of slightly different acidity located inside the microcavities of the zeolitic structure.^{12,13} Indeed, thanks to its Lewis basic character, CO can interact with Lewis acids sites,

like cations, forming carbonyl complexes. This molecular probe has a small dipole moment but a rather high polarizability. Therefore, the stretching frequency of CO adsorbed on alkaline/alkaline earth cations (through the carbon atom) exhibits a shift to higher frequencies with respect to the stretching frequency of the free gaseous molecule (2143 cm^{-1}), resulting from polarization and from the consequent increase in the force constant of the C-O bond. The C-bonded carbonyls show an upward shift proportional to the strength of the Lewis acidity of the cations involved in the interaction, allowing the evaluation of the actual accessibility of the cations present inside the zeolite to a small molecule in the gas phase.^{14,15} The interaction of CO with NaLTA and CaLTA followed by IR spectroscopy is reported in Figure 4.4.

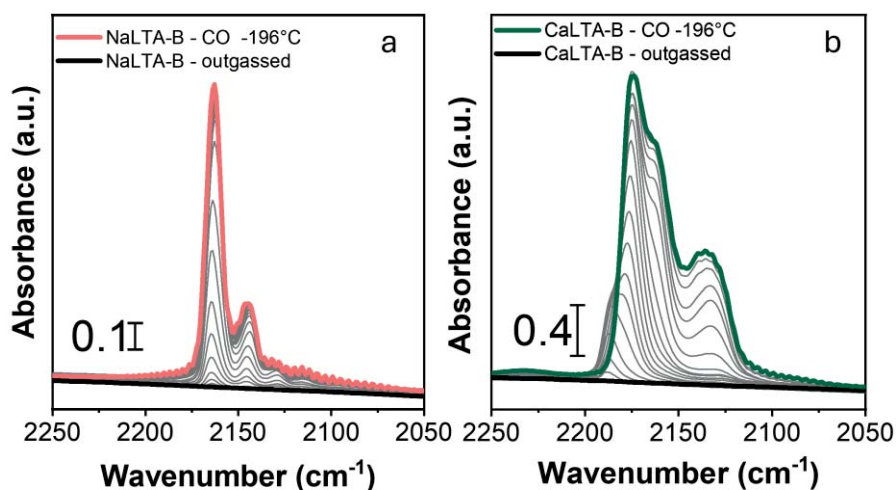


Figure 4.4. IR spectra of CO adsorption at -196°C on activated samples, recorded at different CO coverages and reported in the CO vibrational modes region of: NaLTA (a) and CaLTA (b). Coloured, grey and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively. The figure is adapted from reference 4.

The spectra of CO adsorption at the nominal temperature of -196°C on the commercial NaLTA are reported in Figure 4.4 a. The CO stretching region displays the presence of two well-resolved signals. The sharp band at 2163 cm^{-1} is assigned to $\text{Na}^{+}\text{-CO}$ adducts, whereas the component at 2145 cm^{-1} is due to the C-O stretching mode of CO molecules bridging two Na^{+} ions.¹⁶ Finally, the weak band at around 2130 cm^{-1} is due to a small fraction of liquid-like CO phase. The interaction of CO with CaLTA (Figure 4.4 b) shows a band at $\sim 2174\text{ cm}^{-1}$ which exhibits an

upward shift till $\sim 2186\text{ cm}^{-1}$ upon outgassing. According to Montanari et al.¹⁴ the signal at 2174 cm^{-1} can be associated to $\text{Ca}^{2+}(\text{CO})_2$ dicarbonyls (less energetically stable) which decompose during outgassing to give Ca^{2+}CO monocarbonyls, more energetically stable and shifted at higher wavenumbers. The component located at 2163 cm^{-1} , which readily disappears by decreasing CO pressure, can be assigned to Na^+ carbonyls, in accordance with the atomic percentages of the EDX elemental analysis (Table 4.1). The broad and labile band detectable at $\sim 2135\text{ cm}^{-1}$ can be confidently associated to the liquid-like CO. It is worth noting that the signal associated to liquid like CO is particularly intense for CaLTA suggesting the presence of a lower limitation in the probe molecule diffusion and adsorption inside the CaLTA cages. In summary, for both samples, IR spectroscopy using CO as a molecular probe revealed the presence of adsorption sites (Na^+ and/or Ca^{2+}) with different strengths available to interact with CO and thus with CO_2 .

The adsorption/desorption isotherms and the Specific Surface Area (SSA) of the samples, computed applying the BET equation, are reported in Figure 4.5. Firstly, adsorption/desorption isotherms of N_2 at -196°C were carried out to evaluate the effect of the presence of different cations inside the microporous cavities on the textural properties of the materials (Figure 4.5 a and b). As already known in the literature, the narrow micropores of a type A zeolite cannot be assessed by N_2 adsorption at cryogenic temperature due to its slow diffusion kinetics.^{17,18} Indeed, the restricted diffusion prevents nitrogen molecules from entering the microcavities of this zeolite, hindered by the presence of a huge number of cations. On the other hand, the CaLTA sample exhibits a reasonable SSA computed with N_2 at low temperature. In LTA framework, the substitution of Na^+ ions located near the aperture of the pores with Ca^{2+} cations, having a lower ionic radius, facilitates the diffusion of N_2 inside the microporous structure.^{19,20} A further proof of the presence of a larger fraction of void volume accessible to the probe molecule is provided by the high content of liquid like CO phase detected during IR adsorption experiments in the CaLTA compared to NaLTA sample (Figure 4.4 b). A valuable adsorptive for a correct assessment of the porosity of ultramicroporous materials is CO_2 , usually measured at 0°C (Figure 4.5 a and d).¹⁷ Even if the CO_2 , with its large quadrupole moment could be responsible for specific interactions with the cations of the zeolites, this measurement can still be useful to evaluate the specific surface area of materials which cannot be assessed by nitrogen or argon adsorption at cryogenic temperature, as reported elsewhere.^{18,21,22} In this case, the synergistic effect of its slightly lower kinetic diameter ($3.3\text{ \AA}$)²³ and the

higher temperature of adsorption results in an easier entrance and diffusion into the ultramicropores of the zeolite.²⁴ Indeed, a steep increment in SSA value can be observed for NaLTA (from 26 m²/g to 378 m²/g, measured respectively in N₂ and in CO₂) while the specific surface area of CaLTA obtained by CO₂ adsorption at 0°C (447 m²/g) is totally comparable to the value computed by N₂ adsorption at -196°C (438 m²/g). It is worth noting that the SSA obtained by CO₂ adsorption at 0°C of CaLTA sample is higher compared to the pristine NaLTA beads (378 m²/g) due to the lower concentration of divalent Ca²⁺ cations required in the zeolite framework to compensate the negative charge and, at the same time, to their smaller ionic radius. Lastly, the difference in SSA values between CO₂ and N₂ displayed by NaLTA sample suggests a great selectivity of those materials toward CO₂.

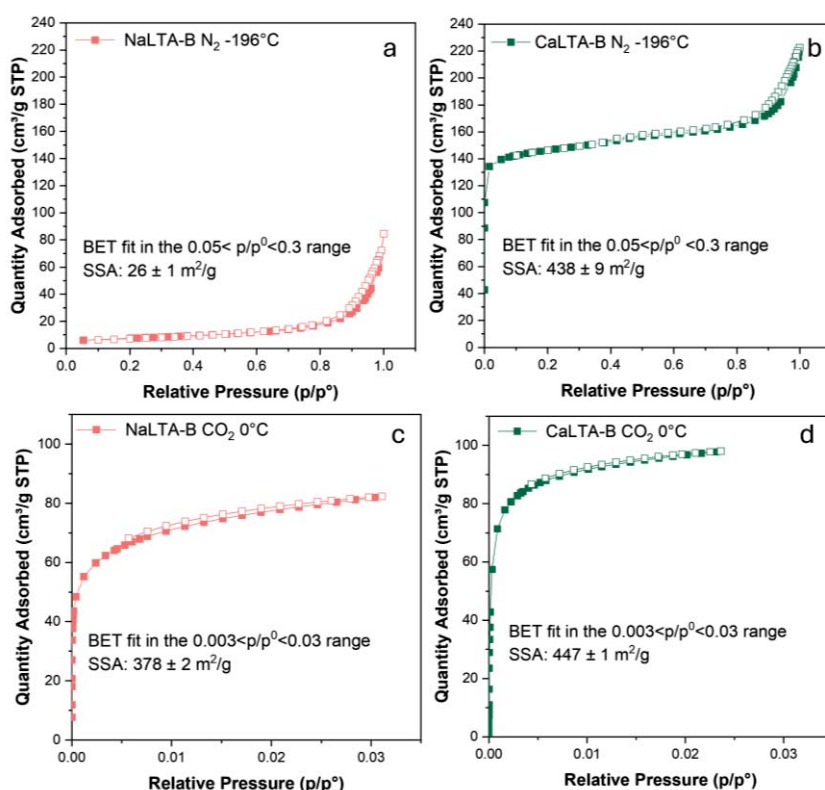


Figure 4.5. Adsorption/desorption isotherms of N₂ at -196°C (a, b) and of CO₂ at 0°C (c and d) of NaLTA (a, c) and CaLTA (b, d) with the corresponding BET SSA values. The figure is adapted from reference 4.

Once the fundamental characterisation had been carried out, the pure CO₂ adsorption capacity of NaLTA and CaLTA in beads form was evaluated in a similar

way to that previously performed for the powder samples (Figure 4.2). CO₂ adsorption/desorption isotherms at 25°C, 60°C and 90°C until 1100 mbar were collected, as reported in Figure 4.6 a and d. Their adsorption capacities at 100 and 1000 mbar were reported in the respective histograms (middle and right frames of Figure 4.6) to better highlight the adsorption trend at different temperatures. The pressure of 1000 mbar was chosen to evaluate the adsorption capacity at atmospheric pressure, while 100 mbar is the CO₂ pressure that will be employed in breakthrough curves (the CO₂ adsorption tests were performed with 10 vol.% CO₂, total pressure during the tests = 1000 mbar, partial CO₂ pressure during the tests = 100 mbar). Also in this case, an expected decrease of the capture capacities with temperature is observed for both the samples. As for powder samples, the uptake of CaLTA-B is higher than that of NaLTA-B as shown by the histograms at 1000 mbar (Figure 4.6 c and f). On the other hand, at lower absolute pressures (100 mbar), the uptake of the two samples was almost equivalent especially at higher temperatures (60°C and 90°C) (histograms in figure 4.6 b and e), in line with what was found for the corresponding powders (Figure 4.2 c and e). However, contrary to what has been observed previously, in the CaLTA-B shows the smallest decrease in performance by increasing the adsorption temperature: the CO₂ adsorbed ranges from 4.06 mmol/g at 25°C and 1000 mbar to 2.86 mmol/g at 90°C and 1000 mbar (-30%), whereas for NaLTA-B a slightly higher loss of about 35% was observed in the same temperature range (from 3.42 mmol/g at 25°C and 1000 mbar to 2.22 mmol/g at 90°C and 1000 mbar). It is worth noting that a general loss of adsorption capacity is observed for both samples passing from powder to beads. In particular, NaLTA shows a 20% decrease in CO₂ uptake when passing from powder to beads at 25°C, and a slightly higher loss of around 30% is observed when the temperature is increased to 60°C and 90°C (percentage calculated from the NaLTA-P values at 1000 mbar shown in Figure 4.2 and the NaLTA-B values at 1000 mbar shown in Figure 4.6 a and c). On the other hand, in case of CaLTA a constant decrease of about 20% is observed for all the three temperatures (percentage calculated from the CaLTA-P values at 1000 mbar shown in Figure 4.2 and the CaLTA-B values at 1000 mbar shown in Figure 4.6 d and f).

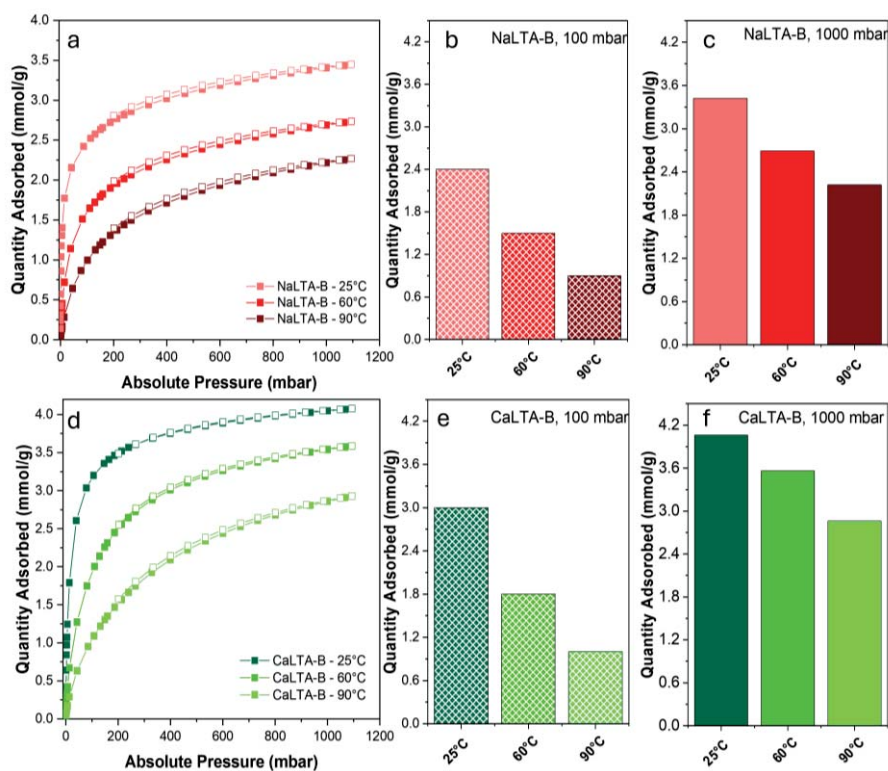


Figure 4.6. CO₂ adsorption/desorption isotherms at 25°C, 60°C and 90°C of NaLTA (a), CaLTA (d) in beads form. Quantity adsorbed in mmol_{CO₂}/g_{adsorbent} at 100 mbar absolute pressure at 25°C, 60°C and 90°C of NaLTA (b) and CaLTA(e). Quantity adsorbed in mmol_{CO₂}/ g_{adsorbent} at 1000 mbar absolute pressure and 25°C, 60°C and 90°C of NaLTA (c) and CaLTA(f). The figure is adapted from reference 4.

The CO₂ capture capacity of the materials was also investigated by performing a secondary adsorption run at 25°C, to study the reversibility of the process and evaluate the possible real use in cyclic adsorption/desorption experiments (Figure 4.7). After collecting the primary CO₂ isotherm at 25°C, the samples were outgassed for 1h at 25°C and a secondary isotherm was collected at the same temperature. The irreversibly adsorbed CO₂ fraction, which was not possible to eliminate by a simple outgassing, can be computed by evaluating the difference between the primary and the secondary isotherms. The primary and the secondary isotherms of NaLTA-B did not completely overlap and a decrease in CO₂ adsorption capacity of -4.7% at 1000 mbar was observed. On the other hand, a total reversibility is observed for CaLTA. These results suggest that the ion exchange procedure with Ca²⁺ affects the overall adsorption capacity at 25°C and, in parallel, provides a full reversibility of the CO₂ adsorbed by the material. The slightly higher reversibility of CaLTA-B compared to NaLTA-B could be due to a lower limitation of

diffusion inside the CaLTA cages, as evidenced by both IR spectroscopy and BET analysis, as well as the probable presence of weaker adsorption sites in CaLTA, as suggested by the formation of the low energetically stable $\text{Ca}^{2+}(\text{CO})_2$ dicarbonyls formed by interaction with CO (Figure 4.4 b). It is worth highlighting that the cyclic adsorption capacity is strictly related to the possible regeneration conditions of the material and, therefore, it is of great importance for the use in real capture applications.

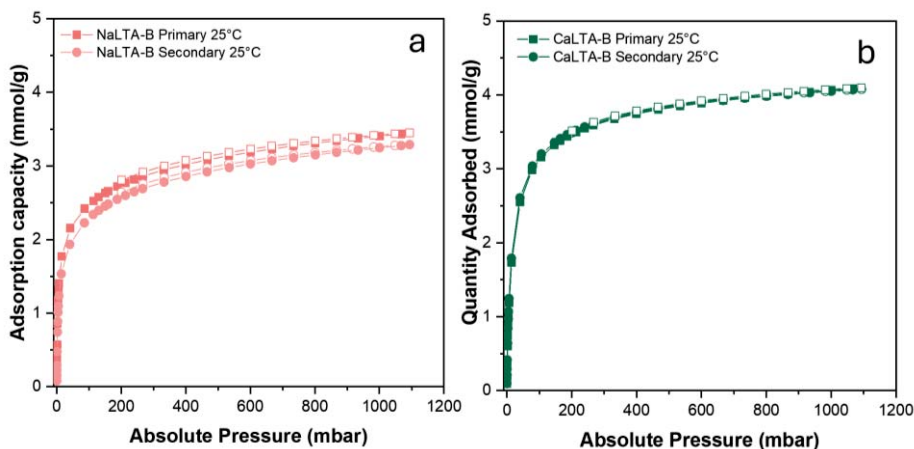


Figure 4.7. Primary and secondary CO₂ adsorption/desorption isotherms at 25°C of NaLTA (a) and CaLTA (b). The figure is adapted from reference 4.

Lastly, the isosteric heat of adsorption was evaluated for LTA samples by applying equation 4.1 reported on the isotherms collected at 25°C, 60°C and 90°C, in the 0.2 - 2 mmol/g range of quantity adsorbed (Figure 4.8). This isosteric heat of adsorption (Q_{st}), also reported as the opposite of the isosteric enthalpy of adsorption ($-\Delta H_{ads}$), is the heat released when an adsorptive molecule interacts with a surface site.²⁵ The Q_{st} curves of NaLTA and CaLTA show a quite flat and constant trend, between 54-50 kJ/mol and 44-40 kJ/mol respectively. The lower isosteric heat of CaLTA sample testifies the weaker interaction between CO₂ and the Ca^{2+} cations compared to Na^+ , perfectly in agreement with the total reversibility displayed by this material upon a secondary CO₂ adsorption and the lower stability of dicarbonyls formed by interaction of CaLTA-B with CO (Figure 4.7 and 4.4 b, respectively).

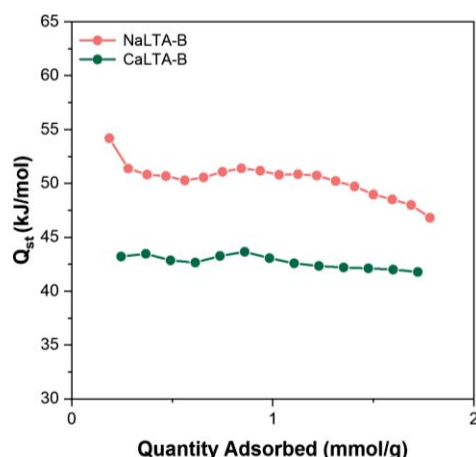


Figure 4.8. Isosteric heat of CO_2 adsorption (Q_{st}) as a function of the quantity adsorbed, calculated from the isotherms at 25°C, 60°C and 90°C. The figure is adapted from reference 4.

All the previously reported data were collected with pure CO_2 in a static environment. However, the possible applications of those materials as adsorbents rarely require capture in static conditions. For this reason, dynamic adsorption experiments under 90:10 N_2/CO_2 flow, trying to mimic post combustion conditions, were also performed (Figure 4.9 a and c). The results are shown in Figure 4.9, where the CO_2 adsorption capacities of the materials at different temperatures (25°C, 60°C and 90°C, i.e., the same temperatures employed for the static experiments with pure CO_2) are reported as a function of time. The breakthrough curves are compared with the “blank” test, namely the reactor without the adsorbent material. As expected, by increasing the temperatures, the adsorption capacities decrease causing a shift of the breakthrough curves to shorter times. Similarly to what was carried out for volumetric measurements the corresponding adsorption capacity is reported in the histograms of Figure 4.9 b and d. As for static experiments, also in this case the sample with the higher adsorption capacity is CaLTA-B, capturing about 3.3 mmol/g at 25°C, compared to 3.1 mmol/g of NaLTA-B. However, as previously observed the difference in uptake between the two samples decreased with the temperature. As a matter of fact, both samples show a CO_2 adsorption capacity of 2.4 mmol/g at 60°C and of 1.7 and 1.5 mmol/g at 90°C for NaLTA and CaLTA, respectively. By comparing the breakthrough measurements with the volumetric isotherms at 100 mbar of pure CO_2 , some differences in the computed amount of CO_2 adsorbed are detectable, even if the trend among samples at the different temperatures is substantially the same (see

Figure 4.6 b and a and Figure 4.9 b and d). The reason for such variations could be due to the different experimental set-up (one working under a N_2 - CO_2 flow, the other one working under equilibrium conditions with pure CO_2).

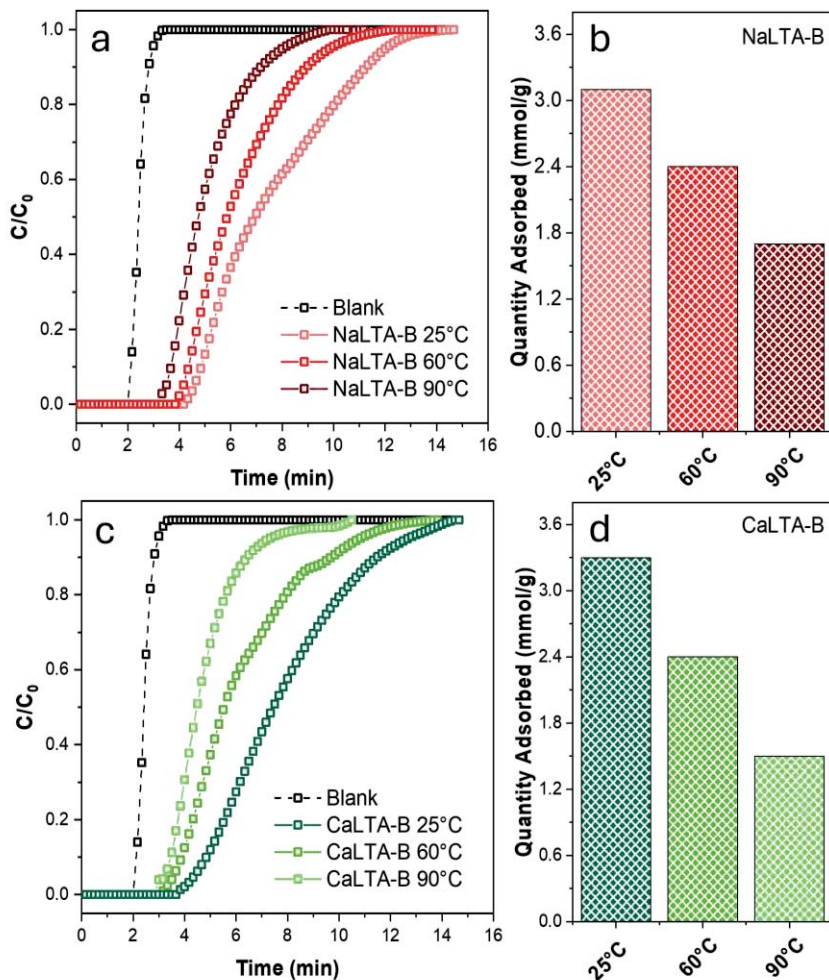


Figure 4.9. CO_2 breakthrough adsorption curves over the time at 25°C, 60°C and 90°C of NaLTA (a) and CaLTA (c). Computed adsorption capacity ($mmol_{CO_2} g^{-1}_{adsorbent}$) at the different temperatures for NaLTA (b) and CaLTA (d). The measurements were performed and kindly provided by Dr. M. Dosa under the supervision of Prof. M. Piumetti (Polytechnic University of Torino). The figure is adapted from reference 4.

In conclusion, both NaLTA-B and CaLTA-B show suitable CO_2 adsorption performances under both static and dynamic conditions over a wide temperature range. They also possess some other desirable characteristics such as low cost and reversibility under mild regeneration conditions. Between the two samples, CaLTA

shows the highest uptake at 25°C, but as the temperature increases, in both static and dynamic conditions, the difference in uptake between the two samples decreases until reaching very similar values in static conditions at 90°C and 100 mbar (0.9 mmol/g for NaLTA-B, 1 mmol/g for CaLTA-B, Figure 4.6 b and e) and even higher CO₂ uptake of NaLTA-B with respect to CaLTA-B in dynamic (1.7 mmol/g and 1.5 mmol/g at 90°C for NaLTA and CaLTA respectively, Figure 4.9). For this reason, in the next step, which consists in investigating the possibility of synthesising an LTA zeolite for direct ink writing, only NaLTA was considered for the moment, even though it would be interesting to explore CaLTA in the future.

4.3 Binderless 3D LTA monoliths

As highlighted in the introduction, another approach to further enhance the properties of solid adsorbents for more practical applications is to shape them into alternative configurations, as for example monolithic structures. These self-standing structures offer several advantages over conventional packing systems such as pellets, beads or granules. They improve overall performance by reducing pressure drops and improving mass and heat transfer characteristics, ultimately leading to a more cost-effective and efficient capture technology. Additionally, monoliths are structured materials having parallel gas flow channels with controllable shape, diameter and density per cross-sectional area.²⁶ However, one of the main challenges lies in maintaining unchanged the CO₂ capture capacity when passing from conventional systems like powder or beads to monoliths.

In this regard, after studying the NaLTA and CaLTA in both powder and beads form, we started a collaboration with the Advanced Ceramics and Glasses group of University of Padova, specialised in additive manufacturing techniques. In particular, Dr M. D'Agostini under the supervision of Prof. G. Franchin and Prof. P. Colombo has worked on the development of a synthesis protocol for the direct ink writing of NaLTA. Prior to the development of the ultimate synthetic protocol (reported in paragraph 4.1 and subject of an Italian patent application)⁸, different tentative were performed to optimize the procedure of synthesis. In particular, much effort was invested in the development of binderless monoliths, in which the only component beside the active phase is an additive used to achieve the appropriate rheological properties required for the printing process. The

experience gained in the characterisation of NaLTA and CaLTA in powder and beads form was particularly useful in driving the synthetic approach. The measurement of the accessibility of Na^+ cations in the zeolite structure by means of IR spectroscopy using CO as a molecular probe is sufficient to provide a first estimation of the availability of the material adsorption sites. Indeed as observed in the previous paragraph, when the cations inside the microporous cavities are full accessible to small molecules in the gas phase the interaction of CO with the NaLTA caused the appearance of a sharp band at 2163 cm^{-1} assigned to $\text{Na}^+\text{-CO}$ adducts, together with a shoulder at 2145 cm^{-1} due to CO molecules bridging two Na^+ ions (see Figure 4.4 a). On the contrary, in the absence of these signals, a partial or total inaccessibility of the Na^+ sites to CO_2 should be assumed, since its kinetic diameter is even smaller than that of CO ($3.76\text{ \AA}$ and $3.30\text{ \AA}$ for CO and CO_2 , respectively).²⁷ Consequently, since CO_2 adsorption generating both linear molecular species and carbonates occurs mainly in the cavities, a decrease in CO_2 uptake capacity is expected.²⁸ A proof of those considerations is reported in Figure 4.10 where IR spectroscopy using carbon monoxide (CO) as a molecular probe was performed on the first attempt of synthesis of NaLTA monoliths (Figure 4.10 a) and a CO_2 adsorption/desorption isotherm at 25°C was performed and compared with the one of NaLTA in beads form (Figure 4.10 b).

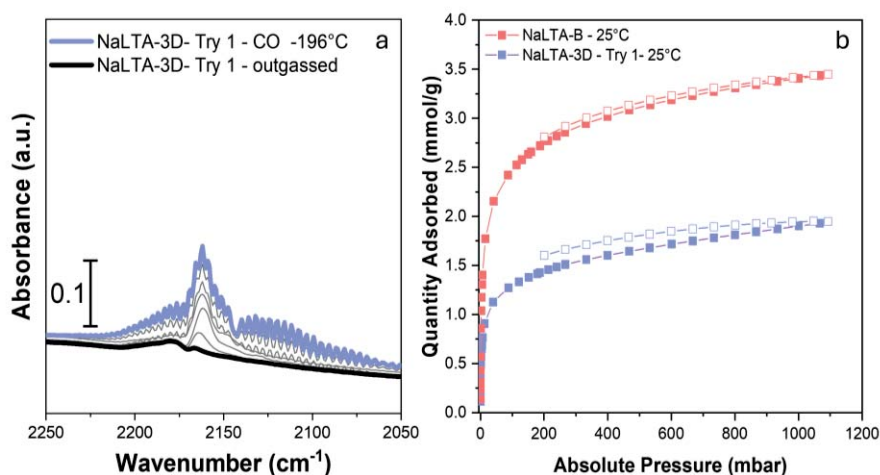


Figure 4.10. IR spectra of CO adsorption at -196°C on the first attempt of NaLTA-3D, recorded at different CO coverages and reported in the CO vibrational modes region (a) and CO_2 adsorption/desorption isotherms at 25°C of the first attempt of NaLTA 3D in comparison with NaLTA in beads form (b). In figure a coloured, grey and black curves represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively.

Contrary to what was observed in Figure 4.4 a, in these spectra the rotovibrational profile of the CO molecule in the gas phase is evident and only weak signal at 2163 cm^{-1} can be observed, suggesting the partial inaccessibility of the Na^+ sites. This hypothesis is confirmed by the much lower CO_2 uptake of this sample observed in the CO_2 adsorption-desorption isotherm at 25°C . In fact, this first attempt of synthesis reached only 1.91 mmol/g at 1000 mbar , $\sim 45\%$ less than the sample in beads form. The same characterisation approach was therefore carried out on the various synthesis attempts, in order to quickly discriminate the suitability of the synthesis process. While initially the inaccessibility of the active sites was probably due to the presence of fractions of amorphous samples and impurities (results not shown for the sake of brevity), once the correct crystallinity was achieved, the presence of the additive, which has to be included in the ink to ensure the correct density and good mechanical properties, was still responsible for hindering the full accessibility of the sites. Different thermal treatments were therefore performed on the samples and the IR characterization using CO at -196°C was carried out until the complete accessibility of the sites was achieved (results not shown for the sake of brevity). As mentioned in paragraph 4.1 the full accessibility of Na^+ sites was achieved through washing with DI water and a thermal treatment at 400°C for 10 h in air. Using this ultimate synthesis process and post-synthetic treatment, different monoliths were prepared, using also different geometries. In particular, three monoliths with Scaffold, Fractal and Hybrid geometries were developed in Padova by Dr M. D'Agostini under the supervision of Prof. G. Franchin and Prof. P. Colombo (Figure 4.11 a for the picture). The presence of LTA crystal structure was checked by means of XRD (Figure 4.11 b) which confirms the formation of the LTA topology in both the initial powder and the 3D-printed monoliths, with good stability after heat treatment up to 600°C . The pattern is indicative of a fully crystalline material and no major extraneous phases are observed, although three low intensity peaks (at 17.5° , 27.9° and 28.5°) can be discerned in the original LTA powder, which disappear in the 3D printed monolith. A possible explanation is that they may be due to a small amount of unidentified, unreacted Na-aluminosilicate species that are readily redissolved when the powder is added to the LTA synthesis gel to make the slurry for 3D printing, resulting in the final printed monoliths being composed entirely of LTA zeolite without any binder.

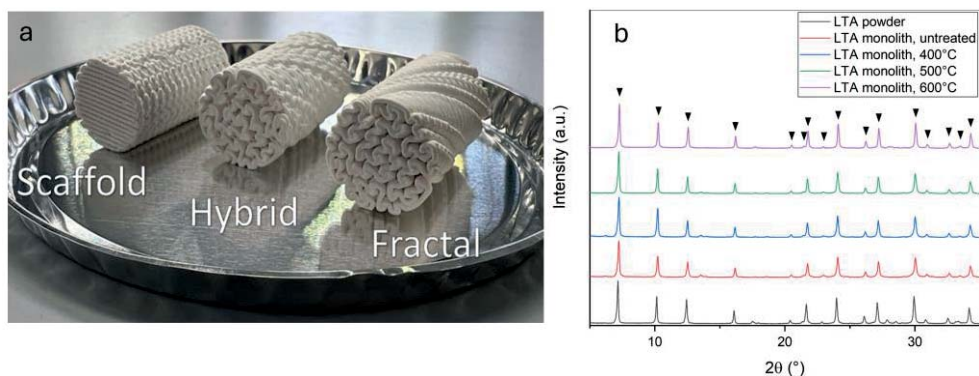


Figure 4.11. Picture of the different printed geometries of LTA binderless monoliths (a) and X-ray diffraction patterns of the original LTA powder and LTA monoliths at RT and after heat treatment at 400°C, 500°C and 600°C (b). The measurements were performed and kindly provided by Dr. M. D'Agostini (University of Padova).

The mechanical strength of the monoliths was also checked in Padova displaying a Weibull scale factor of 2.4 MPa, a value of compressive strength several times greater than what previously reported for LTA printed monoliths with comparable design and geometric porosity using bentonite clay as binder.²⁶

As mentioned above, evidence of the accessibility of adsorption sites in the LTA monoliths comes from *in situ* IR spectroscopy and also from the evaluation of the Specific Surface Area (SSA). (Figure 4.12 a and b).

Differently to what previously observed in Figure 4.10 a, the interaction of CO with the optimized NaLTA-3D monolith give rise to the appearance of the sharp band at 2163 cm^{-1} proving the accessibility of small molecules to Na^+ cations. Similarly, the SSA of the monoliths, carried out directly with CO_2 at 0°C , since the narrow microporosity of this zeolite prevents the evaluation of its textural properties with N_2 at cryogenic temperature, shows a value of $342\text{ m}^2/\text{g}$, only slightly lower than that of the commercial beads ($378\text{ m}^2/\text{g}$, Figure 4.5 c).

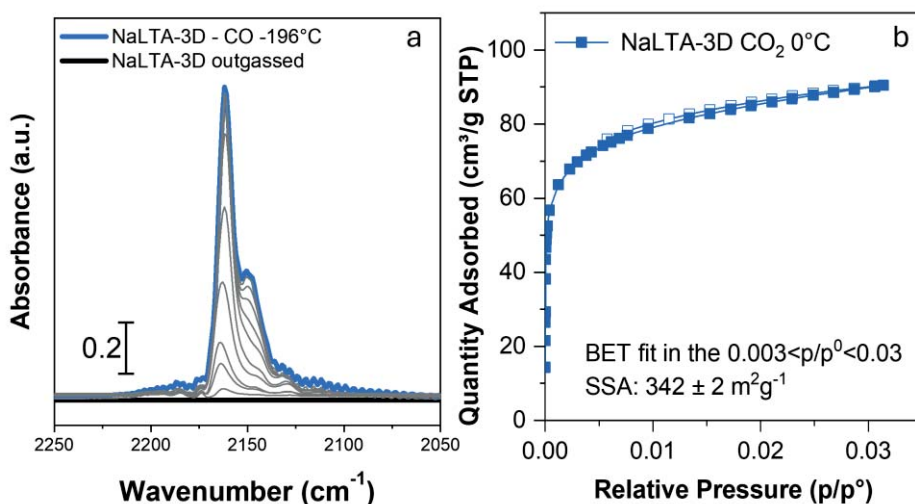


Figure 4.12. IR spectra of CO adsorption at -196°C on the NaLTA-3D, recorded at different CO coverages and reported in the CO vibrational modes region (a) and CO₂ adsorption/desorption isotherms at 0°C with the corresponding SSA evaluations (b). In figure a coloured, grey and black curves represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively.

In order to assess the uptake capacity of the material, the CO₂ adsorption/desorption isotherms of the monolith were collected at three different temperatures (25°C, 60°C and 90°C) and compared with the one previously measured for NaLTA in powder and beads form (Figure 4.13 a, d and g).

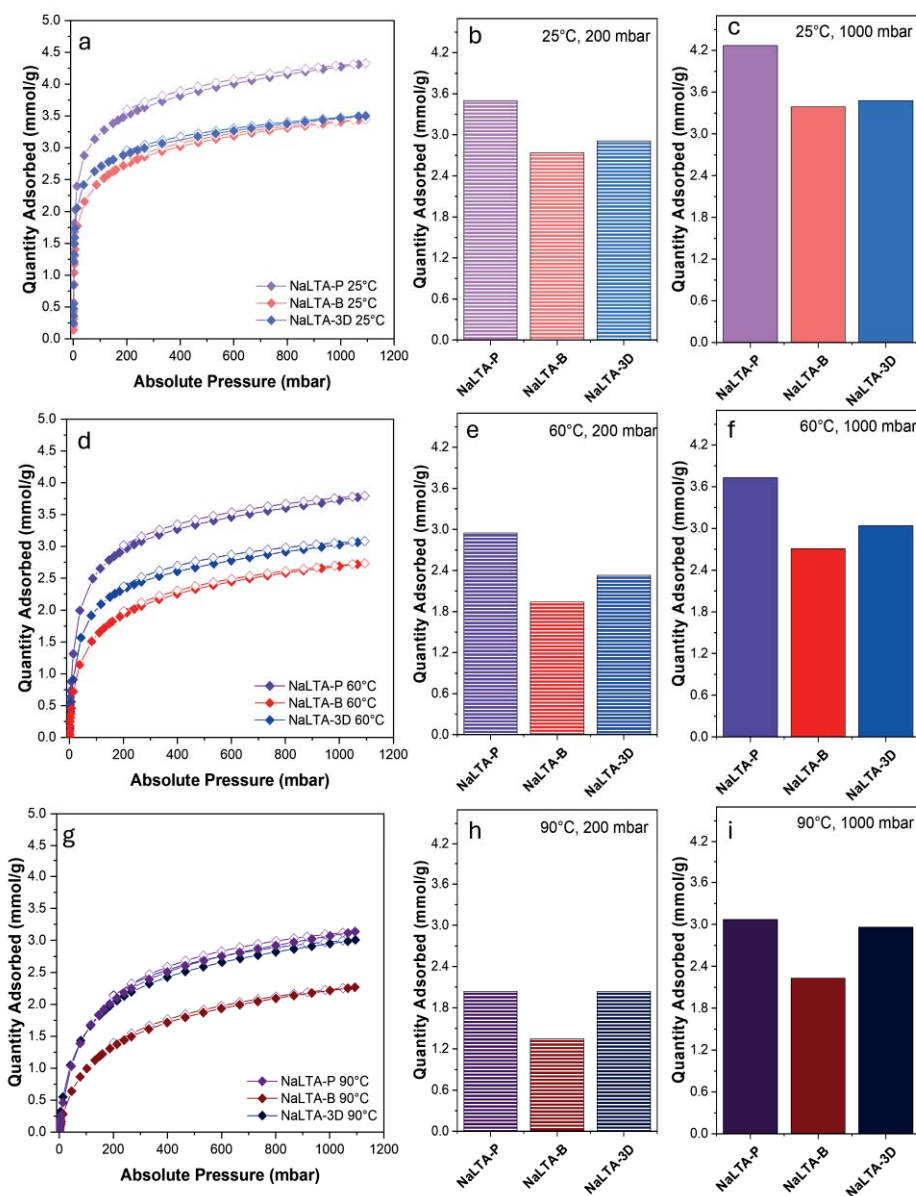


Figure 4.13. CO₂ adsorption/desorption isotherms of NaLTA in powder, beads and monoliths at 25°C(a), 60°C (d) and 90°C (g). Quantity adsorbed in mmol_{CO₂} /g_{adsorbent} at 200 mbar absolute pressure of the different samples at 25°C (b), 60°C (e) and 90°C (h). Quantity adsorbed in mmol_{CO₂} /g_{adsorbent} at 1 bar absolute pressure of the different samples at 25°C (c), 60°C (f) and 90°C (i).

For these measurements, the NaLTA monoliths with scaffold geometry were considered, but since the volumetric measurement is performed under static conditions, the shape of the material does not play a role in the adsorption capacity and the same results are expected with the different geometries. The adsorption capacities at 200 and 1000 mbar were also reported in the respective histograms (middle and right frames of Figure 4.13). It should be noted that, as also mentioned in chapter 3, 200 mbar is the CO₂ pressure used in the breakthrough curves with monoliths, as the CO₂ adsorption tests were carried out at 20 vol% CO₂ and not 10% due to set-up limitations. At 25°C, the powder sample has the highest CO₂ uptake at both 200 mbar and 1000 mbar, whereas the commercial beads and the 3D monolith exhibited almost identical adsorption/desorption isotherms (Figure 4.13 a, b and c). However, by increasing the temperature at 60°C, the beads showed the lowest adsorption/desorption (Figure 4.13 d). The decrease in CO₂ capture capacity of the commercial beads results to be much higher than the one displayed by NaLTA in powder and in monolith form. As a matter of fact, at 1000 mbar, the beads lost almost 20% of the adsorption capacity observed at 25°C, while the other two samples lost only ~13%. Similarly at lower pressures (200 mbar) the CO₂ capture loss for the beads is of ~30% and of ~16% and ~20% for the powder and the 3D samples, respectively. The different behaviour the NaLTA-B sample could be related to the presence of an unknown binder in the commercial beads which affects the CO₂ adsorption properties with respect to the pure powder and the binderless monolith. Interestingly, when the temperature was further increased to 90°C, the monolith achieved almost the same CO₂ capture capacity of the powder at both 200 mbar and 1000 mbar, showing a much better performance than the commercial beads (Figure 4.13 g, h and i).

Lastly, the breakthrough experiments were then carried out using a 20:80 %vol CO₂/He. It should be noted that in order to carry out these measurements a new different set specifically customised for the monoliths was developed. Therefore, some parameters such as the carrier gas, which is He instead of N₂, and the CO₂ pressures have been modified with respect to the conditions previously used and adapted to some limitations present in the new setup (see Chapter 3 for specific information).

Firstly, LTA beads were tested as reference at 60°C and 90°C (Figure 4.14 a and b). Contrary to the volumetric measurement, the breakthrough experiments on monoliths were not performed at 25°C due to the difficulty of maintaining a

constant temperature close to room temperature with the new setup customized for the monoliths, which could lead to errors due to temperature fluctuations. The reactor was filled with a volume of sample comparable to the 3D printed monoliths (around 30 mm of height), resulting in 5,25 g of beads. After this test the breakthrough curves of the monoliths having three different geometries were collected (Figure 4.14 c-f)

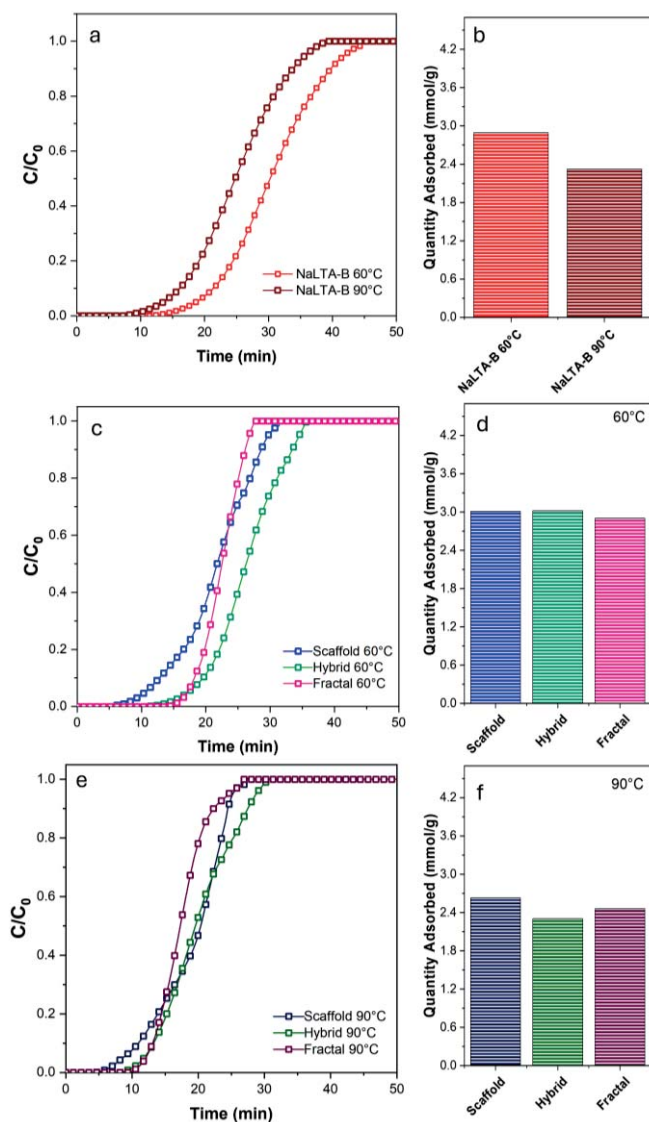


Figure 4.14. CO₂ breakthrough adsorption curves displayed as a function of time of NaLTA beads (a) and NaLTA monoliths having different geometry at 60°C (c) and 90°C (e) and the corresponding computed adsorption capacities (mmol_{CO2} g⁻¹_{adsorbent}) (b, d and f).

In the case of NaLTA-B, the expected decrease of the breakthrough time with the temperature was observed, passing from 42 minutes at 60°C to 35 minutes at 90°C. Consequently, the adsorption capacity decreased from 2.89 mmol/g at 60°C to 2.32 mmol/g at 90°C. It is worth noting that, since the saturation time depends on the amount of sample in the reactor, the one obtained with the previous setup

(Figure 4.9), in which a smaller amount of sample was used, was much lower than the one measured in this case. By comparing the breakthrough measurements with the corresponding volumetric isotherms at the same CO₂ relative pressure (200 mbar), the quantitative values obtained by the dynamic measurements are slightly higher than the static ones (Figure 4.13 b, e and h and Figure 4.14 b, respectively). The variation could be due to the different experimental conditions employed in the two setups (equilibrium/static versus flow measurements). An evaluation of the adsorption kinetics could be done based on the shape of the breakthrough curves. For both curves, the slope remains similar indicating that the adsorption mechanism is not influenced by the temperature. The steepness of the curve is not particularly pronounced, meaning that the diffusion of the gas through the reactor is probably hindered by the packaging of the beads.

The three LTA monoliths having different geometries were then tested. At 60°C the adsorption capacity is very similar with a value of 3.01, 3.02 and 2.90 mmol/g for scaffold, hybrid and fractal geometry respectively. A similar trend is maintained at 90°C with adsorption values of 2.63, 2.30 and 2.46 mmol/g.

A preliminary comparison with commercial LTA beads is possible by evaluating the adsorption capacity: at both temperatures, the monoliths exhibit equal or slightly higher values compared to the commercial sample, highlighting the potential of the 3D-printed materials. In particular, all three monoliths showed a higher CO₂ uptake than the beads at 60°C (2.89 mmol/g), while at 90°C only the scaffold and fractal monoliths showed a higher uptake than the beads sample (2.32 mmol/g). Regarding adsorption kinetics, as expected, variation in printing geometries results in different performance outcomes. For both temperatures, the fractal monolith presents a steeper breakthrough curve, indicating a higher adsorption rate and suggesting potentially greater permeability and lower pressure drops for this geometry. Conversely, the other two geometries exhibit a less pronounced breakthrough curve, implying that the gas mixture encounters greater resistance when it flows through the column. It leads to an inhomogeneous saturation of the column and to a more pronounced “S” shape of the curve. Some final considerations can be made by comparing the curves of the monoliths with those of the NaLTA-B. The fractal monolith has a steeper curve and lower breakthrough time than the NaLTA-B, underlining the potentiality of this latter geometry over the commercial beads. On the other hand, both the Scaffold and Hybrid geometries show breakthrough times and slope more similar to the commercial beads, although with some differences: scaffold has the same breakthrough times

as the NaLTA-B but a smaller slope, while Hybrid has the same slope but longer breakthrough times. These initial results may indicate the superiority of the fractal geometry over the commercial beads, but further kinetic studies need to be carried out to confirm this initial supposition.

4.4 Concluding remarks and future perspectives

In conclusion, LTA was selected due to a combination of affordable price and good adsorption capacities observed in case of sample in powder form (from 4.1 to 3.0 mmol/g at 1 bar in the $25^{\circ}\text{C} \leq T \leq 90^{\circ}\text{C}$ range). Due to those interesting characteristics the study of the material was extended firstly, to LTA in beads form (NaLTA-B and CaLTA-B) and then to monoliths synthesised by Direct Ink Writing technique (NaLTA-3D). The LTA-B were studied in their raw form, having Na^+ as extra-framework cations, and after ion exchange with Ca^{2+} in order to possibly increase the CO_2 adsorption capacity. The success of the exchange procedure was proved by means of EDX analysis, while XRD patterns highlighted the preservation of the crystalline structure. IR spectroscopy was used to investigate the accessibility of the different ions present inside the microporous structure as well as the strength of their interaction with the adsorbates. The specific surface area of the materials, measured using both N_2 and CO_2 , showed that CaLTA was accessible material for N_2 molecules, while NaLTA was accessible only to CO_2 suggesting a great selectivity of the materials toward CO_2 . Their potential application as solid CO_2 adsorbents was investigated by collecting both pure CO_2 adsorption/ desorption isotherms and breakthrough curves under a N_2/CO_2 flow in the 25°C - 90°C temperature range. Both the isotherm and the breakthrough curves of the materials exhibit a similar trend in CO_2 capture capacity with small discrepancies due to the different experimental conditions.

In conclusion, the NaLTA monoliths were successfully synthesized using different geometries. The insight gained from the advanced characterisation of beads and powder LTA samples was particularly useful in assessing the availability of the active sites for CO_2 interaction in the new shaped materials, so driving the optimal synthesis procedure. Static adsorption measurements performed on the monoliths assessed a CO_2 capture capacity comparable to, or even exceeding, that of commercial beads at high temperatures. Moreover, similar adsorption properties

in dynamic conditions were observed for both beads and monoliths. The different geometries explored in this study exhibited comparable adsorption capacities, with different kinetics. These promising results pave the way for further advancements in both synthesis and characterisation of LTA monolithic samples.

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5. CO₂ CAPTURE IN MOFs: THE CASE OF F4 MIL-140A (Ce)

Along with the zeolites discussed in the previous chapter, Metal Organic Frameworks (MOFs) are considered promising candidates as solid adsorbents for CO₂ capture.¹ As mentioned in Chapter 2, the main feature of these materials is the tunability of their structure, which has led to the synthesis of different frameworks, including the so-called "phase-change" or flexible MOFs, which are of particular interest for gas separations because they exhibit a steep gas uptake when a threshold partial pressure of a given adsorbate is reached, with potential advantages in terms of achievable working capacity, selectivity and energy efficiency.^{2,3} In this regards, an ultramicroporous MOF based on Ce^{IV} and tetrafluoroterephthalate (F4 MIL-140A(Ce)), was recently synthesised in mild conditions and in aqueous medium and tested for CO₂ capture showing a non-hysteretic step-shaped CO₂ adsorption isotherm, with steep uptake increase at pressure < 0.2 bar at 25°C.⁴ Such a behaviour was not observed when the MOF is exposed to other gases, e.g., N₂ or C₂H₂, proving this material possesses a high CO₂/N₂ selectivity and a reverse CO₂/C₂H₂ selectivity. The combination of these unique properties makes it crucial to understand the mechanism of CO₂ adsorption in order to develop new materials with the same operating principle, but with enhanced separation performances. For this reason, in the present chapter F4 CeMIL-140A(Ce) synthesised by Prof. M. Taddei at University of Pisa was deeply characterized to unveil the mechanism behind the flexibility of the MOF in both dry and humid conditions. Also in this case, particular attention has been paid to the shaping and a first attempt to produce 3D printed monoliths was also carried out by the group of Prof. P. Colombo in Padova. The 3D MOF was deeply characterized as well to understand if the flexible behaviour of F4 MIL-140A(Ce) could be preserved in the self-standing composite.

The characterization of F4 CeMIL-140A(Ce) and the study of the mechanism of CO₂ adsorption reported in paragraph 5.2 is extensively based on the publication: "Cavallo, M.; Atzori, C.; Signorile, M.; Costantino, F.; Venturi, D. M.; Koutsianos, A.; Lomachenko, K. A.; Calucci, L.; Martini, F.; Giovanelli, A.; Geppi, M.; Crocellà, V.; Taddei, M. Cooperative CO₂ Adsorption Mechanism in a Perfluorinated Ce^{IV}-Based Metal Organic Framework. *J. Mater. Chem. A* 2023, 11 (11), 5568–5583". On the

other hand, the study of the CO₂ adsorption mechanism in the presence of H₂O and the shaping of the MOF reported in paragraph 5.3 are still ongoing activities.

5.1 Materials and methods

F4 MIL-140A(Ce) was synthesized by Prof. M. Taddei (University of Pisa) following the procedure previously reported by Shearan et al.⁵ F4 MIL-140A(Ce) is built from the connection of one-dimensional inorganic building units, made up of octacoordinated Ce^{IV} ions, carboxylate groups belonging to the linker and μ_3 -O species, via the perfluorinated aromatic rings of the linker. This structure features narrow triangular channel-like pores lined with the fluorine atoms belonging to the linkers (Figure 5.1 a). F4 MIL 140A(Ce) contains one water molecule per Ce atom, located in the proximity of the metal atom and at distances compatible with a number of non-covalent interactions with the organic linker (Figure 5.1 b).

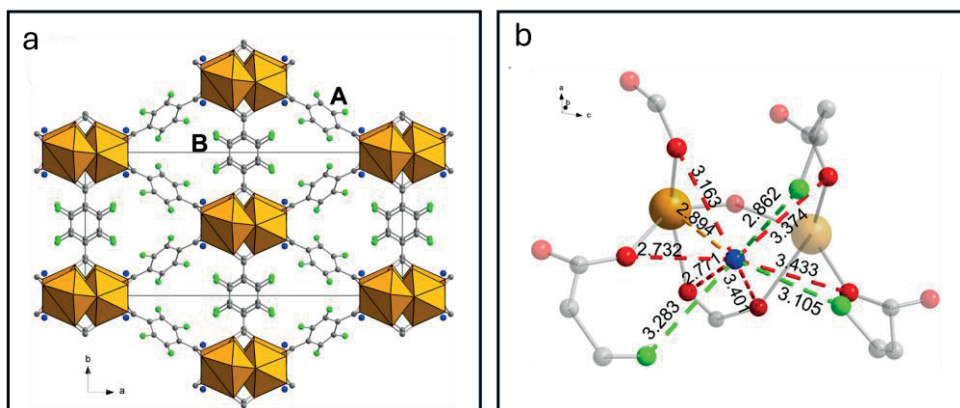


Figure 5.1. Crystal structure of as-synthesised F4_MIL-140A(Ce) viewed along the crystallographic c axis (a) and local environment around the water molecule (b). In (a), the two crystallographically independent linkers sitting on an inversion centre and on a two-fold axis are identified with A and B, respectively. In (b), a threshold distance of 3.5 Å between the O atom of water and surrounding atoms was chosen to identify possible interactions, represented as dashed lines having the same colour of the interacting atom. Non-interacting atoms in (b) are shaded. Colour code: Ce, orange; F, green; C, grey; O, red; H₂O, blue. H atoms are not shown because the structure was determined from PXRD data. The structures were obtained by Prof. M. Taddei and the figure was adapted from reference 6.

High pressure CO₂ adsorption-desorption isotherms up to 5 bar were measured with a Quantachrome iSorb High Pressure Gas Analyser at 25, 40, 55 and 70 °C by Prof M. Taddei. About 200 mg of sample was used for the adsorption studies. The sample

was degassed at 120 °C under dynamic vacuum for 12 h prior to analysis and at 120 °C for 1 h in between subsequent measurements. The isosteric heat of adsorption (Q_{st}) was extracted using the linear version of the Clausius-Clapeyron equation in the loading range 0.1-2.2 mmol/g (see Equation 4.1).

N₂, Ar and CO₂ physisorption isotherms were collected on a Micromeritics ASAP 2020 at -196 °C, -186 °C and 0 °C, respectively, as previously described in Chapter 3. Prior to the measurement, the sample was heated overnight at 120°C under vacuum. Specific surface areas were determined by using the Brunauer–Emmett–Teller (BET) method, following the Rouquerol consistency criteria.⁷ Cumulative pore volume and pore size distribution were derived from adsorption isotherms by applying the NL-DFT method (see Table 5.1 for specific information). The linear BET fit is not reported for sake of brevity

In situ IR spectroscopy was performed on a Bruker Vertex 70 (see Chapter 3 for further information). Before the analysis, F4 MIL-140A(Ce) was evacuated in vacuum at 120°C for 12 h. Both CO and N₂ adsorption at cryogenic temperature were studied following the procedure previously reported in Chapter 3. H₂O adsorption was carried out by sending incremental doses of H₂O (from 0.1 to 20 mbar) at beam temperature on the fully evacuated F4 MIL 140A(Ce). The CO₂ interaction with F4 MIL-140A(Ce) was studied by sending increasing CO₂ doses on the sample at beam temperature, after applying the same activation procedure previously described. The increasing doses of CO₂ were chosen to be compatible with the equilibrium pressures involved in the adsorption/desorption isotherm at 40 °C which is approximately the temperature of the IR beam.

The molar differential heat of CO₂ adsorption was experimentally evaluated on F4 MIL-140A(Ce) by means of a heat flow microcalorimeter (Calvet C80 by Setaram) connected to a high-vacuum ($\approx 10^{-4}$ mbar) glass line equipped with a Varian Ceramicell 0-100 mbar gauge and a Leybold Ceramicell 0-1000 mbar gauge. The sample was evacuated in vacuum at 120°C for 12 h before being placed into the calorimeter under isothermal conditions. The measurement was performed at 30°C by following a well-established step-by-step procedure described elsewhere.⁸ *In situ* IR spectroscopy following CO and CO₂ interaction with the sample was repeated on a partially evacuated F4 MIL-140A(Ce) (i.e. evacuated in vacuum at RT for different times) using the same condition previously described to understand the mechanism of adsorption under “wet” conditions. CO₂ adsorption/desorption isotherms up to 1.1 bar were also measured with a Micromeritic 3Flex at 30 °C on a partially

evacuated sample. Some specific measurement conditions were adopted to perform this study: (i) leak test time of 2s (ii) samples outgassed *in situ* at room temperature for different times and weighed before performing the measurement.

Lastly, a first attempts of shaping have been performed by Dr. M. D'Agostini (University of Padova) through Direct Ink Writing using 60% of F4 MIL-140A(Ce) and 40% of Na Bentonite as binder. In order to assess the possibility of obtaining a patent on the shaping methodology, the details of the synthesis and shaping process will not be discussed in the present thesis. *In situ* IR spectroscopy using CO as a molecular probe on the different powder components and on the 3D MOF, previously ground into powder, was performed using the same methodology previously discussed. All the materials were previously evacuated at 120 °C for 12 h. CO₂ adsorption/desorption isotherms at 25 °C were collected on the same samples with a Micromeritics ASAP2020, using the same activation procedure.

5.2 Unveil the mechanism of CO₂ adsorption in F4 MIL-140A (Ce)

Firstly, CO₂ adsorption/desorption volumetric isotherms of F4 MIL-140A (Ce) were collected at 25, 40, 55 and 70 °C in the 0-5 bar pressure range to study the pure CO₂ adsorption capacity of the material (Figure 5.2 a). All the isotherms exhibit a peculiar step, which progressively moves to higher pressure by increasing temperature. Additionally, the pressure range over which saturation occurs becomes broader. The maximum amount of adsorbed CO₂ on F4 MIL-140A(Ce) is around 2.6 mmol/g at 25 °C and 5 bar and shows the usual decrease upon increasing the temperature (2.2 mmol/g at 70 °C and 5 bar). The isosteric heat of adsorption (Q_{st}), extracted from the fitted isotherms using the linear version of the Clausius-Clapeyron equation (Figure 5.3 b), ranges between 35 and 45 kJ/mol.

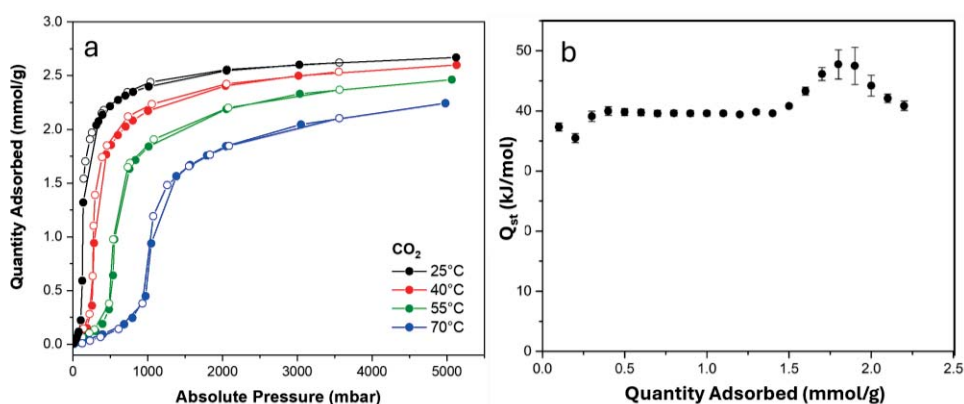


Figure 5.2. Adsorption/desorption isotherms collected on F4 MIL-140A(Ce) at 25°C (black), 40°C (red), 55°C (green) and 70°C (blue) up to 5000 mbar (a) and plot of isosteric heat of CO₂ adsorption (Q_{st}) versus loading obtained from the isotherms (b). The “bump” between 1.5 and 2.0 mmol/g loading is probably an artefact originating from the uncertainty in the fitting in that region, where the isotherms display a change of gradient near saturation and few or no experimental data are available. The measurements were performed by Prof. M. Taddei and the figure was adapted from reference 6.

The sharp uptake of gas (i.e. the isotherm step) moves to higher pressures by increasing the temperature. This peculiar adsorption feature allows easily adapting the phase transition mechanism of this MOF to the partial pressure of common post-combustion streams. Additionally, this characteristic isotherm is known to be particularly suitable for adsorption processes thanks to the large working capacity that can be achieved upon small swings in temperature and/or pressure. Such step-shaped isotherms have previously been observed in other MOFs exhibiting higher CO₂ adsorption capacities at saturation, as in the amine-appended Mg₂(dobpdc)³ (3.4 mmol/g at 25 °C and 5 bar) and in ELM-11 (3.6 mmol/g at 25 °C and 0.3 bar)⁹. However, in the former case, the material displays a much higher isosteric heat of CO₂ adsorption (around 70 kJ/mol), whereas in the latter the phase transition occurs in a higher pressure range (0.3 bar at 0 °C). This leads, on one hand, to stronger interactions and, consequently, to higher regeneration energies and, on the other hand, to a small adsorption of CO₂ at low pressures. To further investigate the peculiar adsorption mechanism of F4 MIL-140A(Ce), its textural properties were accurately studied by collecting low pressure adsorption/desorption volumetric isotherms using three different adsorptives: N₂ at -196°C, Ar at -186°C and CO₂ at 0°C (Figure 5.3 and Table 5.1). The isotherms were measured consecutively using the same MOF powder. Therefore, the differences observed with the selected probe molecules can be attributed to the nature of the probe molecule at the analysis temperature.

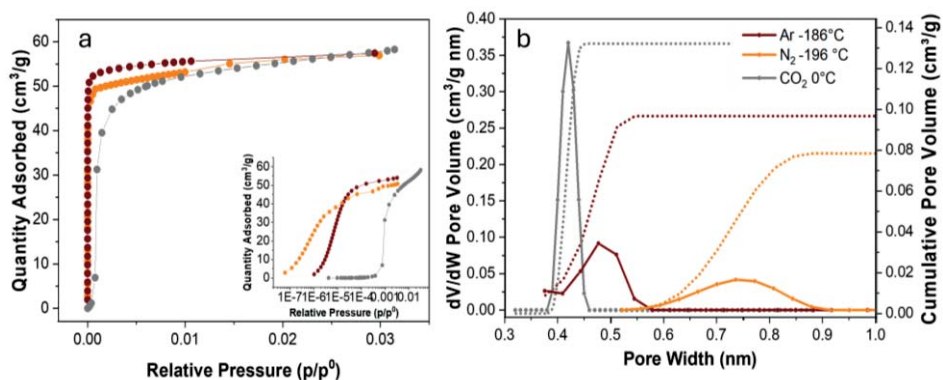


Figure 5.3. Volumetric adsorption isotherms in the $0 < p/p^0 < 0.03$ pressure range (semi-logarithmic isotherms in the same pressure range displayed in the inset) of: Ar at -186°C (dark red), N_2 at -196°C (orange) and CO_2 at 0°C (grey) on F4 MIL-140A(Ce) (a) and pore size distributions (solid line) and cumulative pore volume (dotted line) computed by NL-DFT on the same isotherms (b). The figure is adapted from reference 6.

Ar and N_2 at cryogenic temperature show the typical type I(a) isotherm characteristic of microporous materials, while CO_2 at 0°C exhibits the less common step-shaped isotherm specific of the so-called “phase change” adsorbents (Figure 5.3 a), in agreement with the previous results reported by D’Amato et al.⁴ The semi-logarithmic isotherms reported in the inset of Figure 5.3 a show that the pore filling with Ar occurs at higher relative pressure regions compared to N_2 . The difference in relative pressures becomes more significant if the MOF possesses open metal sites, highlighting the advantage of using monoatomic inert Ar for the characterization of ultramicroporous MOFs. The BET specific surface area (SSA) values (Table 5.1) display an incremental trend, suggesting a different interaction of the molecules with the material.

Table 5.1. Textural Properties of F4 MIL-140A(Ce) evaluated by means of three different molecular probes: Ar at -186°C, N₂ at -196°C and CO₂ at 0°C. Adapted from reference 6.

Probe	Temperature (°C)	BET SSA (m ² /g)	Micropore volume (cm ³ /g)	Micropore size (nm)
Ar	-186	213.8 ± 0.3 ^a	0.096 ^c	0.48 ^f
N ₂	-196	244.8 ± 0.7 ^a	0.083 ^d	0.74 ^g
CO ₂	0	262 ± 1 ^b	0.13 ^e	0.42 ^h

^a BET SSA were determined in the 0.0032 < p/p0 < 0.036 range, applying the Rouquerol consistency criteria.

^b BET SSA was determined in the 0.0028 < p/p0 < 0.031 range, applying the Rouquerol consistency criteria.

^{c,f} Calculated using the cumulative pore volume graph and the pore size distribution graph, respectively (Figure 5.3 b), obtained from NL-DFT analysis of the adsorption isotherm employing a cylindrical pore geometry and considering the model “NL-DFT- Argon on Oxides at 87 Kelvin” present in the Microactive software.

^{d,g} Calculated using the cumulative pore volume graph and the pore size distribution graph, respectively (Figure 5.3 b), obtained from NL-DFT analysis of the adsorption isotherm employing a cylindrical pore geometry and considering the model “N2 - Cylindrical Pores- Oxides Surfaces” present in the Microactive software.

^{e,h} Calculated using the cumulative pore volume graph and the pore size distribution graph, respectively (Figure 5.3 b), obtained from NL-DFT analysis of the adsorption isotherm employing a slit pore geometry and considering the model “CO2 – GCMC Carbon” present in the Microactive software.

The BET SSA obtained by Ar isotherm (213.8 m²/g) is lower compared to N₂ (244.8 m²/g). The spherical Ar molecules display a more ideal packing on the surface compared to diatomic N₂ molecules, whose orientation on the surface can be affected by the possible presence of open metal sites able to interact with N₂ itself. As a consequence, an uncertainty in the evaluation of the cross-sectional area of nitrogen gas is very likely, resulting in an overestimation of the computed BET area with this probe.^{10,11} The highest BET area value is the one derived from the CO₂ isotherm at 0 °C (262 m²/g), suggesting that a structural rearrangement might occur when F4 MIL-140A(Ce) interacts with CO₂, as highlighted by the peculiar step-shaped isotherm collected by using this molecule as adsorptive (Figure 5.2 a).

The pore size distribution (PSD) was also evaluated by applying the non-local density functional theory (NL-DFT) to the adsorption isotherms. It is well-known that the PSD computed by NL-DFT methods depends on the selected kernel of isotherms. However, despite the high number of MOF structures reported to date, proper DFT kernels to study the unique pore size and shapes of these microporous materials are still missing.¹¹ For this reason, the PSD data for MOFs should be considered as merely indicative of the intrinsic porosity of the investigated MOF. The PSDs computed from the three molecular probes are compared in Figure 5.3 b and Table

5.1. N₂, a non-ideal molecule for the analysis of microporous materials, gives the highest value (~0.74 nm), while Ar and CO₂ PSDs show the presence of a family of ultramicropores of around 0.48 and 0.42 nm diameter, respectively, values in better agreement with that estimated on the basis of the crystal structure of as-synthesised F4 MIL-140A(Ce) (0.48 × 0.58 nm, measured from the atomic centres).^{4,6} The result obtained with N₂ does not surprise, indeed it is known that this probe can significantly overestimate the PSD of MOFs with very small micropores, especially if the pore dimension is close to the kinetic diameter of the molecule (0.364 nm for N₂).¹¹ The micropore size obtained by both Ar and CO₂ is more reliable and the latter one results to be very narrow. This could be a further proof of a possible structural rearrangement of the material in the presence of CO₂, which allows the detection of the actual micropores size just with an adsorptive inducing a “phase change” adsorption. Still, it is worth noting that N₂ and Ar show a compatible micropore volume while CO₂ displays a higher value, which might be seen as a further proof of a structural transition caused by this molecule.

Significant information about the mechanism of CO₂ adsorption can be obtained from *in situ* IR spectroscopy. However, prior to this analysis the best evacuation condition of the material was investigated. As previously mentioned, in the as-synthesised F4 MIL-140A(Ce) one H₂O molecule per formula unit is present in the proximity of a Ce atom.⁴ Hydrogen bonding-like interactions are also likely to exist with F atoms and carboxylate groups from the surrounding organic linkers (Figure 5.1 b). According to thermogravimetric analysis, previously performed by D’Amato et al.,⁴ the removal of H₂O is completed at 150 °C, suggesting that it is strongly adsorbed. The evacuation process of F4 MIL-140A(Ce) was further investigated using *in situ* IR spectroscopy, observing that the activation at 120 °C for 12 h under vacuum was effective to remove the adsorbed H₂O before the spectroscopic experiments (see black spectrum in Figure 5.4). The evacuated F4 MIL-140A(Ce) was then exposed to increasing pressures of H₂O, observing significant changes in the IR spectrum, especially in the 3700-3500 cm⁻¹ and 800-770 cm⁻¹ spectral ranges (Figure 5.4 b and 5.4 c). It is worth noting that usually, the evolution of the spectra is followed after outgassing, but with this procedure, which also involves *ex situ* heating, some spectral changes could be lost. For this reason, to better follow the evolution of some specific bands, the experiment was carried out by sending incremental doses of H₂O vapour.

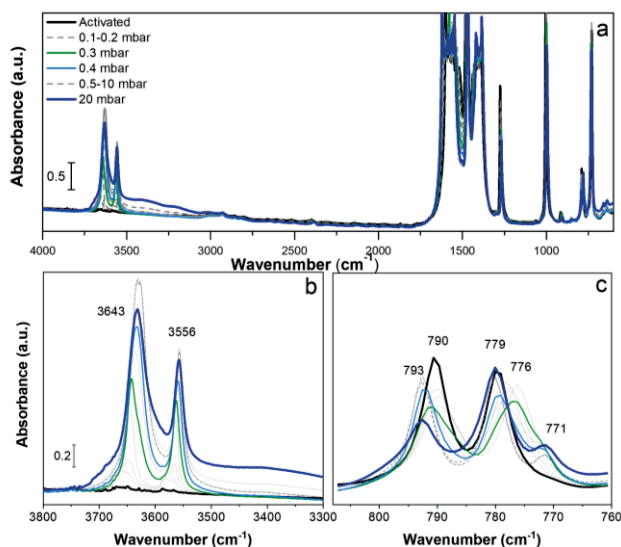


Figure 5.4. IR spectra of F4 MIL-140A(Ce) collected dosing 0.1-20 mbar of H₂O on the evacuated sample, reported in the full spectral range (a) and in the 3800-3300 cm⁻¹(b) and 810-760 cm⁻¹(c) regions. Adapted from reference 6.

In the former spectral region, two well-defined bands at 3643 and 3556 cm⁻¹ appear upon sending increasing H₂O doses. The presence of those peculiar narrow bands in the O–H stretching region is ascribable to the interaction of H₂O with specific acid sites.¹² In the 800-770 cm⁻¹ region, two initial bands at 790 and 779 cm⁻¹ are observed in the evacuated sample (see black spectrum in Figure 5.4 c). After sending 0.3 mbar of H₂O (corresponding to about 0.3-0.4% relative humidity, assuming a local temperature of around 40-45°C under the IR beam; vapour pressure of H₂O at 40°C is 74 mbar, at 45°C is 96 mbar) the 779 cm⁻¹ band shifts to 776 cm⁻¹, before going back to the original position upon further increasing the H₂O pressure. A new band at 771 cm⁻¹ also appears at high H₂O pressure. The 790 cm⁻¹ signal decreases until 0.3 mbar of H₂O, then it slowly shifts to 793 cm⁻¹, changing again its intensity. The spectral modifications observed upon H₂O contact in this region are probably due to changes occurring on the fluorinated rings. A more specific assignment of the bands present in those two spectral regions is provided by DFT calculations: in the high frequency region, the signals at 3643 and 3556 cm⁻¹ can be disambiguated as the O–H stretching mode of water forming distinct H-bonds with F atoms on aromatic rings and O atoms from carboxylates, respectively.⁶ The assignment of bands in the low frequency region is less trivial, due to the coupling of different vibrations generating complex vibrational modes. In a simplified view, the observed signals can be attributed to the out-of-plane bending modes of carboxylate groups

with respect to the aromatic rings. The coexistence of multiple features is explained by the presence of two crystallographically independent linkers (Figure 5.1), as well as from the perturbation induced by adsorbates on the linkers themselves. It is worth noting that the main changes in the 800-770 cm^{-1} spectral region were observed with a H_2O dose of 0.3 mbar (green curve in figure 5.4). This suggests that the exposure of the sample to a specific H_2O pressure is responsible for a sudden change in the structure, hinting at an adsorption process similar to the one displayed by CO_2 and possibly involving the same adsorption sites. This is supported by the very similar saturation loading for both CO_2 and water of about 2.5 mmol/g, corresponding to one adsorbate molecule per formula unit (in case of H_2O this latter results comes from the TGA analysis reported by D'Amato et al)⁴

In situ IR analysis using CO and N_2 as molecular probes at liquid nitrogen temperature was performed to further study the presence of Lewis acidic adsorption sites in the fully evacuated MOF (Figure 5.5)

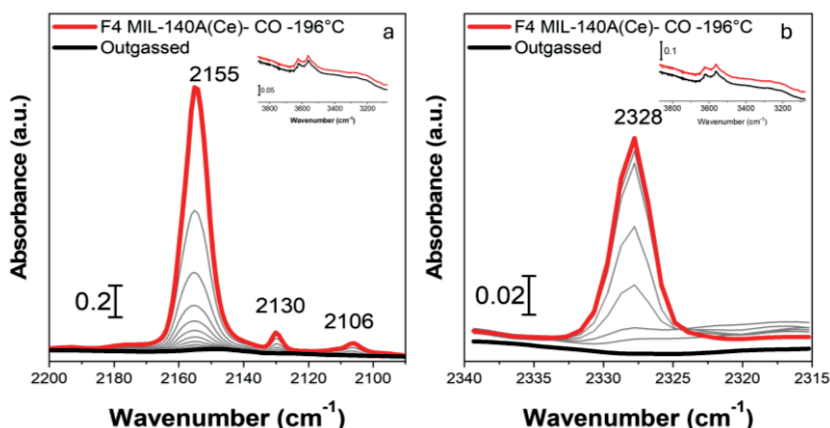


Figure 5.5. IR spectra of F4 MIL-140A(Ce) after adsorption of 60 mbar of CO at -196°C (a) and after adsorption of 60 mbar of N_2 at -196°C (b) and following outgassing. The spectra were plotted by subtracting the spectrum of the evacuated material. In the insets, the raw data of the corresponding hydroxyl stretching region is shown. The figure is adapted from reference 6.

The interaction of CO with F4 MIL-140A(Ce) at liquid nitrogen temperature (Figure 5.5 a) gives rise to three main bands at 2155, 2130 and 2106 cm^{-1} . The most intense band at 2155 cm^{-1} can be assigned to CO adsorbed on Ce^{4+} sites.¹³ Bands at similar frequencies have also been attributed to the interaction of CO with mildly acidic OH groups.^{14,15} However, the absence of changes in the OH stretching region at 3645 cm^{-1} suggests that the latter hypothesis is not realistic (see inset of figure 5.5 a). The weak band at 2130 cm^{-1} is tentatively assigned to CO interacting with Ce^{3+} sites,

whose presence in F4 MIL-140A(Ce) in small amounts was previously revealed,⁴ although another hypothesis is the presence of physisorbed CO into the pores which is usually reported to be in the 2145-2131 cm^{-1} region.^{14,16} Since the rate of disappearance of the band at 2130 cm^{-1} is the same as that of the 2155 cm^{-1} component upon CO desorption, and this is not the first signal that decreases in intensity, the latter hypothesis is to be considered unlikely. The band at 2106 cm^{-1} is due to the isotopic shift of the ^{13}C - ^{16}O interacting with Ce^{4+} . The ratio between the band at 2155 cm^{-1} and this latter one is 1.023, which is nearly equivalent to the isotopic shift factor reported in the literature.¹⁷

N_2 is a much weaker basic probe than CO and becomes IR active due to a decrease in symmetry caused by the interaction with Brønsted or Lewis acid sites. The interaction of N_2 at -196 °C with F4 MIL-140A(Ce) (Figure 5.5 b) causes the appearance of a band at 2328 cm^{-1} , whose assignment is not straightforward, due to the few data reported in the literature. Bands in the range 2332-2328 cm^{-1} are usually assigned to N_2 interacting with hydroxyls and are accompanied by the appearance of signals in the O-H stretching region.¹⁸ Since no significant changes are observed in this latter region, the 2328 cm^{-1} band probably testifies the interaction of N_2 with Ce^{4+} acidic sites. This last interpretation is in agreement with what previously assumed for CO bands and is a proof of a specific interaction of N_2 with the sample. The 2328 cm^{-1} value is in fact comparable to those observed for N_2 adsorbed on MIL-100(Cr) (2290 cm^{-1})¹⁹ and $\text{V}_2\text{Cl}_{2.8}(\text{btdd})$ (2342 cm^{-1}).²⁰ This result clearly demonstrates N_2 is not an inert molecular probe for a MOF with open metal sites and it could be responsible for the higher BET surface area measured with N_2 than with Ar (see Table 5.1).

Once these IR measurements showed that F4 MIL 140A(Ce) has accessible Ce^{IV} sites after H_2O removal, the interaction of the evacuated sample with CO_2 was investigated. Increasing CO_2 pressure in the range between 0.110 and 0.550 bar, at beam temperature (i.e., around 40 °C) were dosed to the activated sample. The CO_2 pressure range was accurately selected by considering the position of the step of the CO_2 isotherm collected at 40 °C (Figure 5.6).

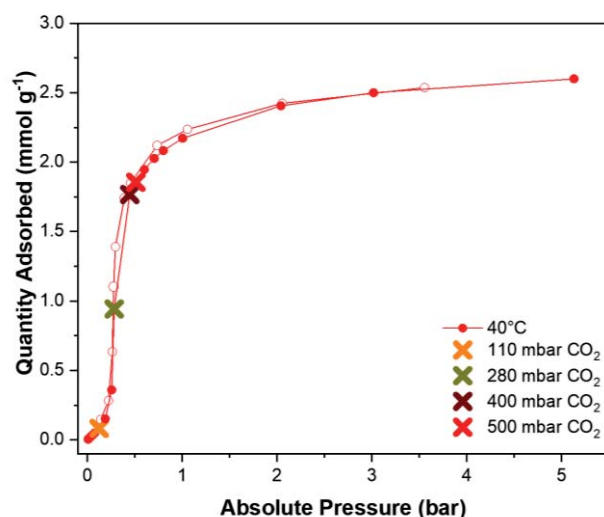


Figure 5.6. CO₂ adsorption/desorption isotherms collected on F4 MIL-140A(Ce) at 40 °C up to 5 bar in which are reported the pressure doses employed during the IR experiment (Figure 5.7). The figure is adapted from reference 6.

The incremental CO₂ doses are responsible for significant changes in the CO₂ asymmetric stretching region between 2400 and 2250 cm⁻¹ (Figure 5.7 a) and in the 800-770 cm⁻¹ spectral range (Figure 5.7 b).

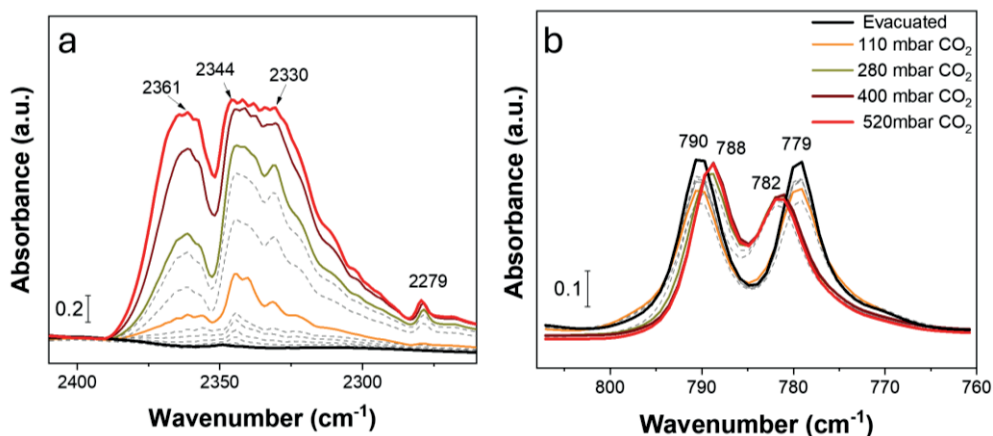


Figure 5.7. IR spectra of CO₂ adsorption on evacuated F4 MIL-140A(Ce) reported in the 2410-2260 cm⁻¹ (a) and 810-760 cm⁻¹ (b) spectral ranges. The same incremental pressure doses of CO₂ reported with coloured crosses in the volumetric isotherm of Figure 5.6 were employed during the IR experiment. Dashed line represents intermediate pressures. The figure is adapted from reference 6.

Upon sending CO₂ doses below the isotherm step (i.e., until around 0.110 bar), a new, quite broad band at 2344 cm⁻¹ appears, slightly shifted to lower frequencies

compared to the antisymmetric CO₂ stretching vibrational mode (at 2349 cm⁻¹). At the same time, no significant changes are detected in the low frequency region, showing only a slight decrease in intensity of the 790 and 779 cm⁻¹ bands. These spectral modifications suggest that, below the isotherm step, CO₂ weakly interacts with the sorbent, likely because access to the open metal sites is prevented by the structural arrangement within channels. By increasing the CO₂ pressure and approaching the isotherm step, a new band at 2361 cm⁻¹, probably due to the interaction of CO₂ with Ce^{IV}, appears, while the 2344 cm⁻¹ band increases, giving rise to an intense band with apparent maxima at 2344 and 2330 cm⁻¹. In general, the assignment of the above-mentioned bands is not straightforward because the rotovibrational profile of gaseous CO₂, which falls in the same spectral region and prevails at high CO₂ coverages, superimposes on those components. Concurrently, the bands at 790 and 779 cm⁻¹ are shifted to 788 and 782 cm⁻¹, respectively, suggesting that changes are occurring on the fluorinated aromatic rings. The CO₂ doses corresponding to the final part of the adsorption step and the beginning of the isotherm plateau cause no further changes in the low frequency spectral range, while both the 2361 and the 2344 and 2330 cm⁻¹ bands go out of scale. The predominance of the band at 2361 cm⁻¹, possibly related to the direct interaction of CO₂ with Ce^{IV} open metal sites, at CO₂ pressures that correspond to the isotherm step could be a further proof of the occurrence of a phase-change adsorption process that enables the establishment of a strong adsorbate/surface interaction.

IR spectroscopy suggests the occurrence of a peculiar adsorption mechanism in which, at low coverage, CO₂ preferentially interacts with the organic linker, while at higher equilibrium pressure, CO₂ triggers a rotation of the fluorinated rings and consequentially the exposure of Ce^{IV} metal sites, which become available to interact with the gas molecule. This adsorption mechanism was further investigated by performing adsorption microcalorimetry at 30 °C to directly measure the CO₂ molar adsorption heat at different coverages (Figure 5.8). Figure 5.8 reports the volumetric CO₂ isotherms (a) and the differential molar adsorption heats (b) of F4 MIL-140A(Ce).

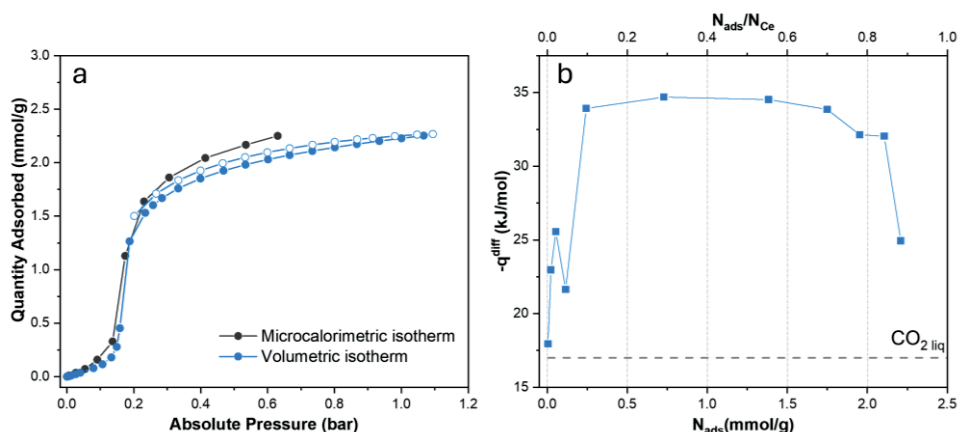


Figure 5.8. Comparison of volumetric isotherms obtained by performing CO_2 adsorption at 30°C with the automatic volumetric instrument (light blue) and with the volumetric line coupled with the microcalorimeter (dark grey) (a). Differential molar adsorption heats curve related to the adsorption of CO_2 at 30°C (b). The dotted horizontal line represents the standard molar heat of liquefaction of CO_2 at 30°C: 17 kJ/mol). This figure is adapted from reference 6.

The volumetric isotherm collected in the 0-0.6 bar pressure range with the microcalorimetric apparatus (dark grey curve in Figure 5.8 a) is perfectly in agreement with the isotherm obtained by the standard automatic volumetric instrument (light blue curve in Figure 5.8 a). The differential molar adsorption heat curve ($-q_{\text{diff}}$, Figure 5.8 b) unusually starts from low values, close to the molar heat of liquefaction of CO_2 (17 kJ/mol). The differential heat then increases until 25 kJ/mol and rapidly decreases to 22 kJ/mol. After this intermediate step, $-q_{\text{diff}}$ reaches a plateau at ~ 34 kJ/mol corresponding to a coverage above 0.2 mmol/g, i.e., exactly where the step in the isotherm is taking place. These unusual values of differential heat clearly suggest that some endothermic modification of the adsorbent is occurring concurrently with the exothermic adsorption of CO_2 . Indeed, microcalorimetry provides the “average” heat of adsorption which could derive from different contributions generated by the interaction between the porous adsorbent and the adsorptive. If the endothermic event is particularly heat-demanding, the resulting net differential heat displays this peculiar trend.²¹ After reaching the value of 34 kJ/mol, $-q_{\text{diff}}$ remains constant until a coverage of 2 mmol/g (a value corresponding to the decrease in the slope of the adsorption isotherm immediately after the step). The relatively high value of $-q_{\text{diff}}$ over a wide range of coverages suggests that CO_2 strongly interacts with a homogeneous set of adsorption sites distributed on the internal surface of F4 MIL-140A(Ce).²² When all the available adsorption sites are covered by CO_2 , the differential heat curve steeply

decreases, again approaching the heat of liquefaction of CO₂. At the step, the differential heat curve is in agreement with the isosteric heat of adsorption plot, indirectly extracted from the CO₂ isotherms by applying the Clausius-Clapeyron equation (Figure 5.2 b). However, the Clausius-Clapeyron model fails in identifying a region of low heat of adsorption before the step takes place. Therefore, the microcalorimetric measurement provided additional evidence for the mechanism hypothesised by the IR spectroscopy, showing a peculiar differential heat curve, characterised by the presence of an endothermic event that takes place at low CO₂ coverage, in perfect agreement with the rotation of the fluorinated rings. After this event, the differential heat converges to an average value compatible with CO₂ interacting with open metal sites.

In conclusion, the combination of volumetric, spectroscopic and microcalorimetric techniques suggest that the CO₂ adsorption in F4 MIL-140A(Ce) occurs through a peculiar cooperative mechanism. In particular, at low coverage, an endothermic event is taking place which can be related to the rotation of the fluorinated rings that leads, at higher equilibrium pressure, to the opening of tight pockets where simultaneous interaction with open metal sites and three F atoms of the linker takes place (see Figure 5.9 for a schematic representation of the mechanism). The step-shaped isotherm of F4 MIL-140A(Ce), resulting from this phase-change behaviour, allows reaching saturation in a narrow range of partial pressure, compatible with real-life post combustion capture requirements, and shows a complete reversible desorption isotherm with a non-hysteretic behaviour. While several MOFs are known to display either adsorption at coordinatively unsaturated metal sites or concerted ring rotation, to the best of our knowledge, the combination of these two features is observed in F4 MIL-140A(Ce) for the first time. Finally, further evidence for this peculiar adsorption mechanism is also provided by a large number of characterisation techniques, including Powder X-ray diffraction (PXRD), X-ray Absorption Spectroscopy (XAS), Solid-state nuclear magnetic resonance (SSNMR) and Density functional theory (DFT), carried out by the other co-authors of the published paper entitled " Cooperative CO₂ Adsorption Mechanism in a Perfluorinated Ce^{IV} -Based Metal Organic Framework ", reported in the appendix of this thesis. ⁶

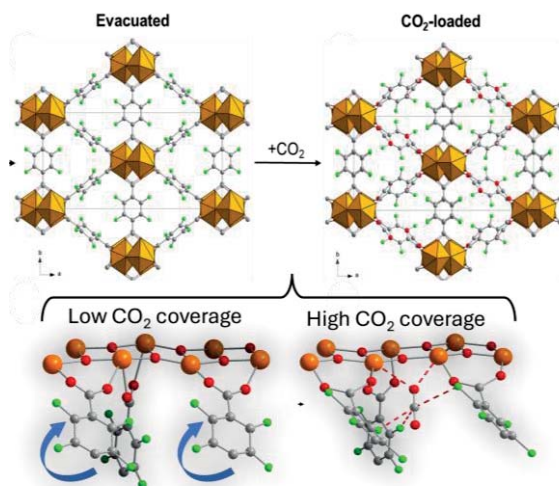


Figure 5.9. Schematic representation of the mechanism of CO_2 adsorption occurring in F4 MIL-140A(Ce). The structures were obtained by Prof. M. Taddei and the figure was adapted from reference 6.

5.3 Moving towards more realistic conditions: the effect of humidity

The peculiar adsorption mechanism exhibited by F4 MIL-140A(Ce) enables it to achieve some of the key features of an ideal adsorbent, mentioned in Chapter 1, such as good capture performance, high working capacity, reversibility and CO_2/N_2 selectivity. However, some of the main characteristics identified for an ideal adsorbent are still missing. To fill this gap, two additional properties are now being investigated: CO_2 capture in presence of water and possibility of shaping.

In particular, water vapour is a common component of flue gas, ranging from 6-18% depending on its source. Understanding the various roles water can play in relation to CO_2 is therefore a critical issue.²³

Unfortunately, a known disadvantage of many MOFs lies in their low stability when exposed to water vapour.^{24–26} However, nowadays, different structures with high hydrolytic stability exist.^{27–29} Even if the framework is stable to moisture, the effect of water on CO_2 adsorption can vary widely, resulting in different effects on CO_2 uptake, such as a constant decrease,^{30,31} increased adsorption capacity only at low water pressures,^{31,32} or even a constant increase in the CO_2 capture capacity of the MOF at all water pressures.^{33,34} The large variability in MOFs structure suggests that

the competitive H₂O/CO₂ adsorption should be studied almost on a case-by-case basis.

In the present case, since F4 MIL140A(Ce) has been synthesised in water, it is stable in the presence of moisture. However, how strongly CO₂ and H₂O compete in the adsorption process, and in particular the effect that the presence of water might have on the peculiar cooperative CO₂ adsorption mechanism observed in F4 MIL140A(Ce), is still unknown. In order to answer this question, we tried to repeat the previous characterizations on a partially hydrated material. It should be noted that all the techniques described so far (IR spectroscopy with molecular probes, volumetry and microcalorimetry) work on completely evacuated samples, so the application of these characterisation methods to partially hydrated samples represent a novelty in their use and, in some cases, pushes the instrumental capabilities to their limits.

Firstly, in situ IR spectroscopy was performed using CO as probe molecule at cryogenic temperature. The same experiment previously performed on the fully evacuated sample obtained after activation at 120°C in vacuum for 12 h (Figure 5.5 a) was repeated on the samples in which a weaker activation condition was performed. In particular, we were interested in the possibility of reaching an intermediate hydration state with some residual water on the sample after different outgassing times. Therefore, the sample was outgassed in vacuum for 2.5 h and 1 h at room temperature and then exposed to CO (Figure 5.10 b and c). The resulting spectra were compared with those of the fully activated sample (Figure 5.10 a).

As previously discussed, the interaction of CO with the fully evacuated F4 MIL-140A(Ce) gives rise to three main bands at 2155, 2130 and 2106 cm⁻¹. The first two were attributed to CO adsorbed on Ce⁴⁺ sites (green dotted line) and to CO interacting with Ce³⁺, respectively, while the latter was due to the isotopic shift of the ¹³C-¹⁶O interacting with Ce⁴⁺. In the first attempt of partial activation, the sample was outgassed at RT for 2.5 h. As can be observed by the higher intensity of the O-H stretching signals at 3643 and 3556 cm⁻¹, some residual water is interacting with the sample (Inset of figure 5.10 b). However, in the CO stretching region only one main band at 2155 cm⁻¹ can be observed suggesting that the Ce⁴⁺ sites are still (almost) fully available for interaction after this evacuation procedure. The effect of some residual water affects the 2130 and 2106 cm⁻¹ signals, which are difficult to detect compared to the fully evacuated sample. Additionally, the lower band at 2155 cm⁻¹ shows the appearance of a shoulder at lower wavenumbers (blue dotted line)

possibly generated by the interaction of CO with a small fraction of OH groups.¹³ A further proof of this last assignment is represented by the slight perturbation of the OH stretching region (inset of Figure 5.10 b)

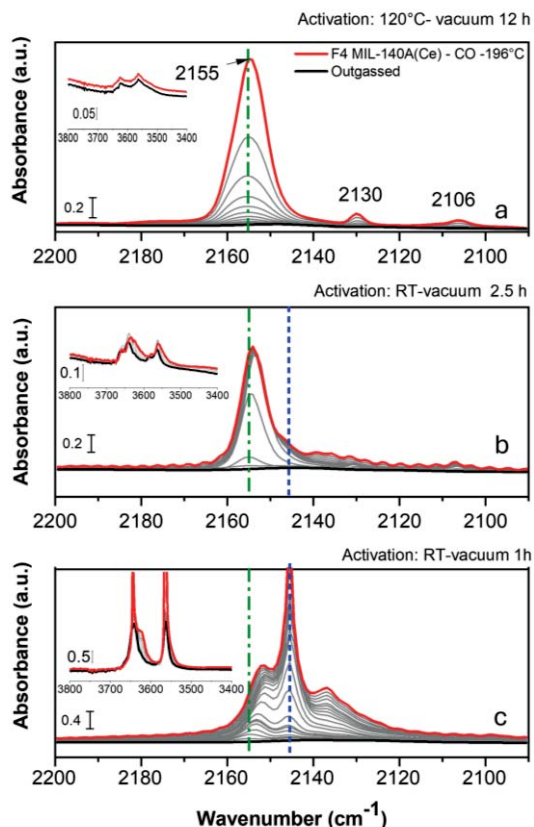


Figure 5.10. IR spectra after adsorption of 60 mbar of CO at -196°C and following outgassing on F4 MIL-140A(Ce) evacuated at 120°C for 12 h (a) at room temperature for 2.5 h (b) and at room temperature for 1 h (c). The spectra were plotted subtracting the spectrum of the evacuated material. In the insets, the raw data of the corresponding hydroxyl stretching region is shown. Green and blue dotted line represent the 2155 and 2145 cm^{-1} bands, respectively.

Since the 2.5 h degassing seems to have activated the sample almost completely exposing a significant proportion of Ce^{4+} sites, a milder evacuation procedure was carried out. The same experiment was therefore repeated on the MOF evacuated in vacuum for only 1 h at room temperature (Figure 5.10 c). As expected, the 3643 and 3556 cm^{-1} bands associated to the O–H stretching signals further increased in intensity (inset of figure 5.10 c), while new components appeared in the CO stretching region. In particular, the most intense band is observed at 2145 cm^{-1} (blue dotted line), followed by a signal at 2151 cm^{-1} which shifts to 2155 cm^{-1} by

decreasing the CO pressure (green dotted line) and a less intense band at 2136 cm^{-1} . This latter band, which rapidly disappears upon outgassing, can be assigned to a liquid-like CO phase. It is worth noting that this band was not observed in the samples activated in harsher conditions. This may further indicate that also the interaction with water causes a structural rearrangement of the material, changing also its textural properties and probably leading to an increase in pore size. The 2145 cm^{-1} band corresponds to the small shoulder appearing in the MOF activated for 2.5 h and assigned to interaction of CO with OH groups. However, in the present case, the milder activation condition results in a more intense signal, due to the increased availability of OH species. Lastly, the presence of H_2O coordinated to the metal sites probably induces a slight change in the vibrational frequency of CO-Ce^{4+} adducts, which appear at 2151 cm^{-1} . After outgassing, the effect of the H_2O perturbation diminishes, until the original signal at 2155 cm^{-1} is restored.

These initial IR measurements indicate that an intermediate activation condition, in which the presence of H_2O prevails, but some Ce^{4+} sites are still available for interaction, can be achieved after 1 h of outgassing at room temperature. To achieve a situation where Ce^{4+} sites are no longer accessible, a much shorter outgassing time is required, making this measurement experimentally not feasible. In fact, in the case of a completely non-activated sample, the access of CO would probably be hindered by the high concentration of H_2O .

Following the characterization previously performed on the fully evacuated sample, the interaction of CO_2 with the partially hydrated F4 MIL-140A(Ce) was investigated. The same increasing CO_2 pressures, previously selected from the CO_2 isotherm collected at 40°C to follow the step (Figure 5.6), were dosed on a partially evacuated sample (Figure 5.11). In particular, F4 MIL-140A(Ce) was outgassed for 1 h, 10 and 0 minutes (i.e. not evacuated) and, then, incremental CO_2 doses (in the range 110-750 mbar) were sent to the sample (Figure 5.11 c-h). The results are compared with the ones obtained from the fully evacuated sample (reported again in Figure 5.11 a, b). The degassing times were chosen to study the CO_2 adsorption mechanism in a state where the Ce^{4+} sites are completely, partially or no longer available. In the latter case, a very short outgassing time is required as this MOF appears to release water very easily.

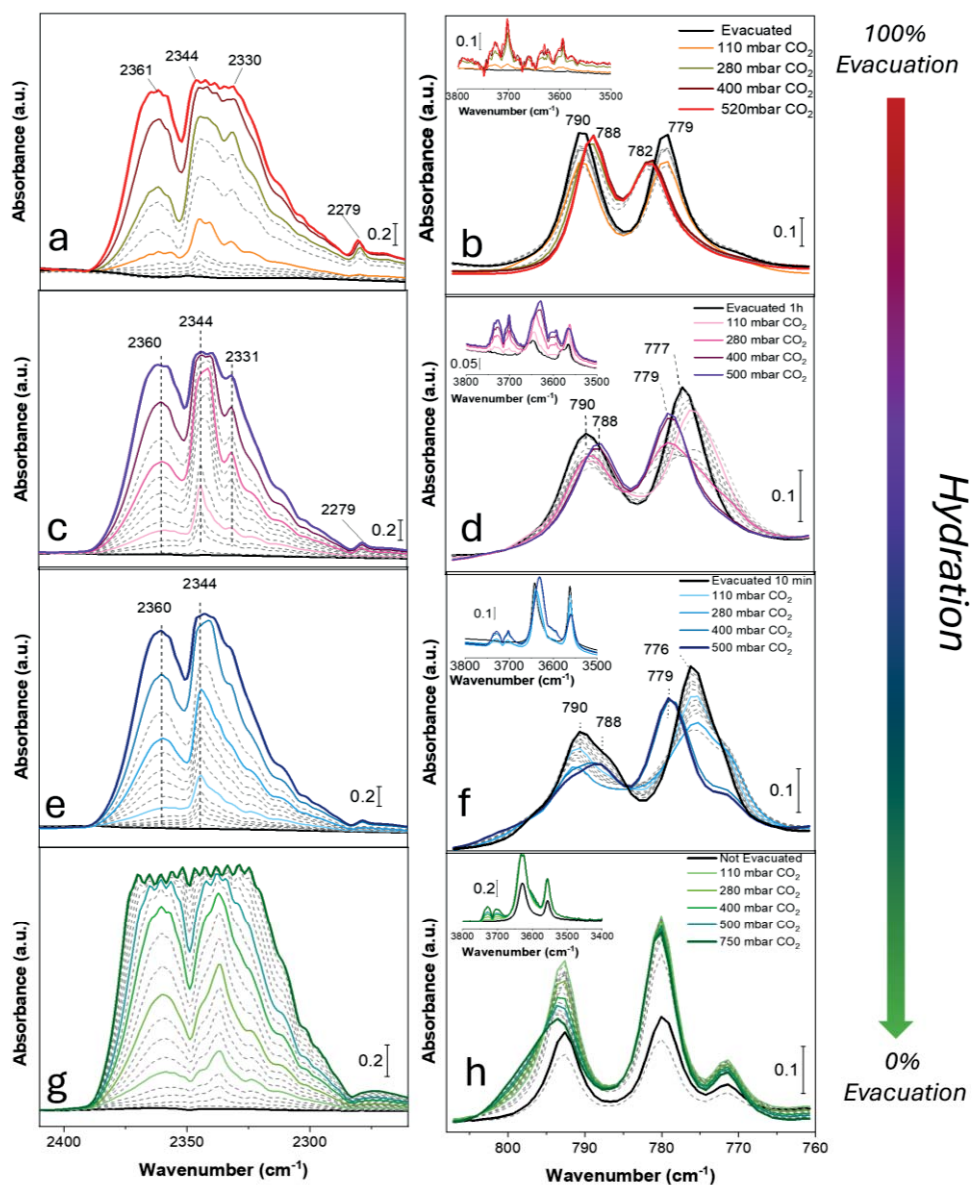


Figure 5.11. IR, reported in the $2410\text{--}2260\text{ cm}^{-1}$ (a, c, e, g) and $810\text{--}760\text{ cm}^{-1}$ (b, d, f, h) spectral ranges, of CO_2 adsorption on F4 MIL-140A(Ce) fully evacuated (120°C for 12h) (a-b), evacuated for 1 h at room temperature (c-d), evacuated for 10 min at room temperature (e-f) and not evacuated (g-h). The same incremental pressure doses of CO_2 reported with coloured crosses in the volumetric isotherm of Figure 5.6 were employed during the IR experiments. Dashed curves represent intermediate pressures. In the insets, the raw data of the corresponding hydroxyl stretching region is shown.

As previously observed, when CO_2 interacts with the fully evacuated sample (Figure 5.11 a-b) at low pressures, a broad band appears at 2344 cm^{-1} and no significant

changes are detected in the 790 and 779 cm^{-1} bands. By increasing the CO_2 pressure and approaching the isotherm step, a new band at 2361 cm^{-1} , tentatively assigned to the interaction of CO_2 with Ce^{IV} , appears and, in the low frequency region, the two initial bands shift to 788 and 782 cm^{-1} , suggesting that changes are occurring on the fluorinated aromatic rings. The CO_2 doses corresponding to the final part of the adsorption step and the beginning of the isotherm plateau cause no further changes.

These results suggested the following adsorption mechanism: (i) at pressures below the step of the isotherm, CO_2 interacts preferentially with the organic linker, whereas (ii) at higher equilibrium pressures (i.e. when the step is reached, between 110 and 180 mbar), CO_2 induces a rotation of the fluorinated rings and leads to the exposure of Ce^{IV} metal sites, which become available for interactions.

When the same experiment is repeated on F4 MIL-140A(Ce) evacuated for 1 h at room temperature (Figure 5.11 c-d), similarly to before, a sharp band initially appears at 2344 cm^{-1} , while no significant changes are observed in the low frequency region. As the CO_2 pressure increases, the 2360 cm^{-1} signal rises, and the 790 and 779 cm^{-1} bands shift to 788 and 779 cm^{-1} respectively. Some differences in the shape of the signals falling in the CO_2 asymmetric stretching region can be observed but, as mentioned above, their correct assignment is prevented by the superposition of the rotovibrational profile of gaseous CO_2 . Another difference from the previous spectra concerns the 790 and 777 cm^{-1} bands: the latter is slightly shifted and more intense than the 790 cm^{-1} signal in the spectrum after 1 h evacuation. As previously observed in Figure 5.4, the change in position and intensity of these bands is due to the different water content. However, the most important variation consists in the pressure at which the shift in the 790 and 777 cm^{-1} bands is observed. In the case of a fully evacuated sample, the main shifts occur between 110 and 280 mbar of CO_2 , while for 1 h evacuation it takes place at higher pressures (i.e. between 280 and 400 mbar). This behaviour suggests that the CO_2 adsorption triggers the same mechanism observed for the fully activated sample, but that the ring rotation occurs at higher pressures.

When the experiment is repeated with the sample evacuated for only 10 minutes (Figure 5.11 e-f), and thus with a higher H_2O content (see inset in Figure 5.11 f), a situation similar to the one described above is observed. In this case, however, the changes in the fluorinated rings (Figure 5.11 f) occur in a higher pressure range (i.e. in between 400-500 mbar).

Lastly, when the experiment is performed on the not evacuated sample (Figure 5.11 g-h) no shift of the fluorinated rings bands is observed, also increasing the pressures till 700 mbar. However, it is worth noting that some significant differences are present in the initial signals, which are located at 793 cm^{-1} , 779 cm^{-1} and 771 cm^{-1} , in agreement with the bands observed sending 20 mbar of H_2O on F4 MIL-140A(Ce) (Figure 5.4 c), suggesting that the high content of H_2O in the structure prevents the occurrence of the same CO_2 capture mechanism.

IR spectroscopy suggests that, at intermediate hydration, the cooperative CO_2 adsorption mechanism can still occur. However, by increasing the MOF hydration (i.e. by decreasing the evacuation time) the pressure range at which the fluorinated ring rotation takes place is shifted to higher pressures, until the presence of H_2O coordinated to Ce^{4+} sites prevents the access of CO_2 and the concerted rotation of the rings.

However, to further prove this assertion, CO_2 adsorption/desorption isotherms on partially hydrated samples were also collected. It is worth noting that to perform this kind of measurements by means of volumetric techniques is not straightforward since the analysis requires the absence of species (as H_2O) that could compete with the adsorbate when equilibrium is reached. In addition, the larger amount of sample required to carry out this type of measurement compared to IR spectroscopy (the difference is of two orders of magnitude) leads to differences in evacuation times for sample activation. To collect isotherms in partially activated conditions, some of the technical parameters required to carry out the volumetric analysis were also modified. The various CO_2 adsorption/desorption isotherms at 30°C , performed on F4 MIL-140A(Ce) evacuated at room temperature for different times, are reported in Figure 5.12 and are the result of numerous tests carried out before establishing the right activation conditions to obtain different hydration conditions.

As expected, the various isotherms show a decrease in CO_2 uptake by increasing the hydration degree, i.e. by decreasing the evacuation time. The maximum amount of adsorbed CO_2 on F4 MIL-140A(Ce) fully evacuated is around 2 mmol/g at 30°C and 1 bar and decreases at 1.3 mmol/g when is evacuated at RT for 6 h. This value slowly decreases till reaching 0.5 mmol/g in case of sample evacuated for 1 h. As previously reported, the CO_2 isotherm of the fully evacuated sample shows the peculiar step occurring in between 100 and 200 mbar. Interestingly, the samples evacuated for 6 h and 4 h, although showing an overall decrease in CO_2 capture capacity, still exhibit the presence of a step occurring at slightly higher pressures: between 200 and 350

mbar when the sample is evacuated for 6 h while upon further decreasing the evacuation time to 4 h., the step shifted to slightly higher pressures (from 300 to 450 mbar). These results are in complete agreement with those obtained by observing the changes occurring in the fluorinated ring vibration range by means of IR spectroscopy and suggest that the cooperative CO₂ adsorption mechanism is only observed when a significant fraction of the Ce⁴⁺ sites is available for interaction. Finally, again as previously assumed, when the H₂O content is higher (green isotherms in Figure 5.12), a classical type I isotherm is visible. This latter evacuation condition refers to a situation where the number of available Ce⁴⁺ sites is limited and is probably similar to that observed in the case of IR spectroscopy using CO as a molecular probe on the sample evacuated for 1 h (Figure 5.10 c). However, due to the different experimental conditions, no direct correlations can be made. Finally, it should be mentioned that the lower CO₂ uptake of the fully evacuated MOF (red isotherm in Figure 5.12) compared to that shown in the previous paragraph (Figure 5.2 a and 5.6) is due to samples obtained from different syntheses.

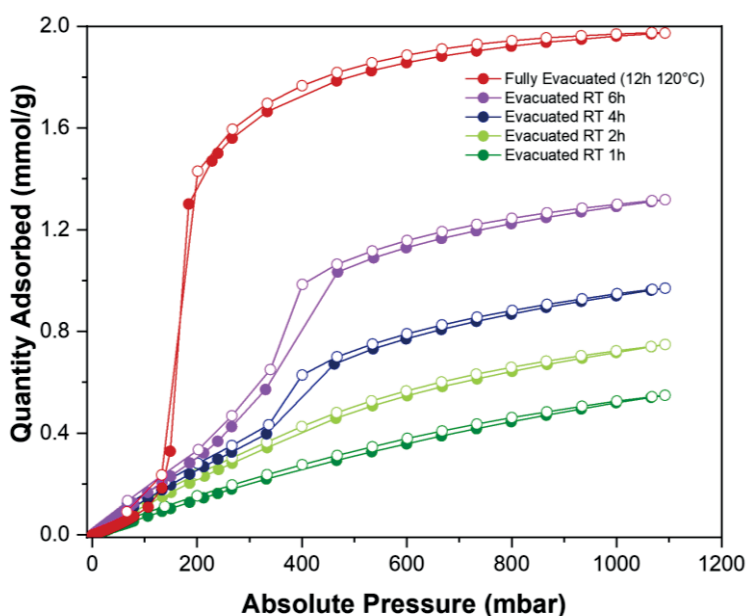


Figure 5.12. CO₂ adsorption/desorption isotherms at 30°C collected on F4 MIL-140A(Ce) fully evacuated (120°C for 12h) (red), evacuated at room temperature for 6 h (pink), evacuated at room temperature for 4 h (blue), evacuated at room temperature for 2 h (light-green) and evacuated at room temperature for 1 h (dark green).

The combination of IR spectroscopy and volumetry was fundamental to understand the mechanism of CO₂ adsorption on F4 MIL-140A(Ce) in presence of H₂O. When the

sample is fully hydrated, the presence of H₂O coordinated to Ce⁴⁺ sites prevents access to CO₂ and the concerted rotation of the rings. In contrast, at intermediate hydration stage, when a certain threshold number of Ce⁴⁺ sites are free, cooperative CO₂ adsorption can still occur, even if higher CO₂ pressures are needed to trigger this mechanism.

5.4 Moving towards more realistic conditions: the effect of shaping

Lastly, as for the other solid adsorbents investigated in this thesis, a first attempt of shaping the MOF was performed at the Advanced Ceramics and Glasses group of University of Padova. Over the last 10 years, interest in the shaping and design of MOF monoliths has grown considerably, resulting in several publications using different shaping methods (See Table 5.2 for a summary of some relevant publications on 3D MOFs for CO₂ capture).

Table 5.2. Summary of different 3D-printed MOFs monoliths reported in the literature for CO₂ capture applications. If not specified, the CO₂ uptake value refers to the adsorption capacity of the material at 25°C and 1 bar measured by means of volumetric techniques.

Samples (Loading)	Binder	Fabrication strategy	CO ₂ uptake powder (mmol/g)	CO ₂ uptake monolith (mmol/g)	Ref.
MIL-101(Cr) (60%)	Bentonite (40%)	Extrusion	1.44 ^a - 1.95 ^b	0.91 ^a - 1.95 ^b	35
MIL-101(Cr) (75%)	Bentonite (25%)			/ ^a -1.36 ^b	
HKUST-1	/	Press/ pelletisation	/	2.68 ^c	31
Ni/DOBDC				6.68	
MIL53 + ZIF-62	/	Crystal glass composite (CGC)	3 ^d	4 ^d	36
HKUST-1	/	Monolithic gels synthesis	/	4.2	37
UiO-66				2.2	
UiO-66-NH ₂				2.1	

UTSA-16 (85%)	PPO (15%)	Extrusion	3.98	2.80	8
	sPS (15%)			3.05	
UTSA-16 (90%)	Kaolin (10%)	Direct Ink Writing	3.5	3.1	38
HKUST-1 (40%)	Torlon	Direct Ink Writing	2.1	1	39
HKUST-1 (60%)				1.2	
MOF-74(Ni) (80%)	15% bentonite +5% PVA	Direct Ink Writing	4.6	4.1	40
UTSA-16(Co) (85%)	10% bentonite + 5% PVA		3.4	2.9	
UTSA-16(82%)	Bohemite(18%)	Direct Ink Writing	/	2.5	41

^a Volumetry 2 bar, 25°C; ^b Breakthrough 40% v/v CO₂, 25°C; ^c Volumetry, 0.8 bar 25°C; ^d Volumetry, 50 bar 30°C;

As illustrated in chapters 1 and 4, the Direct Ink Writing (DIW) technique has attracted a lot of attention due to the possibility of creating different structures by means of digital models. However, one of the main challenges lies in the precise control of the rheology of the ink, which must be printable and retain its structure and shape without losing the specific properties of the original active phase. Therefore, the composition of the ink must be carefully tuned. However, the number of tests needed to select the final composition, which require large amounts of active phase, may be an additional difficulty in applying the Direct Ink Writing (DIW) technique to MOFs, where large scale syntheses, maintaining the original properties, are not straightforward. Therefore, in the present case, the first attempt to shape F4 MIL-140A(Ce) by means of DIW was performed starting from a synthesis which was slightly modified to reach larger scale production (labelled as F4 MIL140A(Ce)-LS). The powder of the MOF was supplied by Swansea University thanks to Prof. M. Taddei. The slightly modified synthesis of the MOF allows the production of a higher amount of sample, but containing impurities of the UiO-66 phase, which is kinetically favoured.⁴ The lower purity of F4 MIL-140A(Ce)-LS leads to differences in the IR spectrum observed during CO adsorption, as will be

explained below, (Fig. 5.13a compared to Fig. 5.5 a), and to a lower CO₂ uptake, which reaches 1.8 mmol/g at 1 bar and 25 °C compared to the previously reported 2.2 mmol/g observed under the same conditions (Fig. 5.14d and Fig. 5.2a, respectively). However, to optimise the printing process, it was necessary to sacrifice some purity in favour of a larger sample quantity. After several trials, the optimised composition of the ink was achieved (Figure 5.14 a for the image). Firstly, the PXRD patterns of the F4 MIL-140A(Ce), F4 MIL-140A(Ce)-LS and NaBT were collected and compared to the one of the 3D monolith (3D F4 MIL-140A(Ce)) previously ground into powder, to prove the persistence of the MOF structure in the printed material (Figure 5.13 c). The first two samples show the presence of F4 MIL-140A(Ce) structure, although some differences visible in the first two reflections as well as in the 13-18° 2 θ range are due to the presence of some UiO-66 impurities.⁵ The bentonite is mainly composed of a montmorillonite phase,⁴² which is almost absent in the 3D monolith, revealing predominantly the presence of the F4 MIL-140A(Ce) structure.

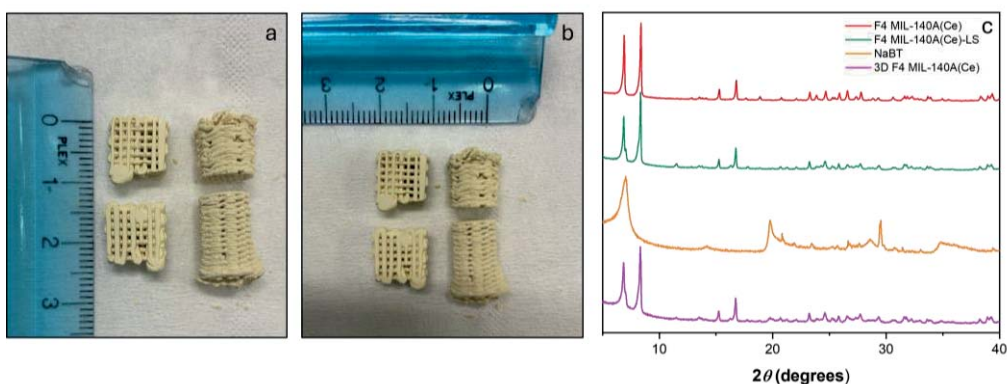


Figure 5.13. Images of the F4 MIL-140A(Ce) monoliths (3D F4 MIL-140A(Ce)) in frontal view (a, b) and XRD pattern of F4 MIL-140A(Ce) (red), F4 MIL-140A(Ce)-LS (aqua green), NaBT (orange) and 3D F4 MIL-140A(Ce) (magenta).

Following the same procedure already reported in Chapter 4, a first analysis of the accessibility of the active sites in the 3D printed material was carried out by means of *in situ* IR spectroscopy using CO as a molecular probe (Figure 5.14 c), comparing the result with that of the individual powder components (Figure 5.14 a and b). All the samples were previously activated in vacuum at 120°C for 12h.

The interaction of CO with F4 MIL-140A(Ce)-LS (Figure 5.14 a) gives rise to the three bands at 2155, 2130 and 2106 cm⁻¹ previously observed in the pure F4 MIL-140A(Ce)

and assigned to CO adsorbed on Ce^{4+} sites, Ce^{3+} sites and to the isotopic shift of the $^{13}\text{C}-^{16}\text{O}$ interacting with Ce^{4+} , respectively. However, two main differences with respect to the previous spectra (Figure 5.2 a) can be observed: a slight downward shift of the 2155 cm^{-1} at the maximum coverage (apparent maximum at 2153 cm^{-1}) and the presence of an additional band at 2138 cm^{-1} . The former slight difference could be due to the overlap of band resulting from the presence of CO interacting with OH.^{14,15} This latter hypothesis is also supported by the shift observed in the OH stretching region in which the 3625 cm^{-1} signal is consumed and parallelly a new band at 3551 cm^{-1} is formed. It is worth noting that the presence of those bands was not observed in case of pure F4 MIL-140A(Ce), while is typically reported in fully activated UiO-66 MOF.⁴³ On the other hand, the latter band at 2138 cm^{-1} is ascribable to a metastable liquid-like CO phase.

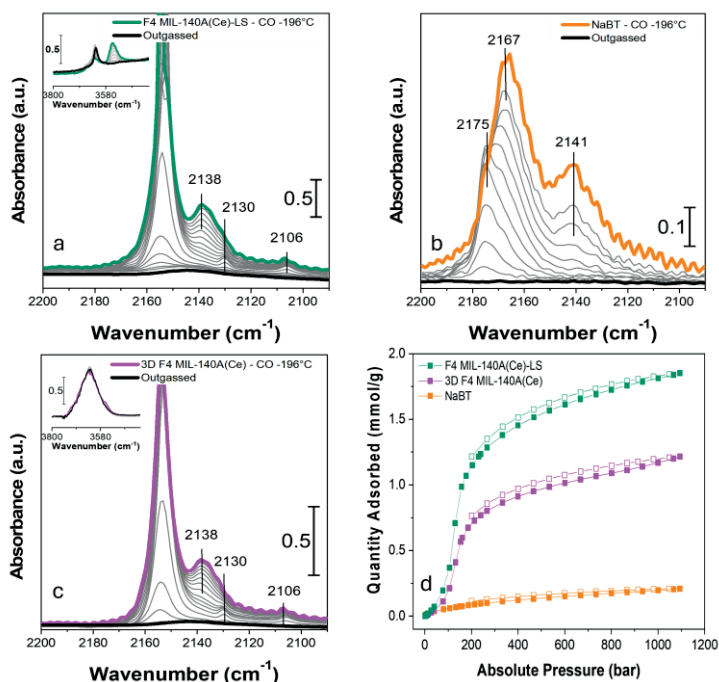


Figure 5.14. IR spectra after adsorption of 60 mbar of CO at -196°C and following outgassing of F4 MIL-140A(Ce)-LS (a), NaBT (b) and 3D F4 MIL-140A(Ce) (c). In the insets, the raw data of the corresponding hydroxyl stretching region is shown. CO_2 adsorption/desorption isotherms at 25°C collected on F4 MIL-140A(Ce)-LS, NaBT and 3D F4 MIL-140A(Ce) (d).

The same characterization was performed on the Na bentonite in which two main bands can be observed: one intense signal at 2167 cm^{-1} which shifts to 2175 cm^{-1} upon outgassing and one less intense band at 2140 cm^{-1} . The former one can be

assigned to the interaction of CO with the Na⁺ cations present in the bentonite. The upward shift observed upon outgassing was previously observed in case of NaY zeolites and attributed to the presence and the conversion of Na⁺(CO)₂ dicarbonyls at 2167 cm⁻¹ into Na⁺CO monocarbonyls (2175 cm⁻¹).⁴⁴ The latter band at 2141 cm⁻¹ was due to liquid-like CO.

Finally, the 3D F4 MIL-140A(Ce) was tested. The sample probably contains a higher amount of H₂O compared to the powder sample, as evidenced by the broad OH stretching band (inset of Figure 5.13c), probably due to the high percentage of Na bentonite present in the shaped material, which is not fully activated under these temperature conditions (120 °C 12h). However, the interaction of CO shows the presence of the same bands described for F4 MIL-140A(Ce)-LS in powder form, indicating the accessibility of the active Ce⁴⁺ sites.

Lastly, the CO₂ capture capacities of the two powder components and of the 3D MOF were tested by collecting adsorption/desorption isotherms at 25 °C. As previously mentioned, the F4 MIL-140A(Ce)-LS powder sample shows a slight decrease in CO₂ adsorption performances with respect to the pure MOF (-18% at 25 °C and 1 bar) due to some UiO-66 impurity in the MOF, but this does not affect the presence of the typical sharp adsorption step in the isotherm. The NaBT exhibits a classical type I isotherm with an almost negligible capture capacity of CO₂ (0.18 mmol/g at 25 °C and 1 bar). Interestingly, the 3D MOF shows an uptake of 1.16 mmol/g in the same measurements condition and the preservation of the step in the same pressure range of the powder sample, suggesting that the CO₂ cooperative adsorption mechanism occurs. Additionally, the CO₂ uptake experimentally measured is perfectly in agreement with the theoretical CO₂ adsorption calculated by summing the individual adsorbed amounts, weighted by the percentage of the different components present in the 3D composite (Table 5.3)

Table 5.3. Experimental and theoretical values of CO₂ adsorption at 25°C and 1 bar of the single components in powder form (F4 MIL-140A(Ce)-LS, NaBT) and the 3D printed monolith (3D F4 MIL-140A(Ce)). The experimental values were obtained from the adsorption isotherm shown in Figure 5.13d at 1 bar, while the theoretical value was calculated by summing the individual adsorbed amounts, weighted by the percentage of the different powder components.

Samples	CO ₂ uptake (mmol/g)	
	Experimental*	Theoretical**
CeMIL powder	1.8	1.08
NaBT	0.18	0.07
3D CeMIL (60% CeMIL + 40% NaBT)	1.16	1.15

* The experimental CO₂ uptake is the quantity adsorbed by the sample at 1 bar ** The theoretical CO₂ uptake in 3D CeMIL is the quantity adsorbed weighted by the percentage present in the 3D CeMIL. The sum of the theoretical CO₂ uptake of the two components is providing the theoretical CO₂ uptake on the 3D CeMIL

5.5 Concluding remarks and future perspectives

In this chapter, F4 MIL-140A(Ce) having a peculiar S shape isotherm which enable to have high working capacity and selectivity was characterized unveiling the occurrence of a peculiar cooperative adsorption mechanism. In particular, at pressures below the step (pressure < 200 mbar), the rotation of the fluorinated rings takes place and leads, at higher equilibrium pressure (pressure > 200 mbar), to the opening of tight pockets where simultaneous interaction with open metal sites and three F atoms of the linker occurs.

After these findings, we recently started to investigate the mechanism of adsorption on a partially hydrated sample, finding that the cooperative CO₂ adsorption mechanism can still occur and shifts to higher pressures until the presence of H₂O, fully covering the Ce⁴⁺ sites, prevents the access of CO₂ and the concerted rotation of the rings. Additional measurements will be carried out in the future to provide more quantitative information.

Finally, also in this case, a first attempt of shaping by DIW was performed showing: (i) the preservation of the step in the isotherm, suggesting that the CO₂ adsorption occurs according to the same mechanism and (ii) a CO₂ capture capacity comparable to the theoretical one (1.16 mmol/g at 25°C and 1 bar). Also in this case additional measurements are being carried out or will be in the future. These include:

- Additional fundamental characterisation including TGA analysis, SEM imaging and mechanical testing.
- Modification of the synthetic composition of the monoliths, increasing the MOF loading and/or changing the rheological agent, while maintaining the capture capacity and mechanical stability.
- Characterisation of both powder and monolith under more realistic conditions (i.e. in flow). Further analysis of competitive H₂O/CO₂ adsorption using breakthrough curves will be carried out.
- Stability over time and after repeated adsorption cycle will be assessed as well as the stability of the monolith to moisture.

However, these latest results, although preliminary, seem promising in the possibility of achieving two of the above-mentioned characteristics (i.e. CO₂ capture in presence of water and possibility of shaping) that an ideal solid adsorbent should have to be considered for real applications.

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6. LAYERED DOUBLE HYDROXIDES FOR CO₂ CAPTURE AT MEDIUM-HIGH TEMPERATURE: FROM POWDER TO 3D MONOLITHS

The third category of materials chosen to assess their potential as solid adsorbents for CO₂ capture consists of Layered Double Hydroxides (LDHs), also known as hydrotalcites. In the previous two chapters, CO₂ adsorption has been investigated in a medium low temperature range ($25 < T < 90^{\circ}\text{C}$). However, especially in post-combustion capture, exhaust streams typically involve higher temperatures ($T > 100^{\circ}\text{C}$). Unfortunately, as the adsorption temperature increases, a drastic loss in the capture capacity is commonly observed for most adsorbents, including zeolites and MOFs.^{1,2} Accordingly, LDHs are among the few materials that can be used for CO₂ adsorption at intermediate-high temperatures, representing significant advantage for their practical applications.^{3,4} Therefore, in this chapter, a LDH sample in both powder and monolith form, previously activated at 400°C (temperature at which the material is converted into the corresponding Layered Double Oxide (LDO) or Mixed Metal Oxide (MMO) structure), were tested for CO₂ capture at 300°C . The CO₂ isotherms show a great fraction of irreversible adsorption in between the primary and the secondary adsorption cycle for both powder and monolithic samples. In order to recover this fraction, a particular property of the material, known as the memory effect, which consists in the ability to recover the initial LDH structure upon contacting LDO with an aqueous solution, was explored. Therefore, after the first adsorption cycle, the samples were exposed to H₂O or KHCO₃ solutions to restore the LDH structure and the CO₂ capture was then re-assessed in the same way to see if the adsorption capacity of the material could also be recovered along with the structure. The most challenging aspect of the work was achieving stable CO₂ isotherms at such high temperatures and developing mechanically robust hydrotalcite monoliths. For this reason, this chapter focuses primarily on testing the adsorption of pure CO₂, with relatively little attention given to the materials characterization and to the study of the CO₂ interaction mechanism. The best results, obtained after numerous tests, will be presented in the following paragraphs although different modifications involving both the synthesis, the regeneration and the characterization conditions could also be explored in the future.

6.1 Materials and methods

As previously mentioned in Chapter 1, LDHs are anionic clays characterized by positively charged metal hydroxides sheets balanced by anions present in the interlayer together with H_2O . Their structure is a modified Brucite structure in which part of M^{2+} ions in the octahedral have been substituted by M^{3+} generating the overall positive charge. The general molecular formula is $[\text{M(II)}_{(1-x)} + \text{M(III)}_x(\text{OH})_2]^{x+} [\text{A}_{x/n}^{n-}] m\text{H}_2\text{O}$ where M(II) and M(III) are respectively the divalent and the trivalent cations, A^{n-} is the anions and x is the fraction of M(III) cation ($x = \text{M(III)} / (\text{M(II)} + \text{M(III)})$) (See Figure 6.1 for a pictorial representation of the structure).

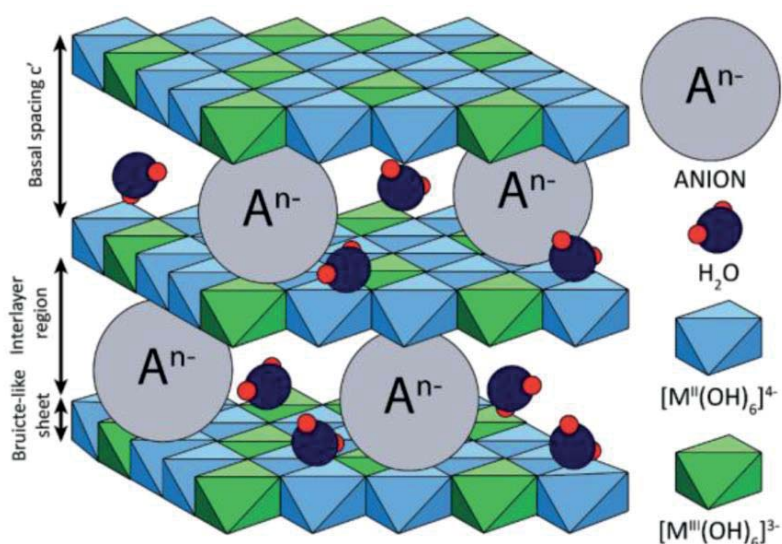


Figure 6.1. Pictorial representation of the LDH structure.⁵

By increasing the temperature, the LDH structure changes. Generally, three different steps can be considered. In the initial step, below 200°C , adsorbed and interlayer water is released, by further increasing temperature ($200\text{--}400^\circ\text{C}$) dihydroxylation takes place and finally, between 400°C and 600°C , loss of the anions occurs. The decomposition of the original structure leads to the formation of amorphous mixed oxides also known as Metal Mixed Oxides (MMO) or Layered Double Oxides (LDOs) having peculiar properties such as high thermal stability, relatively large surface area, homogeneous metal distribution and well-developed porosity.^{6–9} Therefore, the formation of those LDO can occur easily calcinating the

synthesized original hydrotalcite but the temperature should be carefully controlled in the 400-600°C range in order not to form a spinel structure which has not regeneration abilities. As a matter of fact, one of the main qualities of LDO is the so called *memory effect* which is the ability to regenerate, partially or completely, the original layer structure by exposing them to water-based solutions.^{6,10} These properties have stimulated a growing interest in using this material in various applications such as water purification from waste anions, heterogeneous catalysis and CO₂ capture.¹¹ For this latter application, they do not show a promising CO₂ capture capacity at low temperatures due to the presence of H₂O and the limited space between the layers, but as the temperature increases, water and hydroxyl groups are gradually released, leading to easier CO₂ adsorption. Among all the possible LDH structures one of the most promising one for CO₂ adsorption is Mg-Al 3:1 LDH.⁸ Therefore a commercial Mg-Al 3:1 LDH with CO₃²⁻ anions was purchased from Sigma Aldrich in powder form (Lot. Number MKCC5751). In parallel, a LDH monolith was synthesised by M. D'Agostini under the supervision of Prof. G. Franchin and Prof. P. Colombo of University of Padova using the same commercial LDH as active phase (Figure 6.2).

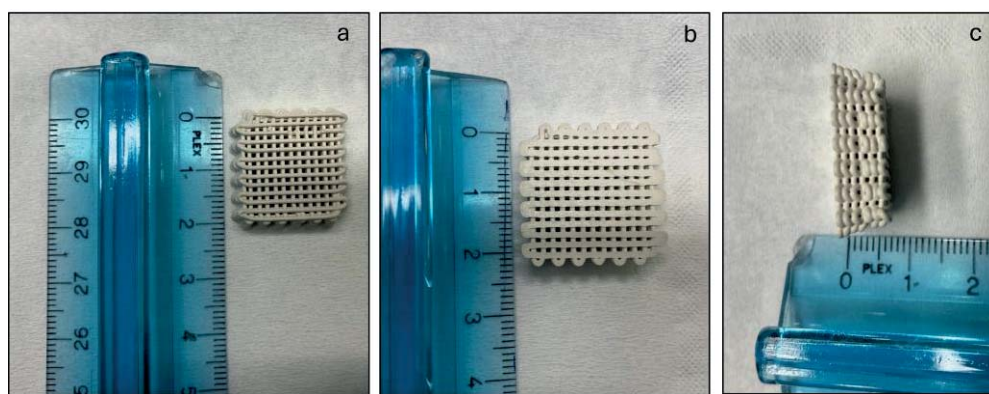


Figure 6.2. Images of the LDH monolith (3D HTlc) in frontal (a), back (b) and side (c) views.

The monolith is composed by 40 wt% LDH (HTlc), 57 wt% sodium geopolymer (NaGP) (molar composition: 3.8 SiO₂ - Al₂O₃ - Na₂O), 3% sodium bentonite (NaBT). Initially, the various component, in the percentage mentioned above, were placed in a steel container under vigorous mixing at 0°C. Contrary to what was previously observed with LTA monoliths, other components were added to the synthesis process in addition to the active phase in order to achieve both the appropriate rheological properties required for the printing process and good mechanical stability of the final 3D structure. In particular, the geopolymer which is an

amorphous aluminosilicates obtained from the dissolution and polycondensation of solid aluminosilicate precursors in alkaline media at low temperature (0-100°C), results to be an excellent binder for the shaping of adsorbent powders thanks to good mechanical properties and a high degree of intrinsic mesoporosity, while Bentonite acts as a rheology modifier.¹² Additionally, an appropriate quantity of water is added to the mixture in order to reach the right viscosity of the ink during the printing process.¹³ Once the gel was homogenised, the obtained slurry was transferred to a syringe for the Direct Ink Writing process carried out with a Delta-type 3D printer (Delta Turbo 2040, WASP, Italy). A pneumatic system pushes the slurry from the syringe into the barrel of an auger-type extruder (LDM module, WASP, Italy), by which it is then distributed at room temperature through a tapered 580 μm nozzle (Vieweg, Germany) to shape the desired object from a CAD model layer by layer. The resulting monolith was cured at 40°C for 7 days. Water was added into the container during the crystallisation step in order to maintain 100% relative humidity and prevent the premature evaporation of water from the monoliths before crystallisation was complete. Lastly the monolith was dried at 40°C for 1 day.

The powder X-ray diffractograms of the various components were collected on a PANalytical X'Pert diffractometer using Cu K α radiation and a power of 45 kV 40 mA in Capillary configuration (2θ range = 5–70°).

Thermo-gravimetric analyses (TGA) were performed using the equipment reported in Chapter 3 under N₂ flow, increasing the temperature up to 800 °C with a heating ramp of 5 °C/min

The CO₂ capture capacity was evaluated by means of a Micromeritics ASAP 2020 at 300°C as previously described in Chapter 3. Prior to the analysis, the samples were activated at 400°C in vacuum for 4 h. It is worth noting that after this thermal treatment an LDO structure is expected, for this reason for the sake of simplicity the LDHs used in the present chapter are generally referred to as "hydrotalcite-like compounds" (HTlc), following the examples found in the literature.¹⁴ In the case of secondary, tertiary and quaternary isotherms, they were performed at the same temperature after outgassing the samples at the adsorption temperature for 1h.

The regeneration of the material was performed by inserting 150 mg of commercial or 3D printed LDH into 20 mL of H₂O or 0.1 M KHCO₃ solution. The flask was put under continuous stirring at 25°C for about 18 hours. After this time, the solution was changed and the procedure was repeated a second time. The final samples

were dried at 100°C for one night. Also for the regenerated materials, prior to CO₂ capture, the samples were activated using the same activation procedure previously reported (i.e. 400°C in vacuum for 4 h), so that the LDO structure was obtained again.

6.2 Evaluation of adsorption capacities of powder and 3D HTlc monolith

Initially, the possible application of HTlc for CO₂ capture at 300°C was evaluated by collecting primary and secondary CO₂ adsorption/desorption isotherms on the commercial powder (Figure 6.3). Prior to each adsorption measurement the samples were pre-treated to desorb all the species which otherwise could drastically decrease the CO₂ accessibility and affect the overall adsorption capacity. However, as previously pointed out for LDHs, an increase in temperature causes a change in structure to LDO (T~400°C for Mg-Al LDH 3:1) and then into a crystalline spinel structure (T~600°C for Mg-Al LDH 3:1).¹⁵ As the adsorption performance is strictly related to the active sites present in the materials, it is easy to assume that a structural change also implies a different CO₂ adsorption capacity. As a matter of fact, a clear dependence of CO₂ uptake on the calcination temperature of LDHs was previously observed in the literature.^{15,16} In particular, the optimal calcination temperature for Mg-Al LDH to enhance CO₂ adsorption has been identified as 400°C, due to the combined effects of an increased specific surface area and greater availability of basic sites. In addition, these activation conditions were able to maximize the physisorbed fraction over the chemisorbed one, improving the reversibility of the material.^{15,16} For all these reasons, the same activation condition was applied to all the samples described in this chapter. After this pre-treatment, a primary CO₂ adsorption/desorption isotherm was carried out (Figure 6.3 square symbols). After the first adsorption run, the sample was outgassed for 1 h maintaining the temperature constant at 300°C, and a secondary (and tertiary) adsorption/desorption isotherm was collected to evaluate the degree of reversibility of the adsorption process (Figure 6.3 cycle symbols).

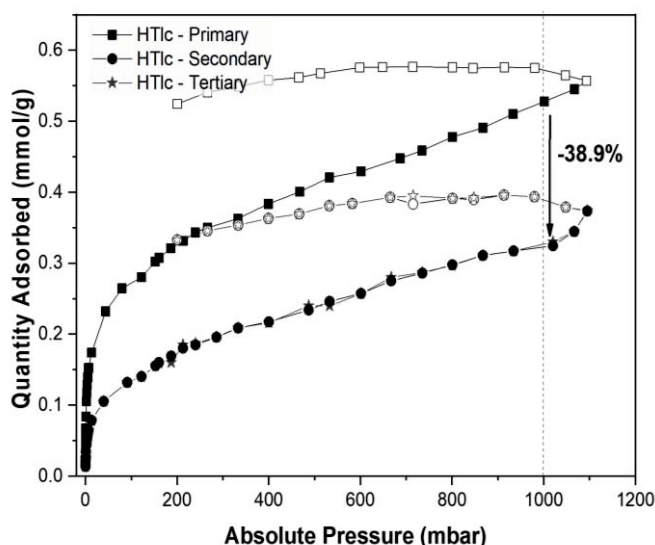


Figure 6.3. CO_2 adsorption/desorption isotherms at 300°C of Mg-Al LDH (HTlc) in powder form. The primary adsorption isotherm is reported with squares, the secondary adsorption isotherm is reported with cycles and the tertiary is reported with grey stars. Full symbols represent the adsorption branch and empty symbols represent the desorption branch.

The HTlc exhibited a type I isotherms in both the primary and secondary run, reaching a CO_2 uptake of 0.53 mmol/g at 300°C and 1 bar in the first cycle.¹⁷ The maximum CO_2 uptake is maintained at a plateau for almost the entire desorption branch until 200 mbar, where the isotherm starts to decrease, suggesting a not fully reversibility of the capture process. No desorption points were acquired at pressures below 200 mbar due to the slow kinetics. As a matter of fact, by outgassing and repeating the measurement, the secondary isotherm revealed a decrease in CO_2 adsorption of almost 40% at the same pressure. As expected, the tertiary isotherm did not further reduce the capture capacity and fully coincided with the secondary one. It is worth mentioning that the adsorption capacity of hydrotalcites change a lot depending on different parameters, such as their composition and synthesis conditions.^{16,18,19} However, the values reported for the same type of hydrotalcites analyzed after activation in the 300°C - 500°C range and in similar measurement conditions (200°C - 500°C) range from 0.17 to 0.85 mmol/g , completely in accordance with what observed for the primary adsorption on the HTlc sample (see Table 6.1). In addition, as far as the secondary isotherm is concerned, a decrease in performance with cyclability has also been observed in the literature.^{15,20,21} In particular, Léon et al. attributed the decrease in CO_2 uptake to

the formation of strong unidentate carbonate species, whereas bidentate and surface bicarbonates lead to highly reversible adsorption.²¹

Table 6.1. Comparison of CO₂ capture capacity of the commercial HTlc (Mg-Al LDH) used in the present chapter and the one reported in the literature analyzed in similar activation (300°C-500°C) and measurement conditions (200°C-500°C).

Sample	Activation condition	CO ₂ Capture temperature	CO ₂ uptake (mmol/g) at 1 bar	Type of analysis	Ref.
Mg-Al LDH (commerical)	400°C 4h + 300°C for 3h	300°C	0.45	Gravimetric	20
Mg-Al-LDH (synthesized by coprecipitation method)	400° 5h	200°C	0.85	TGA	22
Mg-Al-LDH (synthesized by coprecipitation method)	400°C 5h	200°C	0.53	TGA	23
Commercial Mg-Al LDH (EXM 701 by Süd-Chemie AG Company, Germany)	300°C	300°C	0.50	Gravimetric	24
Mg-Al LDH (synthesized by low supersaturation method)	500°C 5h	450°C	0.25	TGA	19
Mg-Al-LDH (synthesized by coprecipitation method)	400°C 5h + 1h in situ at 400°C	200°C	0.53	TGA	18
Mg-Al-LDH (synthesized by coprecipitation method)	400°C 4h at 50 mbar + degas at 200°C 4h	200°C 300°C 400°C	0.49 0.25 0.17	Volumetric	15
Mg-Al-LDH (synthesized by coprecipitation method)	400°C	200°C	0.73	Volumetric	16
Commercial Mg-Al LDH	400°C 4h	300°C	0.53	Volumetric	Present Work

Since simple outgassing at 300°C only partially restored the initial CO₂ adsorption capacity, after performing the secondary isotherm, the sample was exposed to H₂O or KHCO₃ solution to refresh the original LDH structure, exploiting the peculiar memory effect of these materials.¹⁰ The CO₂ uptake was then measured in the same conditions, to assess if the adsorption capacity of the material could also be recovered along with the structure.

In the literature the recovery of the LDH from the corresponding LDO has been widely studied using different solutions both in liquid or gas phases.^{4,10,25,26} However, when the calcined hydrotalcite is exposed to water in the gas or liquid phase, the layered structure is recovered but not the original composition, whereas when carbonate-containing solutions are employed, both structural and chemical compositions are recovered. To make this distinction clearer, Mokhtar et al. suggested that the term hydration should be used in the former cases and reconstruction in the latter.¹⁰ In the present case, the HTlc was exposed to H₂O and KHCO₃ liquid solution and the general term "rehydration" (REH) was used as our interest is more focused on the CO₂ uptake performances rather than the accurate regeneration of the starting material.

The XRD pattern of HTlc as-such (HTlc), after activation (HTlc Act) and rehydrated with both H₂O and KHCO₃ (1st REH H₂O-HTlc and 1st REH KHCO₃-HTlc, respectively) were collected prior to check their CO₂ uptake (Figure 6.4 a). The initial HTlc sample shows the characteristic diffraction pattern of previously reported Mg-Al LDHs.^{26,27} After the thermal treatment the main reflections disappeared while two new broad peaks at 43° and 63°, typical of LDO formation, arose.²⁸ This latter sample was then rehydrated with H₂O or KHCO₃ solution. In both cases, the peaks observed in the initial HTlc sample were totally restored.

The TGA analysis carried out on the HTlc as such and on the two rehydrated samples (Figure 6.4 b) shows a difference in the final weight loss between the sample rehydrated in H₂O, which loses ~36%, and the one rehydrated in KHCO₃, which has a loss of almost 50% of the initial weight. The mass loss and the shape of TGA curve of this latter sample is more similar to the original HTlc (i.e. not thermally treated), suggesting that, in this case, the original LDH sample may have recovered.

The CO₂ adsorption/desorption isotherms at 300°C of the rehydrated samples were then collected (Figure 6.4 c). Both rehydrated samples were able to recover the CO₂

capture capacity of the initial HTlc material, as the isotherms (almost) coincide with the primary one collected on as-such HTls.

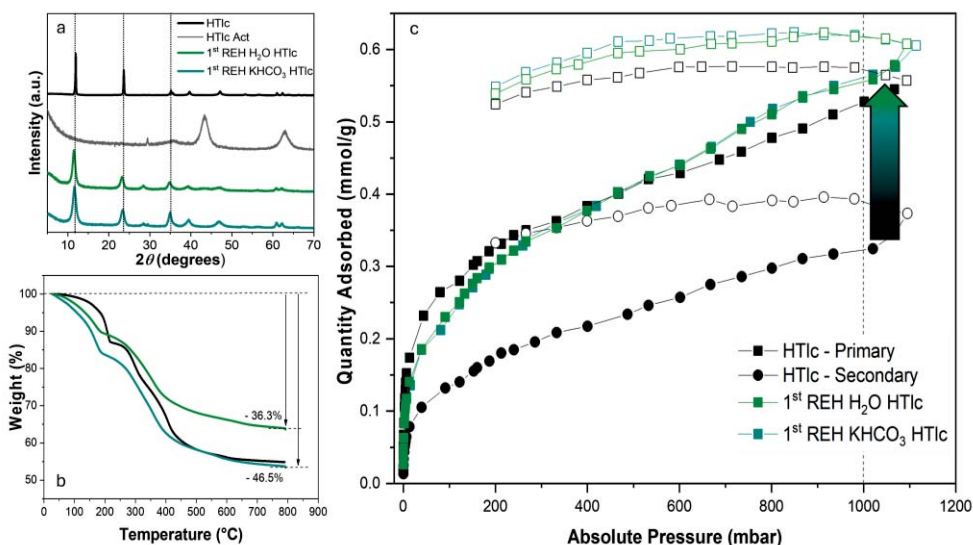


Figure 6.4. XRD pattern of HTlc as-such (HTlc), after activation (HTlc Act) and rehydrated with H₂O and KHCO₃ (1st REH H₂O HTlc and 1st REH KHCO₃ HTlc, respectively) (a), comparison of TGA curves of HTlc as such, 1st REH H₂O HTlc and 1st REH KHCO₃ HTlc (b) and CO₂ adsorption/desorption isotherms at 300°C of the 1st REH H₂O HTlc and 1st REH KHCO₃ HTlc compared with the primary and secondary isotherms of HTlc (c). The primary adsorption isotherm is reported with squares while the secondary adsorption isotherm is reported with cycles. Full symbols represent the adsorption branch and empty symbols represent the desorption branch.

The measurements carried out on the powder sample highlight the potential of this commercial LDH sample for CO₂ capture at medium-high temperatures. The loss in performance observed between the first and second adsorption cycle was successfully recovered by exposing the sample to H₂O solution. The sample was therefore considered as an active phase for the development of 3D monolithic structures produced via direct ink writing.

At the Department of Industrial Engineering of the University of Padova, different synthesis procedures were explored to produce the proper ink for the 3D printing, changing the percentages of the different components and the type of geopolymers used in the synthesis. After various trials, the sample with the best balance between mechanical and adsorption properties was the one composed by 40 wt% LDH (HTlc), 57 wt% sodium geopolymer (NaGP) (molar composition: 3.8 SiO₂ - Al₂O₃ - Na₂O), 3%

sodium bentonite (NaBT) (the detailed synthesis procedure is reported in paragraph 6.1).

The powder XRD patterns of the three separate components (commercial hydrotalcite, geopolymer and bentonite) were collected and compared to the one of the 3D monolith (3D HTlc) previously ground into powder, to prove the persistence of the original hydrotalcite structure in the printed material (Figure 6.5). As previously reported, the HTlc sample shows the characteristic diffraction pattern of the Mg-Al LDHs,^{26,27} while the geopolymer exhibits the a large hump in the 20-40° 2 θ range typical of an amorphous structure, along with the presence of impurities of quartz, muscovite and anatase, commonly observed in the metakaolin original phase.^{29,30} Finally, the pattern of bentonite is mainly composed by a montmorillonite phase.³¹ The diffraction pattern of the 3D HTlc is mainly characterized by the presence of the reflections of hydrotalcites and of some peaks compatible with the previously mentioned quartz and muscovite impurities of the metakaolin. Contrarily, the main reflections of bentonite were not observed, as expected considering the low amount present in the final monolith.

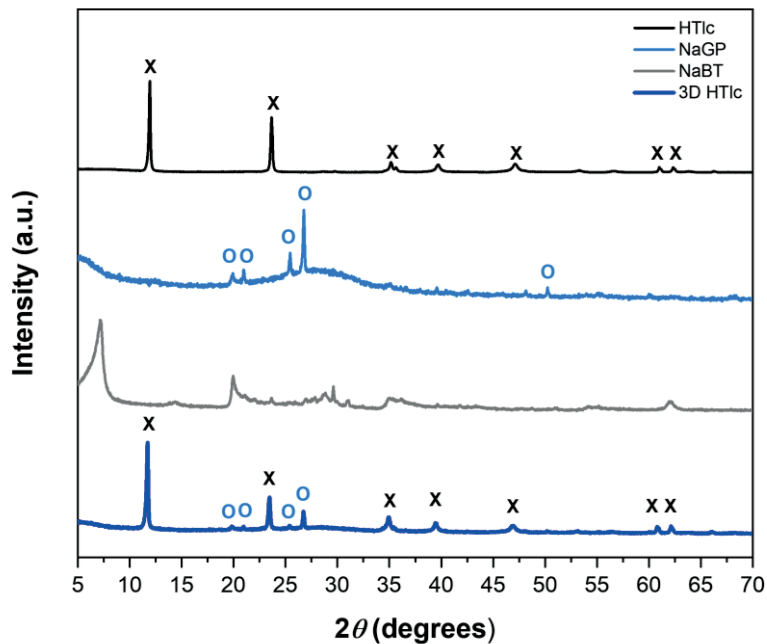


Figure 6.5. XRD pattern of HTlc as-such (HTlc), geopolymer (NaGP) and bentonite (NaBT) in powder from compared with the 3D monolith (3D HTlc). Crosses: main reflections of LDH. Circles: mail reflections of Na Geopolymer.

After checking the crystalline phase of the 3D HTlc sample, the CO₂ adsorption/desorption capacity at 300°C was investigated. The primary and secondary isotherms of the monolith (3D HTlc) are shown in Figure 6.6 and compared with those of the individual powder components. Following the same procedure reported previously, in between primary and secondary isotherm the samples were outgassed at 300°C for 1h. The adsorption capacities at 1 bar and 300°C of all samples are reported in Table 6.2. As for the commercial HTlc in powder form, all samples were previously activated at 400°C for 4h.

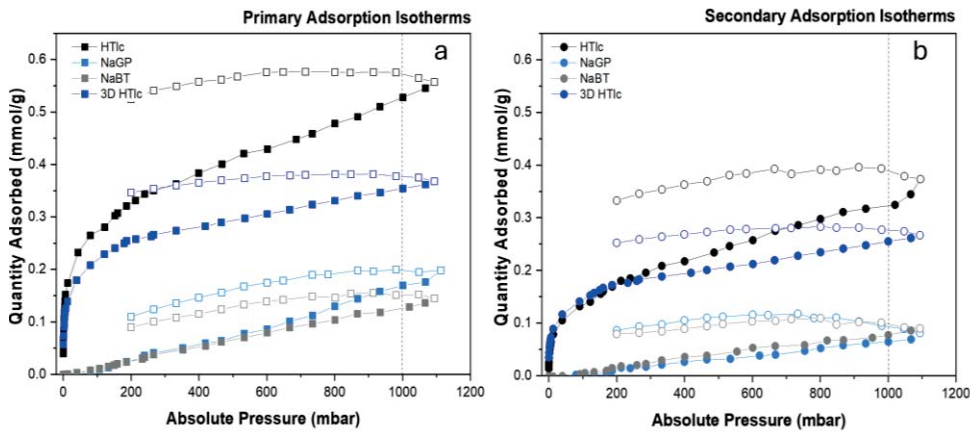


Figure 6.6. Primary (a) and secondary (b) CO₂ adsorption/desorption isotherms at 300°C of the single components in powder form (HTlc, NaGP, NaBT) and the 3D printed monolith (3D HTlc). Full symbols represent the adsorption branch and empty symbols represent the desorption branch.

Table 6.2. Experimental and theoretical values of CO₂ adsorption at 300°C of the single components in powder form (HTlc, NaGP, NaBT) and of the 3D printed monolith (3D HTlc). The experimental values were obtained from the adsorption isotherms shown in Figure 6.6 at 1 bar, while the theoretical value was calculated by summing the adsorbed amount weighted by the percentage of the different components present in the 3D hydrotalcite.

Samples	Primary CO ₂ uptake (mmol/g)		Secondary CO ₂ uptake (mmol/g)	
	Experimental CO ₂ uptake*	Theoretical CO ₂ uptake in 3DHTlc**	Experimental CO ₂ uptake*	Theoretical CO ₂ uptake in 3DHTlc**
HTlc	0.53	0.212	0.32	0.128
NaGP	0.17	0.097	0.06	0.037
NaBT	0.13	0.004	0.08	0.002
3D HTlc (40% HTlc + 57% NaGP + 3% NaBT)	0.35	0.313	0.26	0.167

* The experimental CO₂ uptake is the quantity adsorbed by the sample at 1 bar ** The theoretical CO₂ uptake in 3D HTlc is the quantity adsorbed weighted by the percentage present in the 3D Hydrotalcite. The sum of the theoretical CO₂ uptake of the three components is providing the theoretical CO₂ uptake on the 3D HTlc

As previously reported, HTlc exhibited a type I isotherm in both the primary and secondary adsorption runs, whereas a Henry's adsorption isotherm was observed for NaBT and NaGP, suggesting a much lower affinity for CO₂ for these components, acting only as additives that do not affect the overall CO₂ uptake. Interestingly, similar to the powder sample, 3D HTlc also shows a type I isotherm, implying that in the composite the hydrotalcite, even when present at 40%, represents the active phase in the system and largely contributes to the CO₂ uptake of the material. As a matter of fact, by looking at the primary isotherms, the pure active HTlc phase displays the highest CO₂ uptake, whereas the NaGP matrix and the NaBT additive show a much lower adsorption capacity of about 0.17 and 0.13 mmol/g at 1 bar respectively, as expected for aluminosilicates-based materials at medium-high temperatures.³² On the other hand, the 3D HTlc, although less efficient than the corresponding commercial powder sample, adsorbs 0.35 mmol/g of CO₂ in the first adsorption cycle. This value is slightly higher than the theoretical CO₂ adsorption calculated by summing the adsorbed amount weighted by the percentage of the different components present in the 3D sample, i.e. 0.31 mmol/g (see Table 6.2). By performing a secondary adsorption isotherm (Figure 6.6 b), all samples show a decrease in CO₂ adsorption capacities. As previously observed, the commercial HTlc shows a decrease of almost 40%, reaching 0.3 mmol/g of CO₂ adsorbed at 1 bar, while the other two components, NaGP and NaBT, exhibit a loss of about 62% and 41% respectively, resulting in an almost negligible capture capacity. In contrast, the 3D monolith loses almost 26% between the primary and the secondary adsorption cycle, reaching 0.26 mmol/g at 1 bar, which is higher than the expected theoretical capacity (see Table 6.2).

After the adsorption of CO₂, the 3D monolith was then rehydrated in both H₂O and KHCO₃ solution, trying to restore the initial LDH structure, following the same procedure employed for the HTlc in powder form. In the XRD pattern (Figure 6.7 a) of the 3D sample, previously ground into powder, after thermal activation (3DHTlc Act) the main reflections of the LDH structure disappeared, while two broad peaks at 43° and 63° typical of the LDO arose. The low intensity of the latter reflections was attributed to the lower concentration of HTlc in the composite monolith (40%). After rehydration (1st REH H₂O-3DHTlc), the characteristic reflections of the initial LDH phase just partially reappear, even if the regeneration carried out with KHCO₃ (1st REH KHCO₃-3DHTlc), seemed to be slightly more effective.

The TGA curve of 3DHTlc exhibits a loss of -28 w% at 800°C, while for the rehydrated samples a higher stability of the structure is observed, with a weight loss of -21.5%

and -20.5% for KHCO_3 and H_2O respectively (Figure 6.7 b). This difference could be due to a more difficult regeneration process when the active phase is dispersed in a composite material. It is worth noting that, contrary to what is observed for the monolith, the commercial powder sample rehydrated with KHCO_3 (1st REH HTlc KHCO_3) showed a weight variation more similar to that of the HTlc as such, suggesting the recovery of the initial LDH structure (Figure 6.5 b). However, the differences observed in the TGA analysis did not reflect in a real improvement of the CO_2 capture capacity, suggesting that a similar outcome may occur in the present case.

After the evaluation of the reconstruction process through the TGA measurements, the CO_2 adsorption/desorption isotherms of the rehydrated samples were collected at 300°C (Figure 6.7 c).

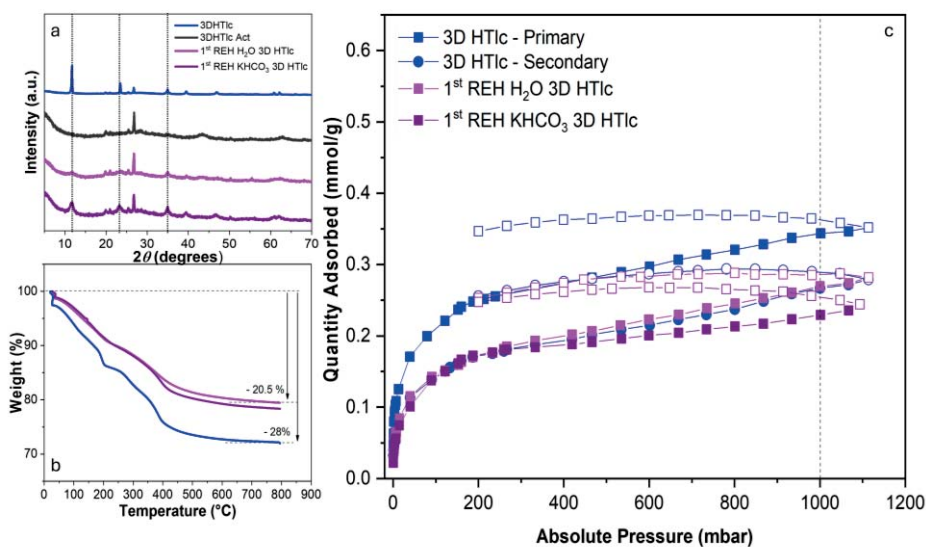


Figure 6.7. XRD pattern of 3D HTlc as-such (3D HTlc), after activation (3D HTlc Act) and 3D HTlc rehydrated with H_2O and KHCO_3 (1st REH H_2O 3D HTlc and 1st REH KHCO_3 3D HTlc, respectively) (a), comparison of TGA curves of 3D HTlc, 1st REH H_2O 3D HTlc and 1st REH KHCO_3 3D HTlc (b) and CO_2 adsorption/desorption isotherms at 300°C of the 1st REH H_2O 3D HTlc and 1st REH KHCO_3 3D HTlc compared with the primary and secondary isotherms of 3D HTlc (c). The primary adsorption isotherm is reported with squares while the secondary adsorption isotherm is reported with circles. Full symbols represent the adsorption branch and empty symbols represent the desorption branch.

Contrary to what was previously observed for the HTlc in powder form, after the rehydration process with both H_2O and KHCO_3 , the monolith did not recover the CO_2 uptake. Indeed, the isotherms collected after rehydration almost coincide with with

the secondary adsorption run of the initial 3D HTlc. The small differences observed between the isotherms of 1st REH H₂O-3DHTlc and of 1st REH KHCO₃-3DHTlc are not relevant and could be considered in the range of the instrumental error, given the small adsorption quantities measured. Considering the above reported results, the rehydration does not seem to be able to restore the CO₂ uptake performance of the 3D material. In fact, this treatment was expected to restore at least the adsorption capacity of the hydrotalcite fraction of the composite (40%).

In order to check if the values obtained by rehydration would remain constant in the subsequent adsorption cycles, a secondary isotherm was measured (Figure 6.8 a). As no difference was observed between H₂O and KHCO₃, this second cycle was only performed on the sample rehydrated in H₂O. Interestingly, a further decrease in the adsorption capacity was observed. As a matter of fact, the quantity adsorbed decreases from 0.26 mmol/g to 0.16 mmol/g at 1 bar and 300°C (-38.5%), passing from the primary to the secondary adsorption (full circles magenta isotherm) after rehydration. Unusually, by performing a second reconstruction step with H₂O (full squares orange isotherm) the adsorption capacity increased again, reaching 0.24 mmol/g (+ 33%) at 1 bar and 300°C, an amount compatible with the primary CO₂ isotherm obtained after the first rehydration step (full squares magenta isotherm). A schematic illustration of the rehydration effect on the CO₂ adsorption capacity of the commercial HTlc and of the 3D HTlc is reported in Figure 6.8 b and c respectively. As previously described, for the hydrotalcite in powder form, the rehydration (with both H₂O and KHCO₃) is able to completely recovered the CO₂ adsorption performance (Figure 6.4 c and 6.8 b). On the other hand, for the 3D printed material, the first rehydration step was not able to refresh the initial CO₂ uptake (Figure 6.7 c and 6.8 c). However, by collecting a secondary CO₂ isotherm on the previously rehydrated material, the capture capacity further decreased. By performing then a second rehydration cycle with H₂O, the CO₂ adsorbed capacity observed after the first reconstruction step was almost restored (Figure 6.8 a and 6.8 c).

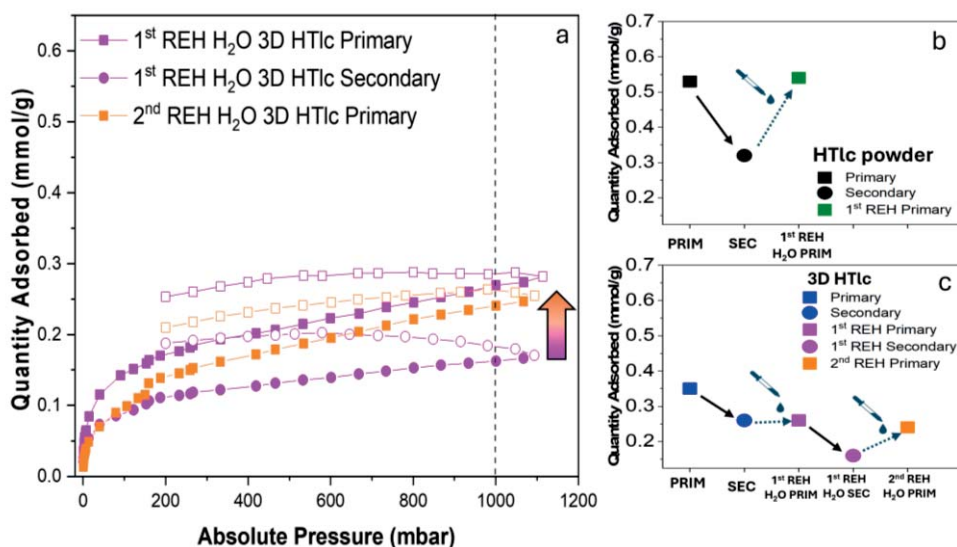


Figure 6.8. Primary and secondary CO₂ adsorption/desorption isotherms at 300°C of the previously rehydrated (with H₂O) 3D HTlc sample (1st REH H₂O 3D HTlc) compared with the primary isotherms collected on the 3D HTlc monolith after a second rehydration step (2nd REH H₂O 3D HTlc) (c). Schematic representation of the quantity of CO₂ adsorbed at 300°C and 1 bar in the different isotherms collected on the HTlc commercial powder (b) and on the 3D HTlc monolith (c). The primary adsorption isotherms are reported with squares while the secondary adsorption isotherm are reported with circles. Black represents the HTlc powder, green the first rehydration of the HTlc powder, blue the 3D HTlc, magenta the first rehydration of 3D HTlc and orange the second rehydration of 3D HTlc. The light blue pipette on the dotted arrow represents the rehydration step between measurements. Full symbols represent the adsorption branch and empty symbols represent the desorption branch.

The slight decrease in CO₂ adsorption observed between the primary and the secondary isotherms of the 3D monolith after the second rehydration cycle (figure 6.8 a) may suggest that the 3D material could be subject to a decrease in adsorption capacity as a result of the prolonged exposure to high temperatures. As a matter of fact, the sample must be exposed to 300°C for 16-18 hours to complete these measurements. To verify this hypothesis, a tertiary and quaternary isotherm were carried out on a freshly synthesised 3D HTlc sample (Figure 6.9 a). Normally, an additional isotherm collected after the secondary one should exhibit the same adsorption values and, therefore, it is rarely reported in the literature. As a matter of fact, since the difference between the primary and secondary isotherm corresponds to the irreversible adsorption fraction, the remaining adsorbed amount should all be reversible in the following cycles.

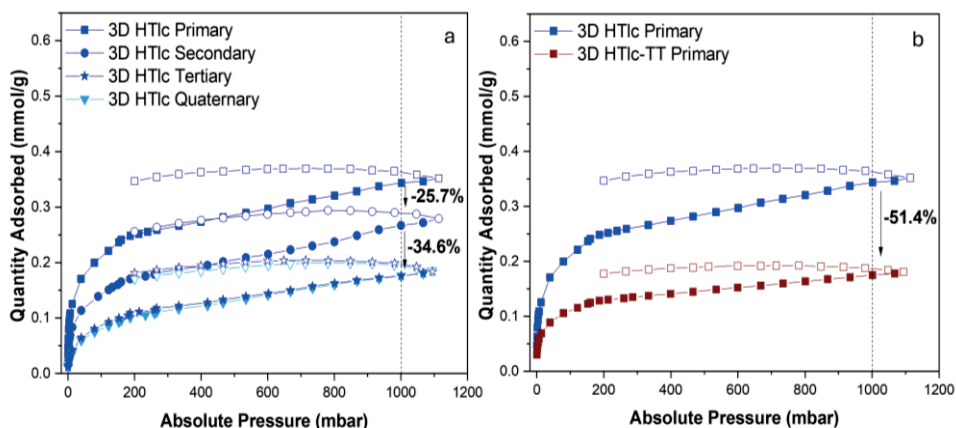


Figure 6.9. Primary, secondary, tertiary and quaternary CO₂ adsorption/desorption isotherms at 300°C of 3D HTlc sample (a) and CO₂ adsorption/desorption isotherms at 300°C of 3D HTlc after being exposed to prolonged thermal treatment in a static oven (3D HTlc-TT) compared to the primary 3D HTlc CO₂ isotherm (b). Full symbols represent the adsorption branch and empty symbols represent the desorption branch.

As previously shown the 3D HTlc, after being activated at 400°C for 4h, adsorbs 0.35 mmol/g at 300°C and 1000 mbar in the primary isotherm, 0.26 mmol/g in the same conditions in the secondary isotherm (-25.7%) and 0.17 mmol/g in the tertiary one (-34.6% with respect to the secondary and -51.4% compared to the primary). A further quaternary isotherm was completely equivalent to the tertiary one. This behaviour confirms the hypothesis that prolonged exposure to high temperatures reduces the adsorption capacity of the 3D monolith. To further prove this, a fraction of the initial 3D HTlc was subjected to a thermal treatment in a static oven resembling the conditions of the measurements (400°C for 4 h and then 300°C for 3 days, the time needed to collect the three consecutive isotherms) and then the CO₂ adsorption was again evaluated. The isotherm of the 3D sample treated in static oven shows a considerable decrease in CO₂ capture, reaching 0.17 mmol/g at 300°C and 1000 mbar (-51.4% with respect to the primary isotherm of the 3D HTlc, in which the sample was heated only for 4 h during the pre-treatment under vacuum), perfectly in agreement with the values obtained in the tertiary and quaternary CO₂ adsorption/desorption isotherm.

6.3 Concluding remarks and future perspectives

As mentioned above, the results reported in this section represent an attempt to apply LDH for CO₂ capture in the medium-high temperature range, taking advantage of the peculiar memory effect of the material to restore the CO₂ adsorption and improve the cyclability performances. While the findings are promising, they are still preliminary and ongoing. These results have provided valuable insights on the potential applicability of the material, but still need to be refined with additional measurements. Below some reflections on the results achieved and on the future investigation to be performed are reported:

- The CO₂ capture capacity of the HTlc powder sample was completely restored by rehydrating it with H₂O or KHCO₃ solution, but additional secondary or tertiary adsorption isotherms and a rehydration cycle should be performed in the future to check the long-term cyclability of this procedure.
- For the 3D HTlc, the initial CO₂ uptake (0.35 mmol/g at 300°C and 1000 mbar), exceeded the theoretical expected value (0.31 mmol/g). However, this uptake was no longer restored by using the current rehydration procedure. In these initial tests, the same rehydration stage that was found to be successful for the powder, was applied to the monolith. However, due to the presence of other additives (NaGP and NaBT), the monolith is a more complex system and perhaps a tailored rehydration procedure should be developed. Indeed, the XRD patterns of the 3D HTlc after the rehydration process with both H₂O and KHCO₃ (1st REH H₂O 3D HTlc, 1st REH KHCO₃ 3D HTlc, Figure 6.7 a) exhibit that the initial LDH reflections are only partially restored, suggesting that the rehydration of the material was not as successful as for the HTlc powder.
- On the basis of the above-reported findings, XRD results to be the most informative technique for quickly evaluating the extent of the reconstruction by rehydration of these materials.
- The rehydration seems to be capable of restoring the CO₂ uptake of 3D HTlc to around 0.24-0.26 mmol/g, corresponding to an increase of ~33-35% (Figure 6.8). This recovered fraction could be associated with a partial recovery of the LDH structure in the monolith, since an increase of about

39% was observed after rehydration for the powder sample. However to prove this hypothesis further analysis should be performed.

- The last experiments showed that when the 3D HTlc is exposed to heat (and CO₂) for a prolonged time, the quantity adsorbed is almost halved with respect to the primary isotherm (0.16/0.17 mmol/g) (Figure 6.9). However, as suggested by the quaternary isotherm, after reaching 0.17 mmol/g of CO₂ adsorption (at 300°C and 1 bar) this value remains constant and do no further decrease. This decrease in adsorption properties could be due to a decomposition of the structure with temperature and/or to a slower conversion of LDH to LDO occurring in the 3D structure. The latter hypothesis assumes that the conversion to LDO is probably not complete after 4 hours at 400°C and continues during all the different measurements performed at 300°C with a slow kinetics. Also in this case, in order to prove this hypothesis additional diffraction patterns will be collected in the following months

Looking at the available literature on the synthesis of shaped hydrotalcite composites for low and/or intermediate temperature CO₂ capture, to the best of our knowledge, only two papers have been published by Papa et al. in 2019 and 2021.^{33,34} In particular, in the first work, a composite material with 28 wt% commercial hydrotalcite (Mg:Al LDH with molar ratios: 1.4, 3.1, 2.2, 2.4) in a geopolymer matrix was synthesised and tested for CO₂ capture at 200°C (measured by thermogravimetric method in a 50:50 CO₂:Ar flow), reaching a value between 0.11-0.14 mmol/g, 30% less than the attended value. In addition, also in this case, a decrease in performance during cyclability was observed due to partial deactivation of the sample.³³ In 2021, a new composite prepared by increasing the hydrotalcite fraction up to 37 wt% was carried out trying to improve the adsorption capacities at low (35°C) and intermediate (200°C) temperatures using two different commercial LDH samples. In this case, the CO₂ capture reaches 0.11-0.14 mmol/g in the first cycle and 0.098-0.11 mmol/g in the second, depending on the Mg/Al ratio present in the initial powdered hydrotalcite sample. In that case the regeneration step between each cycle was performed by heating at 500°C.³⁴

These works underline that although much literature has focused on the potential use of hydrotalcite for CO₂ capture at intermediate temperatures (200-400°C), there is still a deficiency related to shaping that limits its real applicability. The measurements reported in this chapter represent a small step forward in this field due to the slightly higher percentage of hydrotalcite present in the monolith and

the possibility of partially recovering the CO₂ uptake capacity by structure reconstruction.

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7. ELECTROCATALYSTS FOR CO₂ REDUCTION REACTION

As explained in Chapter 2, this section focuses the attention on the first step of 4AirCRAFT Project and deals with the characterization of electrocatalysts involved in the electroreduction of CO₂ to CO. In particular, among the various materials proposed by the project, LDHs resulted to be the most promising ones.

The study reported in this chapter initially focused on catalysts with different elemental compositions: Zn-Al, Ni-Al, Ni-Fe LDH, then the attention shifted to the Zn-Al LDH with the highest faradic efficiency (FE). Zn-Al LDHs with different stoichiometries (2:1, 1:1 and 1:2) were studied by ATR-IR spectroscopy to explore the active sites present in the materials and to understand the reason for the different electrocatalytic performances. Based on the previous results, preliminary studies were carried out to investigate the effect of grinding on the electrochemical performance and on the physicochemical properties of the material. Finally, initial studies were performed using a recently acquired cell capable of combining electrochemical measurements with ATR spectroscopy.

The characterisation of Zn-Al, Ni-Al, Ni-Fe LDHs and Zn-Al LDHs with different stoichiometries (2:1, 1:1 and 1:2) reported in sections 7.2 and 7.3 are largely based on the following publications: " Nakazato, R.; Matsumoto, K.; Yamaguchi, N.; Cavallo, M.; Crocellà, V.; Bonino, F.; Quintelier, M.; Hadermann, J.; Rosero-Navarro, N. C.; Miura, A.; Tadanaga, K. CO₂ Electrochemical Reduction with Zn-Al Layered Double Hydroxide-Loaded Gas-Diffusion Electrode. *Electrochemistry* 2023, 91 (9), 23–00080." and "Cavallo, M.; Dosa, M.; Nakazato, R.; Porcaro, N. G.; Signorile, M.; Quintelier, M.; Hadermann, J.; Bordiga, S.; Rosero-Navarro, N. C.; Tadanaga, K.; Crocellà, V.; Bonino, F. Insight on Zn-Al LDH as Electrocatalyst for CO₂ Reduction Reaction: An in-Situ ATR-IR Study. *J. CO₂ Util.* 2024, 83, 102804". On the other hand, the study of the effect of grinding and of the spectroelectrochemical cell reported in sections 7.4 and 7.5, respectively are still ongoing activities.

7.1 Materials and Methods

The structure of LDH material was previously explained in section 1.2.1 and in Chapter 6. In this case the different LDHs, M^{2+} - M^{3+} LDHs with CO_3^{2-} counterions, were synthesised by Hokkaido University using a traditional coprecipitation process. For the synthesis of Zn-Al LDH with CO_3^{2-} anions, an aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with $Zn^{2+}/Al^{3+} = 2.0, 1.0, 0.50$ mol% was added dropwise into a 0.30 M aqueous Na_2CO_3 solution under stirring at 80 °C. Ni-Al and Ni-Fe LDH were also prepared by replacing the $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with the corresponding $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, respectively with a M^{2+}/M^{3+} ratio of 2.0 mol%. The drop rate was adjusted to 2 mL min⁻¹ by using a syringe pump (SPE-1, AS ONE Corp.). The final pH of the reaction mixture was adjusted to 10 by adding 2.0 M aqueous NaOH solution with a pH meter (pH700, EUTECH INSTRUMENTS Pte. Ltd.). The obtained solution was aged at room temperature for 24 h. The resulting white precipitates were filtrated, washed with distilled water, and dried at 80 °C for 24 h. In case of Zn-Al LDH grounded the as-synthesised sample (Zn-Al LDH 2:1) was ball milled for different times (from 0 till 60 minutes).

The powder X-ray diffraction (XRD) was performed by Hokkaido University by means of XRD diffractometer (CuK α) Mini Flex 600, Rigaku Corp. STEM-EDX measurements were performed by University of Antwerp. The samples were dissolved in ethanol and sonicated for 10 minutes before being drop-casted on a standard TEM grid. STEM-EDX experiments were performed using a ThermoFisher Osiris microscope operated at 200 kV and equipped with a SuperX detector. BF-TEM experiments were performed using a ThermoFisher Tecnai G2 microscope operated at 200 kV and equipped with a Gatan US1000XP CCD camera. HR-TEM images were taken using an image corrected ThermoFisher Titan microscope operated at 300 kV and equipped with a Gatan K2 direct electron detector.

The electrocatalytic CO₂RR experiments were carried out by Hokkaido University. The procedure was described in Chapter 3.

The volumetric and spectroscopic characterizations were performed following the procedures reported in Chapter 3. In the case of Zn-Al LDH 1:2, 2:1 and 1:1 (section 7.3), the spectra were normalised by the underlying area of the structural interlayer carbonates, whereas no normalisation was performed for the measurements

reported in the other sections, where carbonate fitting has not yet been performed. For the volumetric measurements the samples were previously pre-treated under vacuum at 80°C for 4 h. This activation temperature was carefully chosen to preserve the LDH original structure, by examining the variable temperature X-ray diffraction (VT-XRD) pattern of the Zn-Al 2:1 sample. The VT-XRD was performed between room temperature and 450°C using a SmartLab diffractometer (Rigaku, CuK1, $\lambda = 1.541\text{\AA}$). The temperature ramp was set at 5 °C min⁻¹ and the diffractograms were collected in isothermal condition every 10 °C.

7.2 LDHs with different elemental composition: Zn-Al, Ni-Al, Ni-Fe LDH

Initially, three LDHs having different elemental composition, Zn-Al, Ni-Al and Ni-Fe, were selected to perform an initial screening of the electrocatalytic activity. The three electrocatalysts were synthesized and fundamentally characterized by our partners. The X-ray diffraction (XRD) patterns (Figure 7.1 a) showed the presence of (003) and (006) plane peaks, characteristic of the layered structure, while no impurity peaks were detected in any of the products. Peaks in the Zn-Al system were assigned to the previously reported XRD pattern of Zn-Al LDH with carbonate (CO₃²⁻) as interlayer anions.¹ Similarly, for the Ni-Al and Ni-Fe systems, the formation of LDHs with the interlayer carbonate anions was confirmed.^{2,3} However, their peaks were broader than those of Zn-Al LDH, suggesting that the primary grain size was smaller. FE-SEM images showed for Zn-Al LDH the presence of plate-like crystals, typical of LDH structures, with a size of one hundred to several hundreds nm (Figure 7.1 b). The scanning transmission electron microscopy coupled with energy-dispersive X-ray spectrometry (STEM-EDX) mapping showed that elements used as M²⁺ and M³⁺ were homogeneously distributed (Figure 7.1 c, d and e) and the EDX elemental analysis measured an average chemical composition with molar ratios of Zn/Al = 1.96 ± 0.25, Ni/Al = 1.80 ± 0.24 and Ni/Fe = 2.00 ± 0.16 for each product, perfectly in agreement with the starting composition ratio.

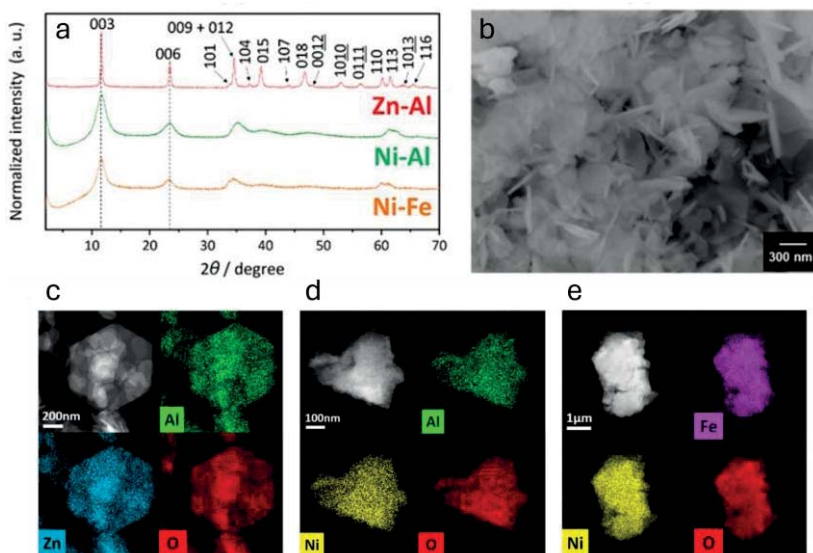


Figure 1.1. XRD patterns of Zn-Al (red line), Ni-Al (green line) and Ni-Fe (orange line) (a), FE-SEM image of Zn-Al LDH (b) and high-angle annular dark field (HAADF)-STEM images and EDX mapping Zn-Al LDH (c), Ni-Al LDH (d) and Ni-Fe LDH (e). Those experiments were performed and kindly provided by Dr. R. Nakazato (Hokkaido University) and Mr. M. Quintelier (University of Antwerpen). This figure is adapted from reference 4.

The samples were then tested for CO₂RR. The faradic efficiency (FE) showed in the case of Zn-Al LDH a high CO formation, dominating at more negative applied potentials, as the highest FE of 67% was obtained at -1.4 vs. RHE (Figure 7.2a). H₂ formation was observed as major side-reaction with a FE ranging from 22% to 30%, while the electron consumption by other reactions gave less than 10% of the FE. On the other hand, in case of Ni-Al LDH, Ni-Fe LDH, or without LDH, H₂ was predominantly formed, suggesting that only Zn-Al LDH acts as a CO₂RR catalyst (Figure 7.2 b, c and d).

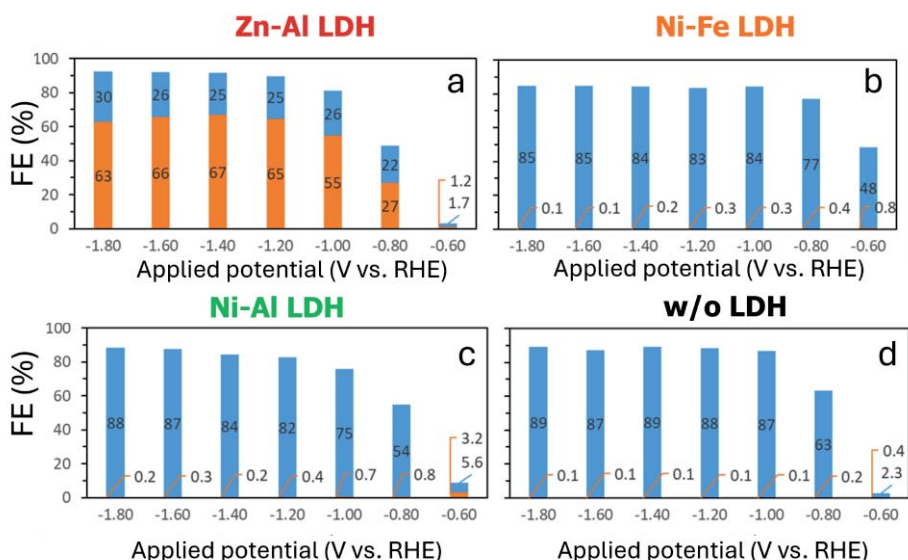


Figure 7.2. Applied potential dependence of Faradaic efficiency (FE) for CO₂ER in 1.0M aqueous KHCO₃ solution using each cathode with (a) Zn-Al LDH, (b) Ni-Fe LDH and (c) Ni-Al LDH, and (d) without LDH. (orange bar: CO, blue bar: H₂). Those experiments were performed and kindly provided by Dr. R. Nakazato (Hokkaido University). This figure is adapted from reference 4.

A deep characterization was then performed to understand the reason of the different electrocatalytic performances of the materials. The CO₂ adsorption capacities of the three LDHs were firstly investigated by collecting volumetric CO₂ adsorption isotherms at 25°C to quantify and identify possible differences in the adsorption capacities of the three electrocatalysts (Figure 7.3 a). Prior to the measurements, the samples were activated at 80°C for 4 h in vacuum. To prove that the original LDH structure is still preserved under those activation conditions, a VT-XRD experiment was performed on the Zn-Al 2:1 sample (Figure 7.3 b).

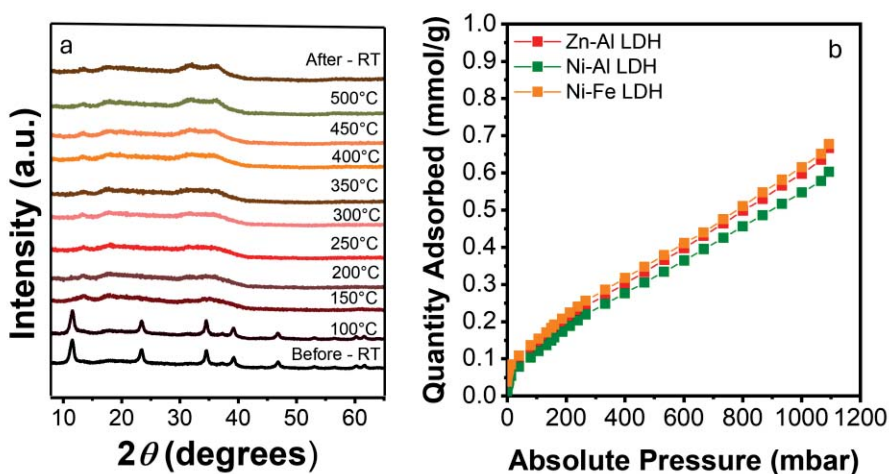


Figure 7.3. VT-XRD of Zn-Al LDH in the 25-500°C temperature range (a) and CO₂ adsorption isotherms at 25°C of: Zn-Al (red curve), Ni-Al (green curve) and Ni-Fe (orange curve) (b). This figure is adapted from reference 4.

VT-XRD measurements showed that the main diffraction peaks of LDH structure were preserved till 100°C. The adsorption/desorption isotherm revealed similar CO₂ adsorption capacities for the three samples with a CO₂ uptake in the range of 0.55-0.59 mmol/g at 1 bar. This result suggested that the reason for the difference in performance in CO₂ reduction reactions was more likely to be found in the nature of the interaction of these materials with CO₂. In order to further investigate this aspect, the same materials were studied by means of IR spectroscopy. Initially, these samples were tentatively tested by means of transmission IR spectroscopy, thanks to the possibility of obtaining information on the available sites and the strength of the interactions by dosing different molecular probes (CO, CD₃CN, CO₂ etc.) on the previously activated samples, as already described in Chapter 4 and 5. However, in all experiments performed in transmission mode, no specific active sites were detected. These results were not an evidence of the absence of interactions but were more likely due to (i) the presence of some residual water in the sample, which cannot be completely removed without changing the structure (see Figure 7.3 a) (ii) the presence of some carbonate anions in the interlayer, resulting in some intense broad bands going out of scale in the carbonate-like region of the IR transmission spectra (1800-1200 cm⁻¹). Therefore, in order to study the active sites present in the samples, an ATR-IR spectroscopical characterization was performed. As a matter of fact, while in transmission measurements all the radiation passes the total thickness of the sample resulting in a spectra out of scale in the region of interest, in ATR, the

penetration depth of the incident radiation, which is reflected multiples times, is much less ($0.5\text{--}2\text{ }\mu\text{m}$). This allows to keep in scale the carbonate region and study the interaction of CO_2 with LDH.

The different samples were deposited as thin layers on the ATR crystal then H_2O , in which N_2 or CO_2 were bubbled inside, was flowed to the sample following the procedure previously described in Chapter 3.

Firstly, the spectra of the dry samples were measured (Figure 7.4).

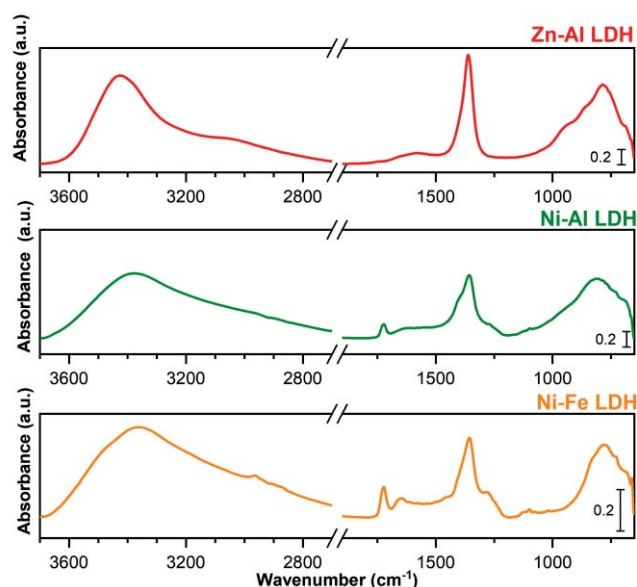


Figure 7.4. ATR-IR spectra in the $3700\text{--}650\text{ cm}^{-1}$ spectral region of dry Zn-Al LDH (a), Ni-Al LDH (b) and Ni-Fe LDH (c). From reference 4.

The three LDH samples exhibited a common broad band in the high frequency region ($3500\text{--}2950\text{ cm}^{-1}$) ascribable to the hydroxyl-stretching vibrations of both structural M-OH species ($3500\text{--}3400\text{ cm}^{-1}$) and molecular water present in the interlayer ($3300\text{--}2950\text{ cm}^{-1}$).⁵ In the low frequency region, a broad band ($1000\text{--}650\text{ cm}^{-1}$), derived from the superimposition of the ν_2 out of plane stretching mode of interlayer carbonate anions ($\sim 860\text{ cm}^{-1}$) and the lattice HO-M-OH and M-OH (M = Zn, Al, Ni, Fe) vibrational modes ($450\text{--}800\text{ cm}^{-1}$), was present.⁶ In the intermediate region, a band at 1640 cm^{-1} , which is typical of the bending vibrations of the interlayer water molecules, and an intense peak at around 1350 cm^{-1} with a weak shoulder at $\sim 1410\text{ cm}^{-1}$ due to the ν_3 stretching mode of interlayer carbonate anions were observed.⁵ It is worth noting that the ν_3 stretching mode of free carbonate

anions is reported to be at 1415 cm^{-1} .⁷ However, a change in the symmetry of the molecule could lead to the splitting of the ν_3 in two distinct components (symmetric $\nu_{3\text{sym}}$ and asymmetric $\nu_{3\text{asym}}$ vibrations) at ~ 1365 and $\sim 1415\text{ cm}^{-1}$. Additionally, the bands in the $1800\text{--}1200\text{ cm}^{-1}$, partially superimposed to the structural water and carbonates signals, are probably related to the formation of surface (non-structural) carbonate species upon the exposure to the CO_2 present in the atmosphere. It should be pointed out that the Ni-Al and Ni-Fe LDHs interestingly exhibited some additional peaks at 1725 cm^{-1} and 1270 cm^{-1} , which are probably due to the presence of a different family of surface “bridged” carbonate-like species.⁷

After completely understanding the spectra of the dry samples, the difference among the three LDHs upon interaction of CO_2 was investigated by adding CO_2 saturated water on the dry samples (Figure 7.5).

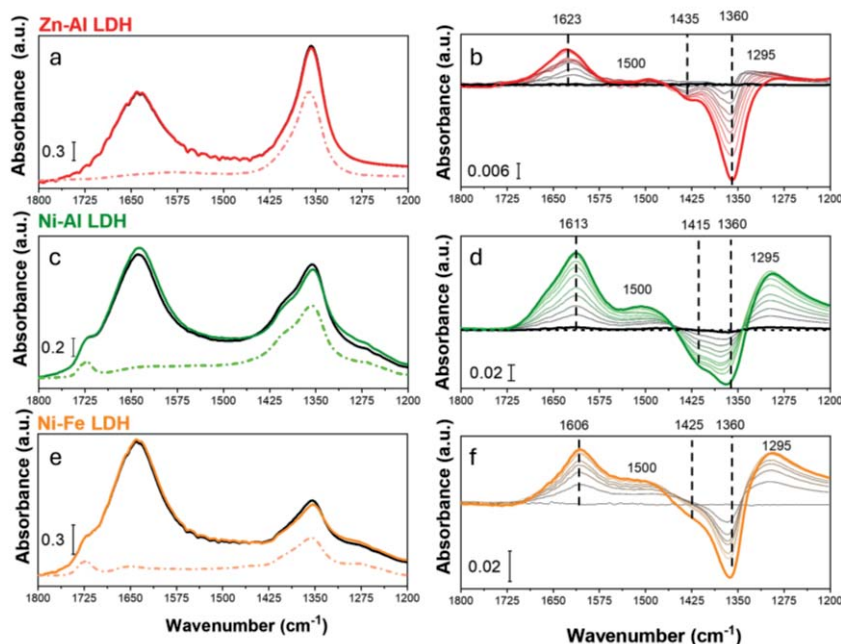


Figure 7.5. ATR-IR spectra in the carbonate-like region ($1800\text{--}1200\text{ cm}^{-1}$) of: Zn-Al LDH (a), Ni-Al LDH (c) and Ni-Fe LDH (e). The corresponding differential spectra (obtained by subtracting the spectra of the wet N_2 -saturated sample to that of the wet CO_2 -saturated sample) are shown on the right side (b, d and f). Dotted coloured, black, and solid coloured curves represent the dry, wet N_2 -saturated, and wet CO_2 -saturated samples, respectively. The curves of intermediate CO_2 coverage are shown in grey. In adsorption differential spectral patterns (b, d and f), the bands relative to species that form or increase upon CO_2 contact are pointing up, bands relative to species that decrease are pointing down. From reference 4.

As shown in Figure 7.5 a, c and e, the contact with water caused an increase in the high frequency region bands associated to the OH stretching vibrations (here not reported for sake of brevity) together with the increment of the 1640 cm^{-1} signal ascribed to the H-O-H bending vibrations, while the interaction of CO_2 with basic sites was responsible for the appearance of surface (non-structural) carbonates-like species ($1800\text{-}1200\text{ cm}^{-1}$ region). However, the appearance of those carbonates on the different LDHs fall in the region dominated by the bending vibration of water and interlayer carbonates anions, whose intense bands strongly affect the identification of the newly formed surface carbonate (See Figure 7.5 a, c and e). For this reason, the identification of the main spectral changes occurring in this region upon CO_2 contact, is possible just by subtracting the spectra of the corresponding wet N_2 -saturated samples (See Figure 7.5 b, d, and f).

For all LDHs, the CO_2 contact was responsible for the increase of the intense band at around 1610 cm^{-1} , which shifted to different wavenumbers depending on the kind of LDHs (1606 cm^{-1} for Ni-Fe, 1613 cm^{-1} for Ni-Al and 1623 cm^{-1} for Zn-Al), and the simultaneous decrease of the signal at 1360 cm^{-1} . However, the Ni-Al and Ni-Fe LDHs behave differently compared to Zn-Al one in the remaining spectral regions. In particular, upon CO_2 contact, the Ni-Al and Ni-Fe LDHs exhibit two broad and intense bands at $\sim 1500\text{ cm}^{-1}$ and at $\sim 1295\text{ cm}^{-1}$, which are nearly absent in the Zn-Al one. Additionally, the decrease of the band at 1360 cm^{-1} occurs simultaneously to the component at around 1420 cm^{-1} , which is located at different frequencies in the three LDHs: 1415 cm^{-1} in Ni-Al, 1425 cm^{-1} in Ni-Fe and 1435 cm^{-1} in Zn-Al. Finally, the bands at 1725 cm^{-1} and 1270 cm^{-1} which are originally present in the Ni-Al and Ni-Fe LDHs and assigned to surface “bridged” carbonates were not changed by CO_2 contact, suggesting the stability of these carbonate species in the as-synthesized LDHs (See Figure 7.5 c and e and corresponding differential spectra d and f).

As already mentioned, free carbonate anions generally show a ν_3 asymmetric CO_3^{2-} stretching at around 1415 cm^{-1} , which split in two different signals when the symmetry is lowered ($\nu_{3\text{sym}}$ and $\nu_{3\text{asym}}$) detectable in the $1800\text{-}1200\text{ cm}^{-1}$ spectral range.⁷ When CO_2 interacts with the LDH basic sites, both the symmetric and asymmetric vibrations are detected, and different carbonate-like species, such as unidentate, bidentate, bridged, and polydentate structures or bicarbonates, are

formed depending on the type and the strength of the surface (Figure 7.6 for a schematic representation of the different carbonate species).⁸

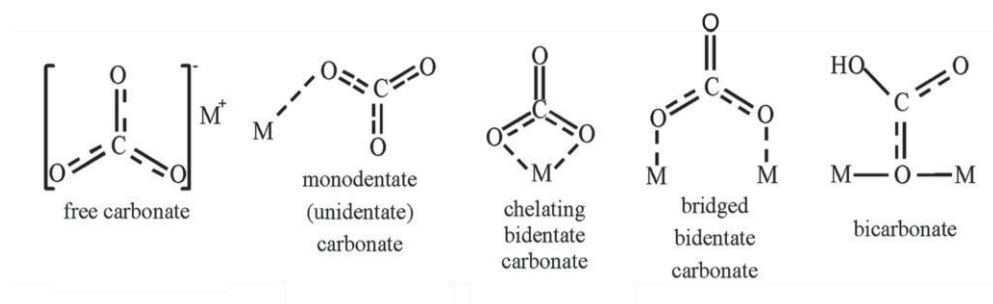


Figure 7.6. Illustration of possible carbonate-like species formed from the interaction of CO₂. From reference 9.

To distinguish between carbonates, the most employed criteria is usually based on the distance between the two “new” stretching components ($\Delta\nu_3$) which is usually inversely proportioned to the basic strength of the sites available in the material. Indeed, the monodentate carbonates, which have low coordination oxygen anions and account for the strongest basic sites, usually display a $\Delta\nu_3$ of $\sim 100\text{ cm}^{-1}$. The bidentate carbonate-like species, which form on acid–base pairs and constitute the intermediate strength basic sites, usually show a $\Delta\nu_3$ of $\sim 300\text{ cm}^{-1}$ for the chelated ones and of $\sim 400\text{ cm}^{-1}$ for the bridged ones.^{7–10} Lastly, bicarbonates are easily discernible due to the presence of the characteristic, sharp C–OH bending (δOH) mode in the $1225\text{--}1240\text{ cm}^{-1}$ spectral range and are usually weakly bonded, while polydentate species in gas phase are usually strongly resistant to degassing conditions.⁷ In the present case a correct assignment of the carbonate species formed upon CO₂ adsorption is not straightforward for at least two reasons: (i) the superposition of the signals generated by structural carbonate and water molecule and (ii) the possible loss of a fraction of deposited sample during the experiment. Additionally, the assignment of carbonates based on $\Delta\nu_3$ splitting can be affected by the polarizing power of the metal cations, the composition of the material, the presence of water and/or cations external to the metal coordination sphere, and many other factors.^{7,11} However, the identification of the main carbonate species formed on LDHs reported in the literature is reasonable following the values of $\Delta\nu_3$ reported above (Table 7.1).

Table 7.1 Comparison of the main carbonate species formed on LDH-derived systems present in literature. For each carbonate the asymmetric O-C-O stretching frequency (ν_{3asym}), the symmetric O-C-O stretching frequency (ν_{3sym}) and their difference ($\Delta\nu_3$) was reported. From reference 12.

Samples	Monodentate (Md) Carbonate (cm^{-1})			Bidentate chelated (Bc) Carbonate (cm^{-1})			Bidentate bridged (Bb) Carbonate (cm^{-1})			Others (cm^{-1})	Ref	Notes
	$\nu_{3(asym)}$	$\nu_{3(sym)}$	$\Delta\nu_3$	$\nu_{3(asym)}$	$\nu_{3(sym)}$	$\Delta\nu_3$	$\nu_{3(asym)}$	$\nu_{3(sym)}$	$\Delta\nu_3$	Bicarbonates		
Mg-Al mixed oxide	1510–	1360–	200	1610–	1320–	310				1650–	13	CO ₂ in gas phase on calcined Mg-Al (Mg/Al ratios 0.5–9.0)
	1560	1400	110									
Mg-Al mixed oxide	1575–	1355–	190	1645–	1300–	325	1730–	1300–	425	1690–	14	CO ₂ in gas phase on calcined Mg-Al (Mg/Al=3, synthesised with K ₂ CO ₃ or Na ₂ CO ₃)
	1590	1385	235									
Co-Al HTlcs Ni-Al HTlcs	-	-	-	1545	1242	303	-	-	-	-	15	Investigation of Co-Al and Ni-Al (3:1) upon thermal decomposition
	1430	1360	70	1590	1333	257						
K promote d Mg-Al LDH	-	-	-	1570–	1365–	185	-	-	-	-	8	Treated at 600°C prior to the measurement. Spectra recorded under CO ₂ /H ₂ O/N ₂ gas flow
				1540	1335	235						

Di Cosimo et al.¹³, who investigated the interaction of CO₂ with Mg-Al mixed oxides having different molar ratios (0.5–9.0), reported the presence of unidentate carbonates at 1510–1560 cm⁻¹ (asym ν_{O-C-O}) and at 1360–1400 cm⁻¹ (sym ν_{O-C-O}) with a $\Delta\nu_3$ in the range of 200–110 cm⁻¹. The bidentate carbonates were detected at 1630–1610 cm⁻¹(asym ν_{O-C-O}) and at 1340–1320 cm⁻¹(sym ν_{O-C-O}) with a $\Delta\nu_3$ of 310–270 cm⁻¹, while bicarbonate species show two bands at 1650 cm⁻¹ and at 1480 cm⁻¹ together with the appearance of the C-OH bending mode at 1220 cm⁻¹. Comparable frequencies were reported in a similar system by Leòn et al.¹⁴ where, unlike to Di Cosimo et al.¹³, two different families of unidentate carbonates and both chelated and bridged bidentate species were detected. Perez-Ramirez et al.¹⁵ reported the presence of monodentate and bidentate chelated carbonates having a $\Delta\nu_3$ lower than the previously mentioned authors, while Coenen et al.⁸, who investigated a K promoted Mg-Al mixed oxide in the presence of wet CO₂, mainly reported the appearance of bidentate species.

Therefore, based on the $\Delta\nu_3$ splitting, the major bands formed upon CO_2 interaction with the samples were tentatively assigned to the formation of predominantly bidentate species ($\Delta\nu_3 > 100$). Additionally, the presence of bicarbonates is highly unlikely due to the absence of the characteristic sharp band at $\sim 1220 \text{ cm}^{-1}$ associated to the COH bending mode.^{7,16} The differences in the spectra of Ni-Al, Ni-Fe and Zn-Al show the formation of different families of bidentate carbonates with different strength and stability which suggests also the presence of different basic sites in the as synthesized LDHs. The differences in the basic sites originally present in the materials together with the different strength of the carbonates species generated by the interaction with CO_2 is probably responsible for the different catalytic behaviour in the three LDHs.

However, given the low (almost zero) CO evolution of two of the samples analysed, a more detailed analysis of the active species was carried out only on the most efficient sample (Zn-Al LDH) and the results are reported in the following section in which some new compositions were also characterized.

7.3 Zn-Al LDH with different $\text{M}^{2+}/\text{M}^{3+}$ molar ratio

The higher activity of Zn-Al LDH with respect to Ni-Al and Ni-Fe LDHs observed in the previous section brings the Zn-Al composition into focus. This sample was further analysed and the effect of the variation of stoichiometry was studied in detail. Two new compositions of Zn-Al LDH were synthesized having different $\text{M}^{2+}/\text{M}^{3+}$ ratio, Zn-Al 1:2, Zn-Al 1:1, and their performances were compared to the Zn-Al 2:1 which was newly prepared. Following the same procedure previously described, the sample was firstly characterized by means of XRD and EDX analysis and a first analysis of CO_2 adsorption capacity was performed (Figure 7.7)

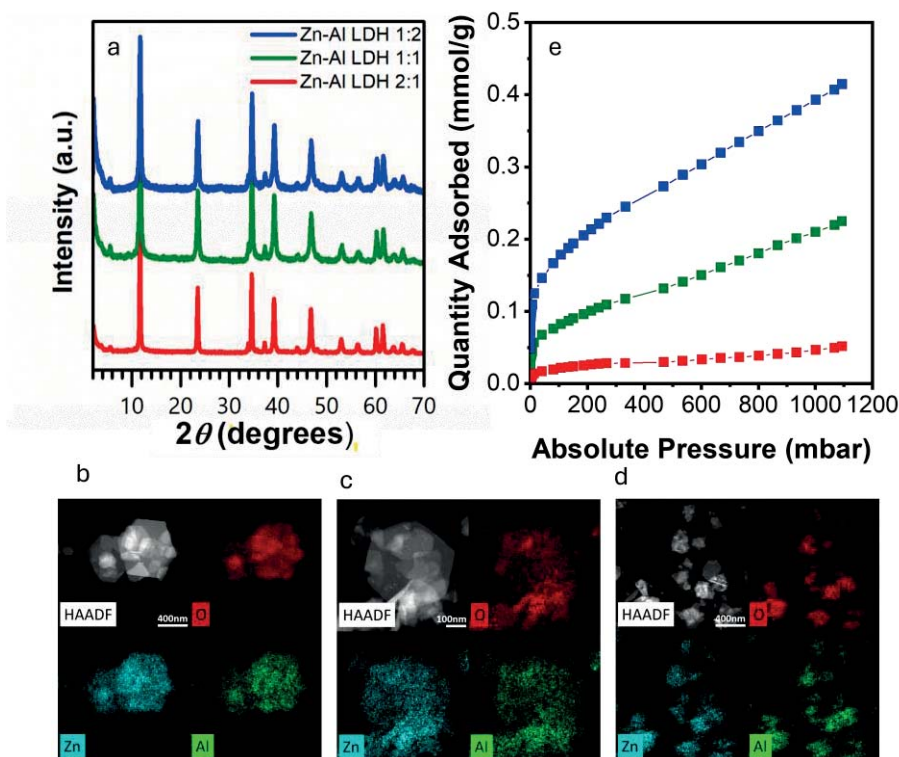


Figure 7.7. XRD diffractograms of Zn-Al 1:2 (blue line), Zn-Al 1:1 (green line) and Zn-Al 2:1 (red line) (a), High-angle annular dark field (HAADF)-STEM images and EDX mapping Zn-Al 1:2 (b), Zn-Al 1:1 (c) and Zn-Al 2:1 (d) and CO₂ adsorption isotherms at 25°C. XRD and STEM images were performed and kindly provided by Dr. R. Nakazato (Hokkaido University) and Mr. M. Quintelier (University of Antwerpen). This figure is adapted from reference 12.

The X-ray diffraction (XRD) patterns (Figure 7.7 a) showed the presence of (003) and (006) plane peaks, characteristic of the layered structure in agreement with what previously reported in the previous paragraph. STEM-EDX elemental analysis (Fig. 7.7 b, c and d) yielded mean Zn:Al ratios of 1.96, 1.56, and 1.19 for Zn-Al 2:1, Zn-Al 1:1, and Zn-Al 1:2, respectively. As a matter of fact, in the Zn-Al 1:1 and Zn-Al 1:2 samples there were also smaller particles present that contained only aluminum which could explain the deviation of the measured mean Zn:Al ratio from the expected value. Considering that no impurity peak was observed in the XRD pattern, the particles containing only aluminum were ascribed to amorphous alumina. The preliminary analysis of CO₂ capture capacity carried out by means of adsorption isotherms at 25°C (Figure 7.7 e), showed, contrary to the previous case, the following trend: Zn-Al 1:2 >> Zn-Al 1:1 > Zn-Al 2:1. The potential application of Zn-Al LDHs as electrocatalysts for CO₂RR to CO was then evaluated in the same conditions

previously described. The applied potential dependence of current density (j) and Faradaic efficiency (FE) are shown in Figure 7.8. The catalytic currents were observed to increase with more negative applied potentials in all the samples, while CO and H₂ still remains the main gaseous products. The partial current densities of CO evolution tended to be larger in the case of Zn-Al 1:1 and Zn-Al 1:2 than in the case of Zn-Al 2:1 while the total current density and the partial current density of H₂ evolution were larger in the order Zn-Al 2:1 > Zn-Al 1:1 > Zn-Al 1:2, thus H₂ evolution tended to be suppressed in favour of CO by decreasing the Zn/Al ratio, reaching the best performances for Zn-Al 1:2.

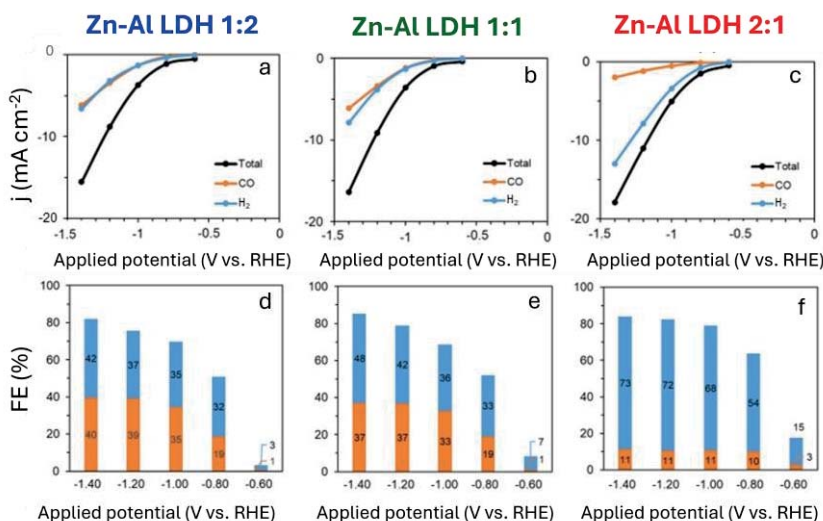


Figure 7.8. Applied potential dependence of current density (j) (a, b and c) and Faradaic efficiency (FE; orange bar: CO, blue bar: H₂) (d, e and f) for CO₂RR in 0.10 M aqueous KHCO₃ solution of Zn-Al 1:2 (a), Zn-Al 1:1 (b), and Zn-Al 2:1 (c). Those experiments were performed and kindly provided by Dr. R. Nakazato (Hokkaido University). This figure is adapted from reference 12.

Since the use of molecular probe using transmission IR spectroscopy does not provide suitable information (see section 7.2) the three samples were studied by means of ATR-IR spectroscopy. The spectra of the dry samples were firstly analysed (Figure 7.9).

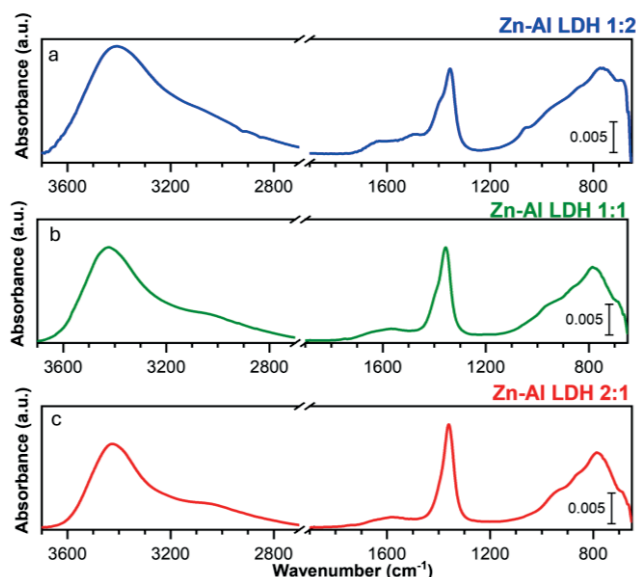


Figure 7.9. ATR-IR spectra in the 3700-650 cm^{-1} spectral region of dry Zn-Al LDH 1:2 (a), Zn-Al LDH 1:1 (b) and Zn-Al LDH 2:1 (c). From reference 12.

As previously discussed, the samples exhibit: (i) a broad band at high wavenumbers ($3900\text{--}2500\text{ cm}^{-1}$) ascribable to the hydroxyl stretching vibrations (ii) another broad band in the low frequency region ($1000\text{--}650\text{ cm}^{-1}$) resulting from the overlapping of the ν_2 out of plane stretching mode of interlayer carbonate anions ($\sim 860\text{ cm}^{-1}$) and the vibrational mode of lattice HO-M-OH ($450\text{--}800\text{ cm}^{-1}$) (iii) the presence of the bending vibrations of the interlayer water molecules (1640 cm^{-1}) and the asymmetric ν_3 stretching mode of the structural interlayer carbonates at around 1400 cm^{-1} and 1365 cm^{-1} due to the splitting caused by the decrease in symmetry.^{17,18}

As explained in the previous paragraph in order to detect the main spectral change occurring in the carbonate region upon CO_2 interaction a subtraction of the spectra of the wet N_2 -saturated samples must be performed. The spectra showing the interaction of the sample with the CO_2 saturated H_2O flow were then obtained (Figure 7.10)

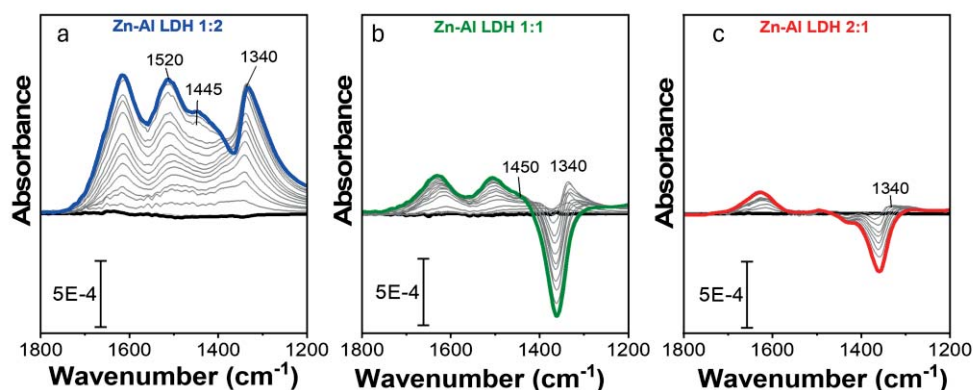


Figure 7.10. In-situ ATR-IR spectra in the carbonate-like region (1800–1200 cm^{-1}) of Zn-Al 1:2 (a), Zn-Al 1:1 (b) and Zn-Al 2:1 (c) under a CO_2 -saturated H_2O flow. The spectra are reported by subtracting the spectra of the wet N_2 -saturated sample to that of the wet (H_2O) CO_2 -saturated one (a, b and c). The black and coloured curves represent the wet (H_2O) N_2 -saturated and wet (H_2O) CO_2 -saturated samples, respectively. The curves of intermediate CO_2 coverages are shown in grey. The spectra were normalized by the underlying area of the structural interlayer carbonates. This figure is adapted from reference 12.

As previously discussed, the bands emerging in this spectral region are associated with carbonates-like species originated from the interaction of CO_2 with the basic sites. In case of Zn-Al LDH 1:2 the spectrum shows a rapid increase of the bands at $\sim 1340 \text{ cm}^{-1}$, followed by a gradual increment of the signal at 1520 cm^{-1} . This latter band probably overlaps to another signal at lower wavenumbers (approximately 1450 cm^{-1}), rising with a similar trend. Additionally, the broadness of the band related to the HOH bending vibrations at 1640 cm^{-1} also suggests the existence of other spectral components superimposed at higher wavenumbers. The spectra collected at higher CO_2 coverage (colored curves) display an unusual minimum at 1363 cm^{-1} , which further complicates the identification of the different components, especially for Zn-Al 1:1 and Zn-Al 2:1 LDHs. This downwards band will be discussed in detail later on. The Zn-Al 1:1 sample shows, similarly to Zn-Al 1:2, a first increase of the 1340 cm^{-1} band followed by the rise of a broad band in the 1580 and 1400 cm^{-1} spectral region. Unfortunately, this sample exhibits an important minimum at 1363 cm^{-1} which partially hides a probable second component at around 1450 cm^{-1} and leads to a difficult identification of the real maxima of the different spectral components. For Zn-Al 1:1 and even more for Zn-Al 2:1, the carbonates evolution seems to be lower compared to Zn-Al 1:2, especially for the bands between 1580 and 1400 cm^{-1} which are nearly absent for Zn-Al 2:1. Indeed, for this sample the prevalent band is the HOH bending at 1640 cm^{-1} , together with the presence of the minimum at 1363 cm^{-1} . Notably, all samples show a decrease in intensity at 1363 cm^{-1} .

cm^{-1} , leading to the appearance of negative bands for Zn-Al 1:1 and Zn-Al 2:1. Since the vibrational frequency of this negative signal coincides with that of the structural interlayer carbonates it could be due to (i) a consumption of interlayer carbonates anions and/or (ii) a loss of deposition by the crystal, generated by the CO_2 -saturated H_2O flow. To minimize the risk of deposition loss and to better appreciate the carbonates bands hidden by the presence of the intense HOH bending mode at 1640 cm^{-1} , a different solvent was used. Even though water was chosen as the solvent closest to the reaction conditions, to further investigate the formation of carbonates upon CO_2 adsorption, the same tests were repeated in C_6H_{12} (Figure 7.11).

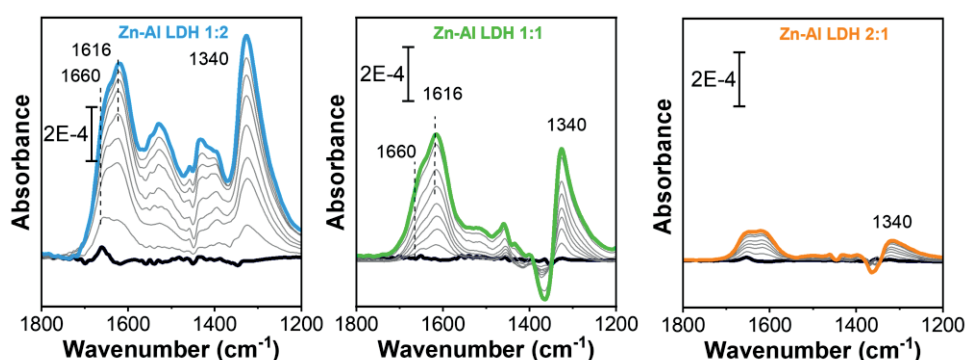


Figure 7.11. In-situ ATR-IR spectra in the carbonate-like region ($1800\text{--}1200\text{ cm}^{-1}$) of Zn-Al 1:2 (a), Zn-Al 1:1 (b) and Zn-Al 2:1 (c) under a CO_2 -saturated C_6H_{12} flow. The spectra are reported by subtracting the spectra of the wet N_2 -saturated sample to that of the wet (C_6H_{12}) CO_2 -saturated one (a, b and c). The black and coloured curves represent the wet (C_6H_{12}) N_2 -saturated and wet (C_6H_{12}) CO_2 -saturated samples, respectively. The curves of intermediate CO_2 coverages are shown in grey. The spectra were normalized by the underlying area of the structural interlayer carbonates. This figure is adapted from reference 12.

The three samples show a carbonates spectral evolution coherent with what was previously observed for CO_2 -saturated H_2O (Figure 7.10). The IR spectra collected in C_6H_{12} are characterized by a band at 1448 cm^{-1} ascribed to the CH_2 scissoring bending mode.¹⁹ However, considering the medium-weak intensity of this signal, it does not preclude the investigation of the carbonates spectral region. As previously observed in H_2O , upon contact with CO_2 -saturated C_6H_{12} flow, the spectrum of Zn-Al 1:2 sample (Figure 7.11 a) shows an increase of the band at $\sim 1340\text{ cm}^{-1}$ along with an increment of the signals in the $1700\text{--}1600\text{ cm}^{-1}$ range, now clearly displaying the presence of two distinct and well-resolved components at 1616 cm^{-1} and 1660 cm^{-1} . The band at 1340 cm^{-1} is characterized by a tail at low frequencies, confirming the existence of an additional component. The $1600\text{--}1370\text{ cm}^{-1}$ region also gradually increases in intensity, revealing the presence of two distinct components, although

the presence of the CH₂ bending mode prevents a clear identification of the maxima. Similarly, Zn-Al 1:1 shows a first increase of the bands at 1616 and 1340 cm⁻¹ followed by the increment of the bands at 1660 cm⁻¹. The latter can probably be coupled with a component falling between 1340 and 1200 cm⁻¹, as suggested by the asymmetric shape of the band with apparent maximum at 1340 cm⁻¹. An increase of the bands in the 1600–1370 cm⁻¹ spectral region is also observed, although less pronounced than in Zn-Al 1:2. Lastly, the Zn-Al 2:1 spectrum is characterized by a scarce evolution of the carbonates bands. For all samples, a spectral minimum at 1363 cm⁻¹ was detected, but less pronounced than that observed in the water stream, suggesting a higher stability of the sample deposition when in contact with a C₆H₁₂ solution.

By looking at the whole carbonate spectral profile, Zn-Al 1:2 displays a greater carbonates evolution than Zn-Al 1:1 and Zn-Al 2:1 in both H₂O and in C₆H₁₂. Interestingly, this result agrees with the volumetry data (Figure 7.7 e), where the Zn-Al 1:2 LDH shows a CO₂ capture capacity at 1 bar higher than for Zn-Al 1:1 and Zn-Al 2:1 (50% and 75% respectively), different from what is shown by the LDH with different elemental compositions (Figure 7.3 b). Another interesting finding is the possibility to better appreciate the existence of two IR components when the experiment is carried out in C₆H₁₂ flow: one with an apparent maximum at 1660 cm⁻¹ and another between 1340 and 1200 cm⁻¹, which were weakly detectable in the tests performed in H₂O. These bands can be associated to a basic oxygen, which preferentially interacts with H₂O rather than CO₂. For this reason, the interactions with these sites are only distinguishable when the experiments are carried out in C₆H₁₂. After this spectroscopic study, the main carbonate-like species generated by CO₂ adsorption were tentatively assigned (Figure 7.12). A fit of the main families of carbonates was performed, keeping the position of the structural interlayer H₂O and CO₃²⁻ components fixed (see light blue and light green curves in figure 7.12, respectively).

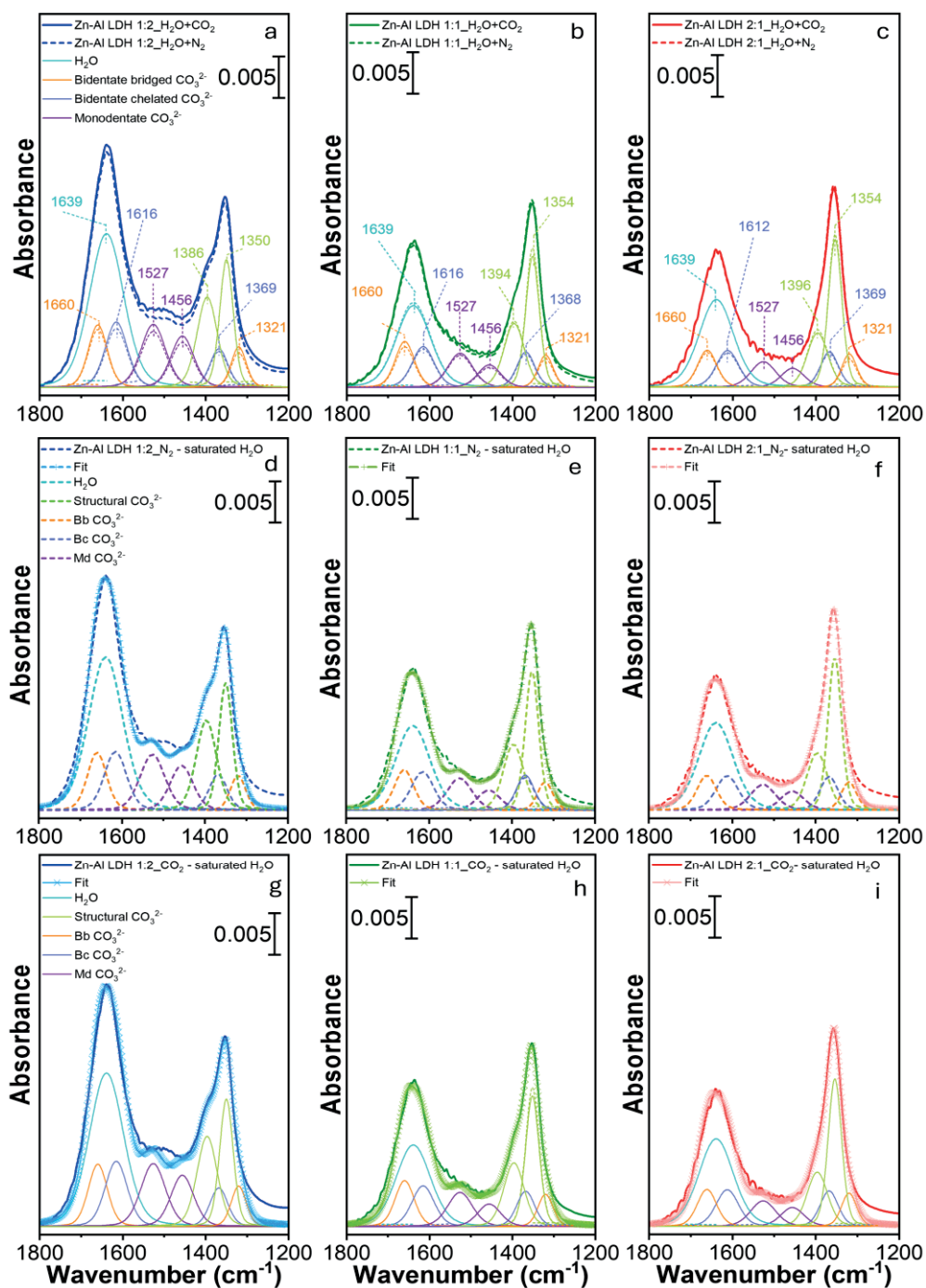


Figure 7.12. Band fitting of carbonate-like species species of IR spectra collected under N_2 -saturated and CO_2 -saturated H_2O flows in the $1800\text{--}1200\text{ cm}^{-1}$ range of Zn-Al LDH 1:2 (a), Zn-Al LDH 1:1 (b) and Zn-Al LDH 2:1(c) and the resulting fit (cross-shaped light blue curves) of N_2 saturated samples (d, e and f) and of CO_2 saturated samples (g, h and i). The spectral components of distinct carbonates species are

evidenced by different colours: orange - Bidentate bridges (Bb), indigo - Bidentate chelated (Bc) and violet - Monodentate (Md). The dashed curves refer to the spectrum and relative components of the wet N₂-saturated sample, while the solid curves refer to the spectrum and relative components of the wet CO₂-saturated samples (i.e the maximum CO₂ loading reached after 30minutes). The components of asymmetrical vibration of structural carbonates are reported in light green and the component of bending vibrations of structural and physisorbed water is reported in light blue. This figure is adapted from reference 12.

In order to develop a consistent identification of the carbonate bands of this work, a correlation was made between the evolution of the signals observed upon CO₂ contact in both H₂O and C₆H₁₂ (Figure 7.10 and 7.11) and the species reported in the literature (table 7.1). Consequently, the main bands have been assigned, mainly referring to the work of Debecker et al⁹, in the following way: (i) signals at 1527/1456 cm⁻¹ to asymmetric and symmetric O-C-O stretching of monodentate carbonates (Md), (ii) components at 1616–1612/1368–1369 cm⁻¹ to asymmetric and symmetric O-C-O stretching of bidentate chelated (Bc) carbonate and (iii) bands at 1660–1321 cm⁻¹ to asymmetric and symmetric O-C-O stretching of bridged (Bb) carbonates. The absence of the characteristic δ_{OH} in the 1225–1240 cm⁻¹ spectral range suggests the non-presence of bicarbonates even if the presence of the liquid phase complicates their identifications.²⁰ This assignment agrees with the bands evolution observed in the differential spectra (Figure 7.10).

As previously pointed out, due to the low intensity of the signals, the carbonate evolution in the samples could be noticed only by subtracting the spectra of the wet N₂-saturated sample from the wet CO₂-saturated one. Indeed, the not-subtracted ATR-IR spectra show only few differences in the intensity of the various components (see difference between solid and dashed spectra in the whole range of Fig. 7.12). To better appreciate the evolution of the carbonate species over time, the band fitting of the spectra at intermediate CO₂ coverage (collected each 7.5 minutes after the switch of N₂ to CO₂) was performed and the area of the different carbonates spectral components was evaluated (Figure 7.13 and Table 7.2).

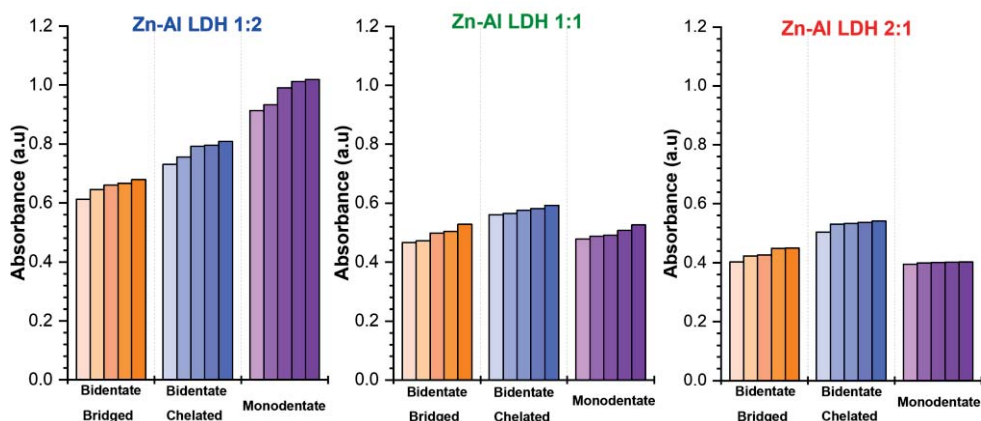


Figure 7.13. Evolution of the carbonate species over time. The band fitting of the spectra at intermediate CO_2 coverage (0, 7.5, 15, 22.5, 30 minutes) was performed (as reported in Fig. 7.12 for the 0 and 30 minutes coverage) and the area of the carbonates components was evaluated by summing the asymmetric and the symmetric contributions of the same carbonate species. The numbers reported are normalized to the area of the fit of the interlayer carbonates. From reference 12.

Table. 7.2. Evaluation of the carbonate species formed upon the interaction of the samples with a CO_2 -saturated H_2O flow. For each sample, the average of the intensities of the histograms in Figure 6 (Average), the sum of bridged and chelated bidentate (Total Bidentate $\text{Bb}+\text{Bc}$), the Monodentate to Bidentate ratio ($\text{M}/(\text{Bb}+\text{Bc})$) and the ratio between the two bidentate species (Bb/Bc) was reported. From reference 12.

	Carbonate species	Average	$\text{Bb}+\text{Bc}$	$\text{Md}/(\text{Bb}+\text{Bc})$	Bb/Bc
Zn-Al LDH 1:2	Bidentate bridged (Bb)	0.652			
	Bidentate chelated (Bc)	0.776	1.430	0.680	0.840
	Monodentate (Md)	0.973			
Zn-Al LDH 1:1	Bidentate bridged (Bb)	0.493			
	Bidentate chelated (Bc)	0.575	1.069	0.466	0.857
	Monodentate (Md)	0.498			
Zn-Al LDH 2:1	Bidentate bridged (Bb)	0.429			
	Bidentate chelated (Bc)	0.529	0.959	0.416	0.811
	Monodentate (Md)	0.399			

Although a comparison of the carbonate between the three samples would likely result in incorrect interpretations, the change over time within the same sample could be assessed. In particular, contrarily to what is observed in the other two LDHs, the Zn-Al 1:2 LDH shows a higher amount of Md carbonates compared to Bb and Bc. However, the sum of bidentate species (Bb+Bc) is always higher than the Md carbonates in all samples. For this reason, to really highlight the differences among the various LDHs in carbonate species formed upon CO₂ interaction, an evaluation of the monodentate to total bidentate carbonates ratio ($Md/(Bb+Bc)$) must be carried out. Interestingly, the $Md/(Bb+Bc)$ ratio of Zn-Al 1:2 is higher than for the other two samples (0.680 for Zn-Al 1:2 LDH versus 0.466 and 0.416 for Zn-Al 1:1 and 2:1 respectively), testifying a larger contribution of monodentate species in Zn-Al 1:2. Since the different carbonate species are strictly connected with the strength of the basic sites, the relative intensities of the IR bands of the various carbonates families provides a powerful tool to discriminate among materials with different basic nature. In particular, the prevalence of the Md carbonates in Zn-Al 1:2 is probably related to the presence of a higher content of low coordination oxygen anions having a strong basic character. On the other hand, Zn-Al 1:1 and 2:1, with a lower $Md/(Bb+Bc)$ ratio, are probably characterized by a higher content of acid–base pairs with intermediate basic strength. The different basic sites are expected to play a crucial role in CO₂RR especially in the initial stage of the reaction. For this reason, the highest electrocatalytic performances of Zn-Al 1:2 could be correlated to the presence of stronger basic sites and to an overall higher affinity of this sample towards CO₂. However, in order to deeply understand their role and the mechanism of reaction, an analysis under *operando* conditions should be carried out, as will be discussed in detail in section 7.5.

7.4 The effect of Grinding

In the previous sections, different LDH samples were investigated as potential catalysts for CO₂RR. First, three LDHs with different elemental compositions were studied and the Zn-Al LDH showed the highest CO evolution. Subsequently, the Zn-Al composition was fixed and the effect of the change in M^{2+}/M^{3+} ratio was investigated, in particular by synthesizing Zn-Al 1:1 and 2:1 in addition to the 2:1 composition. Those results were part of two different publications, Nakazato et al.⁴ and Cavallo et al.¹², reported in the appendix. However, by carefully observing the results reported for the Zn-Al LDH 2:1 composition in the two sections (7.2 and 7.3), a different CO evolution could be detected. As a matter of fact, in figure 7.2 the Zn-Al LDH 2:1 exhibited a high CO formation, with a FE ranging from 67% obtained at -1.4 vs. RHE to 1.2% at -0.6 vs. RHE. On the contrary, the same sample reported in Figure 7.8 showed a much lower CO evolution (from 11% obtained at -1.4 vs. RHE till 3% at -0.6 vs. RHE). Even though the electrochemical results are often subject to variation, the fact that they were performed keeping constant the main parameters (type of cell, electrolyte concentration...) suggests that the difference in performance is due to other factors. Considering the preparation of the samples a “major” difference emerged: in the first case (section 7.2) the samples were grinded before conducting the electrochemical tests while in the other case (section 7.3) the as-synthesized sample were tested. Those considerations suggested that the CO₂RR activity of LDH might be influenced by changes in the physicochemical properties of LDH due to grinding. In order to better understand this aspect and to prove this hypothesis, some further experiments were carried out. However, as mentioned above, these measurements are part of ongoing activities and further investigations still need to be performed.

Firstly, the FE at different applied potentials was measured (by our partners at the University of Hokkaido) in a set of Zn-Al LDH 2:1 that have been ground for different times (Figure 7.14)

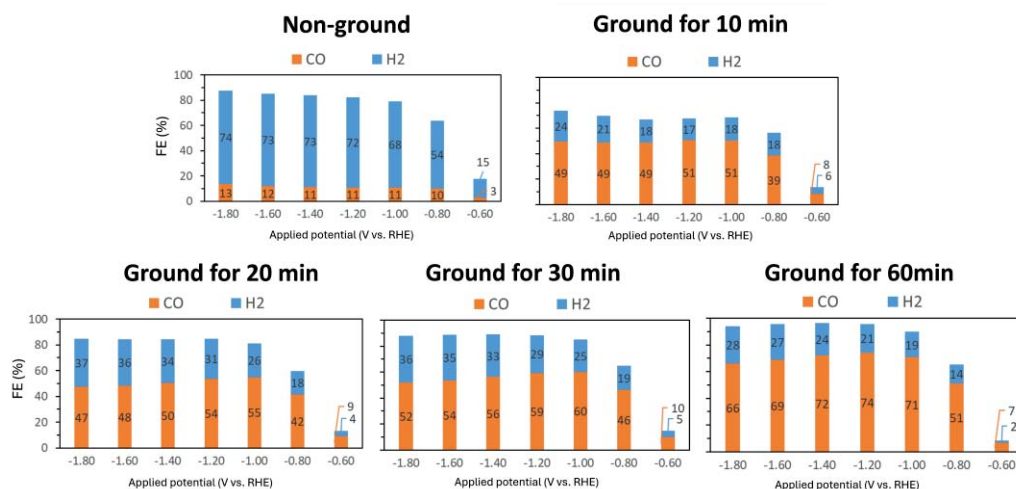


Figure 7.14. Applied potential dependence of Faradaic efficiency (FE) for CO₂ER in 1.0M aqueous KHCO₃ solution using each cathode with Zn-Al LDH 2:1 ground for different times (orange bar: CO, blue bar: H₂). Those experiments were performed and kindly provided by Dr. R. Nakazato (Hokkaido University)

The results evidenced a constant increase in CO evolution in the range -0.6 to -1.8 V vs RHE upon increasing the grinding time. After that the XRD patterns of the same samples were performed (Figure 7.15).

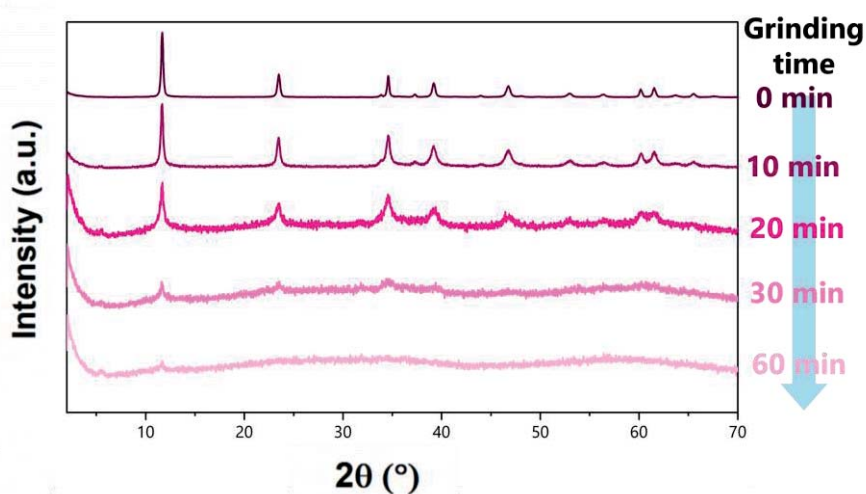


Figure 7.15. XRD diffractograms of Zn-Al LDH 2:1 ground for increasing times. Those experiments were performed and kindly provided by Dr. R. Nakazato (Hokkaido University)

As expected, the XRD showed the characteristic (003) and (006) plane peaks of the layered structure for the as-synthesised Zn-Al LDH 2:1. However, by increasing the grinding times those signals start to decrease till nearly completely disappear in case of 60 minutes grinding. This behaviour suggests that a gradual decrease in the crystallinity of the sample occurs as the grinding time is increased, probably causing a partial collapse of the initial layered structure.

To investigate the behavior of the grinded material upon interaction with CO₂ and/or H₂O, ATR-IR spectroscopy was performed. The Zn-Al LDH 1:2 ground for 60 minutes was deposited on the crystal and the spectra of dry sample and in contact with water (under N₂-saturated H₂O flow) was evaluated (Figure 7.16)

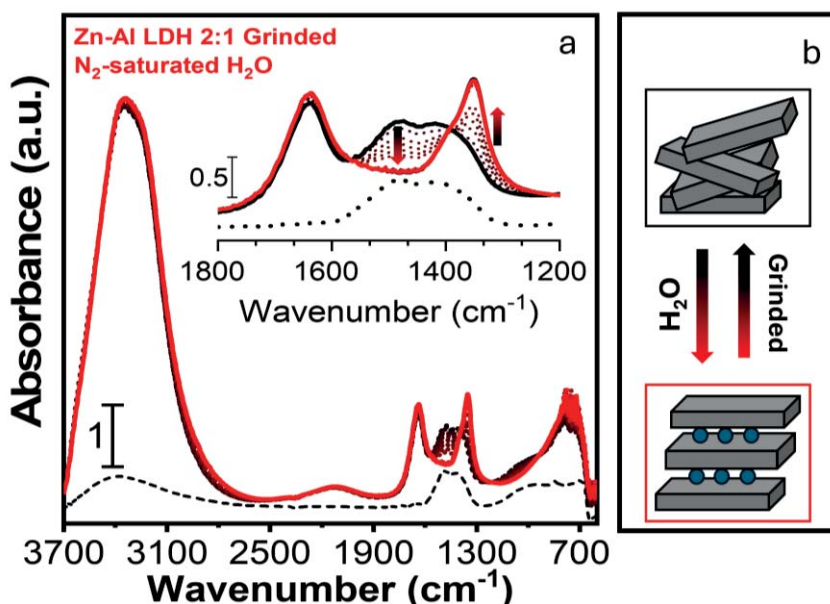


Figure 7.16. ATR-IR spectra in the 3700-650 cm⁻¹ spectral range of the dry Zn-Al LDH 2:1 grinded for 60 minutes (black dashed curve) and under a N₂-saturated H₂O flow (a) and pictorial representation of the changes occurring in the sample (b). The black and red curves represent the wet (H₂O) N₂-saturated samples after 0 and 30 minutes, respectively. The intermediate coverages are shown in dots. A magnification of the 1800-1200 cm⁻¹ spectral region is shown in the inset.

The spectrum of the dry sample (black dashed curve in Figure 7.16) shows the appearance of a broad band at high wavenumbers (3900-2500 cm⁻¹) due to the hydroxyl stretching vibrations and another one in the low frequency region (1000-650 cm⁻¹) due to the overlapping of the ν_2 out of plane stretching mode of carbonate

anions ($\sim 860\text{ cm}^{-1}$) and the HO-M-OH lattice vibrational mode ($450\text{--}800\text{ cm}^{-1}$) as previously discussed. However, in the $1800\text{--}1200\text{ cm}^{-1}$ range, instead of the previously observed peak at around 1350 cm^{-1} assigned to ν_3 stretching mode of interlayer carbonate anions, two different bands having the apparent maxima at 1483 and 1413 cm^{-1} can be detected. Upon interaction with water, an increase in the high frequency region associated with the OH stretching vibrations, together with the increase in the 1640 cm^{-1} signal attributed to the H-O-H bending vibrations, can be immediately detected. By increasing the time of contact with water (dotted curves in Figure 7.16) some changes in the previously mentioned 1483 and 1413 cm^{-1} bands begin to occur. In particular, the 1483 cm^{-1} slowly decrease while a new band at around 1350 cm^{-1} is formed. A similar behaviour is likely to occur at 1413 cm^{-1} , but the changes are partially hidden by the appearance of a shoulder at $\sim 1410\text{ cm}^{-1}$. The just formed 1350 and 1410 cm^{-1} bands do not rise further after reaching their maximum. It is worth noting that these signals coincide with those previously reported in Figures 7.4 and 7.9 in relation to structural interlayer carbonate anions present in the dry LDH samples. The behaviour shown by the grinded sample suggests that the initial partially collapsed structure is slowly restored upon contact with water until it reaches LDH again (Figure 7.16 b for a schematic representation).

When no further changes in the 1483 and 1413 cm^{-1} bands were observed, the inlet gas was switched to CO_2 and the evolution of the spectra was studied by subtracting the wet N_2 -saturated sample (Figure 7.17 a).

Upon CO_2 interaction the spectrum shows an initial increase of the bands at $\sim 1620\text{ cm}^{-1}$ and 1338 cm^{-1} . Additionally, a broad signal in between 1600 and 1400 cm^{-1} also appears. At higher CO_2 coverage the initial 1620 cm^{-1} band increases slightly shifting to higher wavenumbers, on the other hand, the 1338 cm^{-1} signal rises and moved till 1280 cm^{-1} . The broad intermediate band in between $1550\text{--}1450\text{ cm}^{-1}$ is also increased, and a shoulder appears, but the precise identification is hidden by the presence of a minimum at around 1350 cm^{-1} . Comparing this band evolution with that previously shown in Figures 7.5b and 7.10c, the CO_2 interaction in this case leads to the formation of a much more complex spectrum. In particular, the signals around $1600\text{--}1400\text{ cm}^{-1}$ results to be much more intense compared to the previous situation. It is worth noting that the bands falling in that spectral range were previously attributed to the presence of monodentate species associated to the presence of a higher content of low coordination oxygen anions having a strong basic character. In the previous case the highest electrocatalytic performances of Zn-Al 1:2 was tentatively correlated to the presence of the stronger basic sites.

Interestingly, this relationship between the electrocatalytic activity of the sample and the presence of monodentate species seems to be applicable also in the present case.

Lastly, the behaviour of the Zn-Al LDH 2:1 grinded for 60 minutes were also studied in the presence of C_6H_{12} (Figure 7.17b).

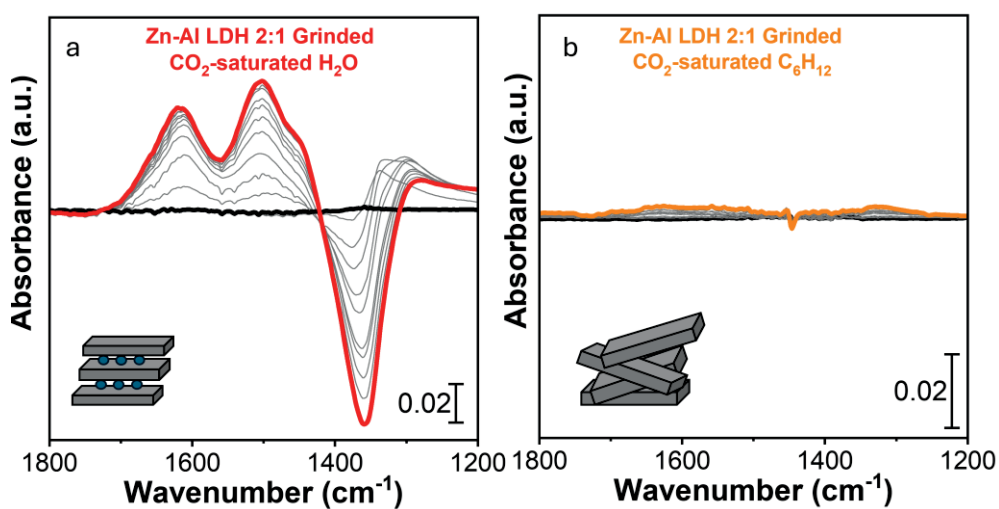


Figure 7.17. In-situ ATR-IR spectra in the carbonate-like region (1800–1200 cm^{-1}) of Zn-Al LDH 2:1 grinded under a CO_2 -saturated H_2O flow (a) and under a CO_2 -saturated C_6H_{12} flow. The spectra are reported by subtracting the spectra of the wet (H_2O/C_6H_{12}) N_2 -saturated sample to that of the wet (H_2O/C_6H_{12}) CO_2 -saturated one. The black and coloured curves represent the wet (H_2O/C_6H_{12}) N_2 -saturated and wet (H_2O/C_6H_{12}) CO_2 -saturated samples, respectively.

While previously this solvent was used to decrease the risk of deposition loss and to better appreciate the carbonates bands hidden by the presence of the intense HOH bending mode, in the present case the solvent also allows the study of the sites present in the ground sample without regenerating the LDH structure. As a matter of fact, in the case of the experiment carried out in H_2O (Figure 7.17a), since the sample was exposed to an N_2 -saturated wet flow before the interaction with CO_2 , only the active sites present in the "just reconstructed" LDH structure were detected.

However, as can be easily observed in case of CO_2 -saturate C_6H_{12} flow no evolution in the carbonate like region can be observed. This behaviour could indicate that the grinding of the sample is responsible for the reduction of active sites that are

unavailable and /or inaccessible to CO₂, and only become re-available through contact with H₂O and the consequent regeneration of the LDH structure.

These results suggest that the differences in electrochemical performance observed in the previous chapters could be due to a difference in grinding time leading to variations in the physico-chemical properties of the initial LDH materials, however they are still preliminary and further analysis will be carried out to fully understand the phenomenon.

7.5 Toward operando conditions: Spectroelectrochemistry

The results reported so far were fundamental to understand the active sites present in different materials and to describe the effect of their interaction with the reactants. However, as already mentioned at the end of section 7.3, a more realistic evaluation of the behaviour of the materials could only be made by observing the evolution of the spectra under the application of a potential, thus moving towards *operando* conditions. Recently, the need to better understand the mechanism of the electrochemical reactions, the formation of reaction intermediates and products has led to the development of various spectroelectrochemical techniques (SEC), which generally refers to the combination of electrochemistry with various types of characterisation techniques such as IR, Raman, NMR, X-ray absorption spectroscopy and others.²¹ Among the various type of SEC techniques, the one involving the use of IR spectroscopy (IR-SEC) is expected to have the biggest potential and to undergo major improvements in the coming decades.²¹ The two most employed IR-SEC techniques are the IR spectroscopy with external reflection element (IRAS) and IR spectroscopy with internal reflection element (ATR-IR). In IRAS the radiation passes through the IR window and a thin layer of electrolyte before reaching the sample deposited onto the working electrode (WE). On the other hand, in ATR the beam reaches the catalyst without passing through the solution. ATR-IR is usually associated to a higher surface sensitivity especially when the WE consists of metallic nanoparticles films able to enhance the infrared absorption (ATR-SEIRAS).²² Given the growing popularity of these techniques and the need to understand the reaction mechanisms of these electrocatalysts, we have recently become interested in the use of ATR-SEC techniques. A cell capable of combining electrochemical measurements with ATR spectroscopy was recently

acquired. Although there is still much to learn, this paragraph reports the first steps taken in the use of the cell, the problems encountered and the objectives to be achieved in the future.

Firstly, an analysis of the cell configuration was carried out together with the development of the setup.

The new Spectro-electrochemical cell, the PIKE Technologies VeeMAX III, was coupled to an infrared spectrometer and connected to a mass flow to perform the analysis in the same way as for ATR-IR (see Chapter 3). However, in this case, once the cell is ready for measurement, it is connected to an external potentiostat (see Figure 7.18 a for a schematic representation). The biggest difference compared to the previous configuration is the use of one single reflection Si wafer as reflection element instead of the multireflection AMTIR crystal present in HATR cell. The Si wafer is placed at the interface of the ATR accessory and the electrochemical cell. On top of the Si wafer, which is acting as WE, should be deposited the electrocatalyst. The configuration of the electrochemical cell, which has been slightly modified with respect to the commercial one, can be classified as an H-Type electrochemical cell, as all the reaction is happening in a liquid electrolyte. However, differently from the H-type cell in which the counter electrode (CE) is placed into the anode separated by an anion exchange membrane, in the Veemax III the electrodes are placed in the same compartment (see Figure 7.18 b for a schematic representation of the two cells). To make it as similar as possible to an H-type cell, a small glass tube has recently been designed to separate the CE (a picture of the actual configuration is reported in figure 7.19 a).

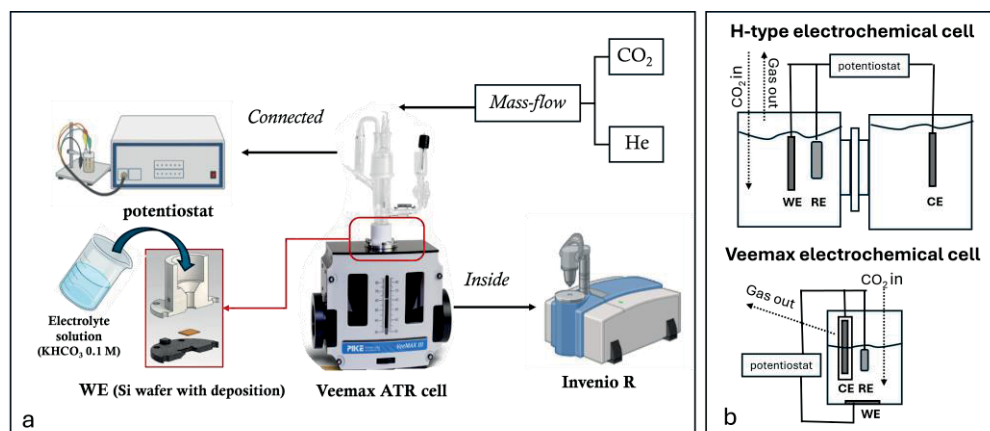


Figure 7.18. Schematic representation of the set-up used during for the spectroelectrochemical measurement (a) and schematic representation of the H-type and Veemax electrochemical cells (b).

The trickiest part to set up is the WE. As a matter of fact, the electrocatalyst deposited on the Si wafer should be at the same time detectable to IR and conductive for the electrocatalytic tests. The most difficult challenge for IR is represented by the low intensity of the signals and the low signals to noise ratio which is influencing a lot the detection of the real maxima of the different bands. As far as conductivity is concerned, the circuit should be closed by the presence of two gold pins in contact with the sample deposited on the Si wafer and connected externally to the potentiometer by means of a screw (see Figure 7.19 b). However, sometimes the contact of the gold pins with the sample is responsible for scratching the deposition, reducing or preventing conductivity throughout the sample. An additional difficulty is the study of electrocatalysts in powder form, which are easily delaminated. As a matter of fact, while this setup has been widely used in homogeneous electrocatalysis or for heterogeneous metallic catalysts, usually deposited on the reflection elements through sputtering, only very few works have been carried out on powder samples.^{23,24}

In this initial stage, we decided to prepare the WE by two different methods: (i) by drop casting the sample onto a first layer (15 nm) of gold previously sputtered onto the Si wafer, and (ii) by drop casting the sample directly onto the Si wafer. In the latter case, to reduce the risk of scratching, a thin copper tape was placed in correspondence of the gold pins (see figure 7.19c for a schematic representation).

In the former case gold was used to ensure a better conductivity in all the sample while in the latter the presence of the catalyst alone ensures that no other material

is taking part to the reactions. In both cases the dropcasting was performed with the addition of 30 μL of binder and 570 μL of ethanol to 10 mg of sample (Zn-Al LDH 2:1 was used). Finally, it should be noted that only the sample in contact with the solution (i.e. inside the circle of the holder, see Figure 7.19 b) takes part in the reaction.

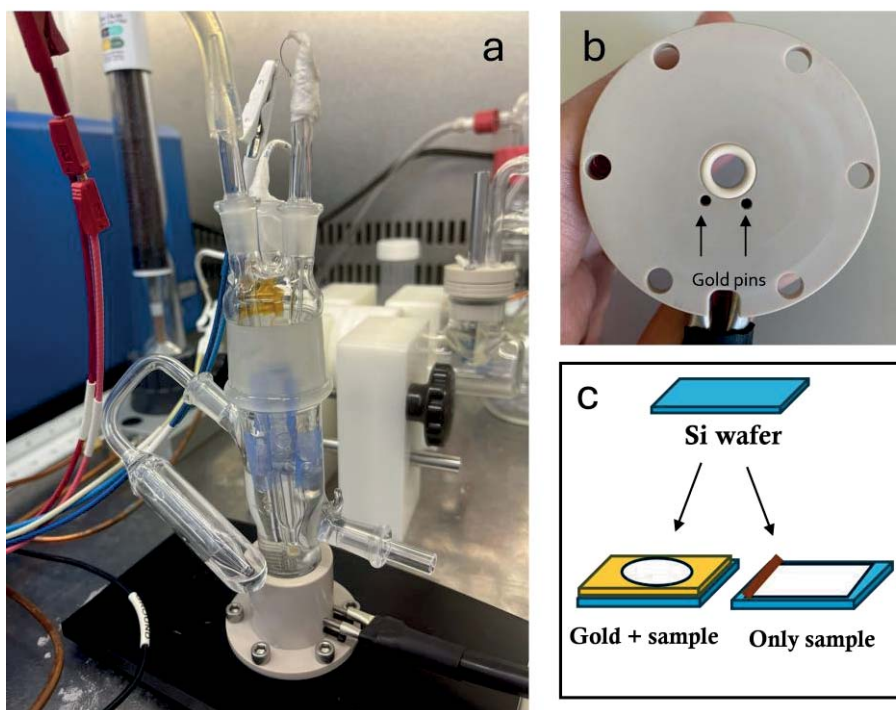


Figure 7.19. Picture of the actual configuration of the Veemax III electrochemical cell (a), picture of the upper part of the WE holder (b) and schematic representation of the two configurations tested for WE (c).

Both depositions were tested under the same conditions as the previously reported ATR experiments: firstly N_2 -saturated electrolytic solution was sent to the sample for 30 minutes and then the gas was switched to CO_2 (see Chapter 3). The main difference with respect to the previous reported measurements is the use of an electrolytic solution of KHCO_3 0.1 M instead of H_2O (the use of KHCO_3 or other basic electrolytic solutions in the case of HATR was not possible due to the safety usage parameters of the AMTIR crystal). This experiment, carried out in the absence of potential, was performed to test the cell and compared with the results obtained in case of HATR cell previously shown in Figure 7.5 b and Figure 7.10 c (Figure 7.20).

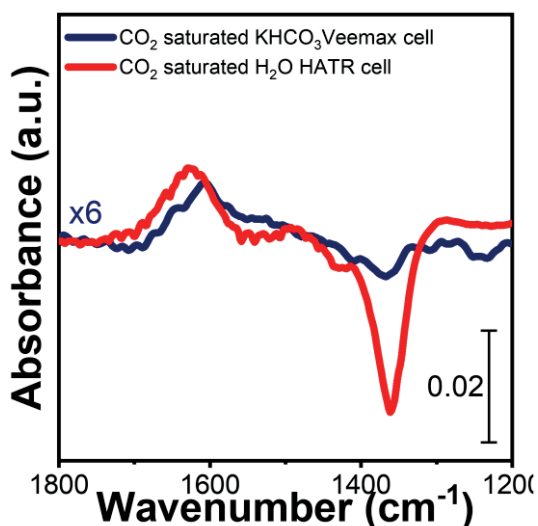


Figure 7.20. ATR-IR spectra of Zn-Al LDH 2:1 under 30 minutes CO₂-saturated flow performed by means of HATR cell (red curve) and by means of Veemax III cell (blue curve). This latter spectrum was multiplied by factor 6 to make a comparison. A solution of 0.1 M KHCO₃ was used for the Veemax III cell, while H₂O was used for the HATR. The spectra are reported by subtracting the spectra of the wet (H₂O/KHCO₃) N₂-saturated sample to that of the wet (H₂O/KHCO₃) CO₂-saturated one

The comparison of the spectra performed with Veemax III cell and the one performed with HATR shows the appearance of bands having a very similar trend. As a matter of fact, the two spectra slightly differ for the main bands appearing at 1640 cm⁻¹ in the previous reported spectra, and shifted to lower wavenumbers in the present one. This difference could be due to the use of KHCO₃ instead of H₂O. Additionally, also in this case a negative band appears at ~1360 cm⁻¹ but in the present case a lower decrease is observed, suggesting the presence of a even more stable deposition. The main drawback of the measure performed with the spectroelectrochemical cell is represented by the low intensity of the signals.

After checking the spectra evolution upon contact with CO₂ saturated flow, a first preliminary measurement of the changes occurring in the sample by applying a potential was carried out (Figure 7.21).

It is worth noting that these are really preliminary tests, and no clear identification of the peaks has been carried out. However, it could be noted that the two configurations possess very different current density and a very different bands evolution. In case of sample deposited on gold a higher current density was measured and a multitude of negative bands was observed in both OH stretching region and carbonate like region (Figure 7.21 b and c). On the other hand, in case of

Zn-Al alone, a smaller current density was measured together with the appearance of some positive signals in the carbonate like region (Figure 7.21 d and f). Additionally in this latter case no changes were observed in the OH stretching region (the small signals visible are probably due to noise of the spectra) (Figure 7.21 e). We hypothesised that those changes are probably due to the presence of gold which is itself an electrocatalyst for CO₂RR and is probably influencing both the current evolution and the reaction performances.

In order to better understand the mechanisms and proof this hypothesis, different other experiments will be carried out. The gold alone will be tested, and the experiments will be repeated multiple times to check those results. Furthermore, in the future the tests will be performed using a chronoamperometry (i.e. at different constant potential). Additionally, we will preferentially work with catalyst alone in order to avoid the influence of gold or other metals in the results.

The same test will also be performed for Zn-Al 1:2 LDH, which showed high CO evolution, and a comparison of the two electrocatalysts will be performed to understand the mechanism of reaction and the role of the different carbonates.

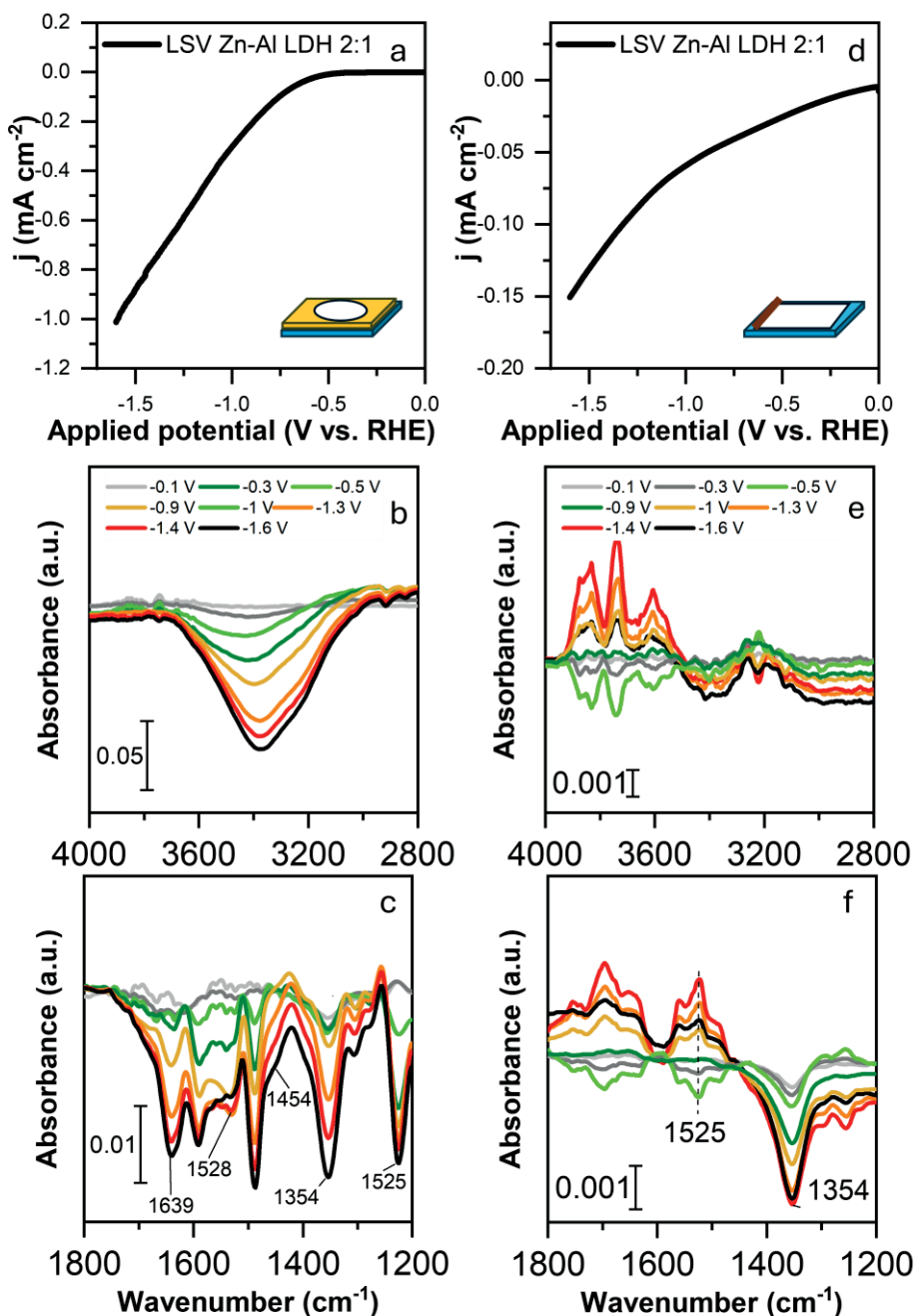


Figure 7.21. Applied potential dependence of current density (j) (a, d) and spectral evolution upon variation of potentials from 0 to -1.6 V in the OH stretching region (4000-2800 cm⁻¹) (b, e) and in the carbonate like region (1800-1200 cm⁻¹) (c, f) of Zn-Al LDH deposited on gold (a, b, c) or deposited directly onto Si wafer (d, e, f). The spectra are reported by subtracting the spectra of the wet (KHCO₃) CO₂-saturated sample at 0 V.

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8. DEHYDRATION OF ALCOHOLS INTO 1-ALKENES USING BIOMIMETIC CATALYST

After producing an appropriate fraction of CO by electrochemical reduction of CO₂, the second step of the reaction employs CO and renewable H₂ as reactants for the synthesis of hydrocarbons. As previously pointed out in Chapter 2, in this second step of the reaction we focused on the “strategy II” which involves a first transformation of CO into 1-alkanols through the microbial transformation developed by Siemens and Evonik Industries and already available in the industry, and a subsequent dehydration to 1-alkenes. In particular, the main activity aimed to characterize a commercial acid-leached bentonite, FULCAT-22F, which was tested as heterogeneous biomimetic catalyst for the dehydration reaction with interesting results. Indeed, this catalyst turned out to facilitate efficiently the dehydration reaction of a range of substituted alcohols (primary, secondary and tertiary) under energy-saving conditions at much lower temperature (60<T<180°C) as most “traditional catalysts” for the same purpose (T>300°C).¹ The characterisation carried out and reported here helped to explain the high reaction yields of the catalysts, as well as the different performances obtained at different temperatures.

The catalytic tests and the characterization of FULCAT-22F is part of the paper “Cavallo, M.; Allahverdiyev, A.; Dosa, M.; Kelly, O.; Crocellà, V.; Bonino, F.; Gröger, H. Overcoming the acidity limitation by introducing tailor-made bifunctionality: How clays outperform strongest Brønsted acids in energy-saving alkene formation via primary alcohol dehydration” that will be submitted to *Journal of Catalysis* very soon.

8.1 Materials and methods

Both fundamental and spectroscopic characterizations were carried out on the heterogeneous FULCAT-22F catalyst provided by BYK Additives Ltd., Widnes, United Kingdom. The catalyst consists of a commercial acid-leached bentonite, a type of claystone composed mostly of Montmorillonite that is a clay mineral from the smectite group. Smectites are a group of clay minerals with a 2:1 phyllosilicate structure consisting of two tetrahedral silica layers and an octahedral alumina sheet

in between (TOT structure). The ideal half-cell chemical formula for Montmorillonite is $M_{0.33} H_2OAl_{1.67}(Fe^{2+}, Mg^{2+})_{0.33} Si_4O_{10}(OH)_2$, where M is a metal cation in the interlayer space between TOT sheets. The tetrahedral cations are Si^{4+} and the octahedral ones are mostly Al^{3+} , Fe^{2+} , and Mg^{2+} . In the octahedral sheets, Al^{3+} is mainly replaced by Fe^{2+} and Mg^{2+} , creating an excess of negative charge in the structure. Different cations are neutralizing the charge and are localized in the interlayer together with water molecules (see Figure 8.1a for a pictorial representation of the structure).²

Montmorillonite exhibits both Lewis Acid Sites (LAS) and Brønsted Acid Sites (BAS), which are influenced by many different factors such as the provenance, the hydration level and the thermal or acid treatment applied to the material. Usually, the BAS arise from structural silanols (weak acidity) and from the dissociation of interlayer water molecules coordinated the cations while the LAS are associated to low coordinated aluminium/iron/magnesium structural species or interlayer cations.³ As there is a direct connection between water and the formation of BAS, the hydration level of the material plays an important role in many catalytic reactions: the higher the temperature the lower the water content in the sample and, consequently, lower amount of BAS are expected. On the contrary, lower temperature applications are usually associated with higher BAS content and lower LAS availability, as they are coordinated with the water molecules.^{4,5} When an acid treatment is applied to the material various modifications may occur, leading to changes in its physicochemical properties, such as specific surface area or pore volume.^{6,7} Additionally, the exchangeable cations are expected to be replaced by protons in the interlamellar space and parallelly the leaching of cations from octahedral sites may occur.^{8,9} These treatments therefore probably lead to the formation of some new BAS in the structure (herein defined as "structural" BAS) different from that originated by the dissociation of the water molecules. Due to all these factors influencing the acidity of the material, it is not easy to make a complete identification of the different LAS and BAS, but a list of the main expected ones is given in Figure 8.1b.

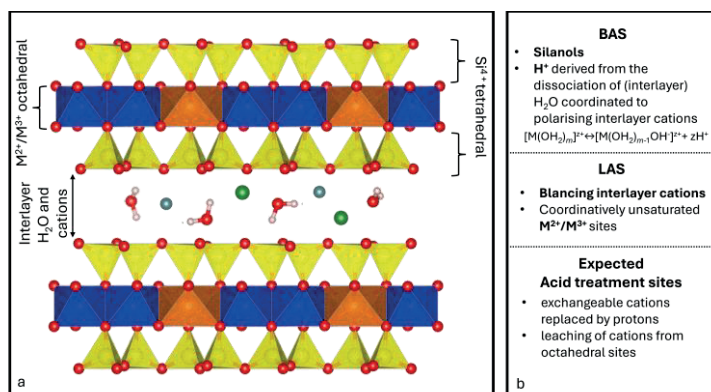


Figure 8.1. Pictorial representation of the original structure of bentonite (structural OH are not shown) (a) and list of the main acid sites expected in the material (b).

The material was tested for the dehydration reaction by our partners from Bielefeld University (Mr. A. Allahverdiyev under the supervision of Prof. H. Gröger). Reactions were generally performed in a 25 ml flask in the 60-180 °C temperature range. For primary and secondary alcohols an *in situ* removal of products by distillation was performed to shift the equilibrium to the product site. In case of tertiary alcohols, only in the initial studies an *in situ* removal by distillation was performed while further reaction have been performed under batch conditions (i.e. without any *in situ* removal). In the case of distillation, at the end of the reaction, a separation of the organic phase from the aqueous phase of the distillation flask was performed. The crude yield and alkene purities were determined by ¹H-NMR after determination of the mass. Under batch conditions, the conversion was determined at the end of the reaction using ¹H-NMR spectroscopy. A detailed description of the setup was reported by Allahverdiyev et al.¹⁰

The sample was then fundamentally and spectroscopically characterized.

In this case Variable Temperature Powder X-ray Diffraction (VT-PXRD) were performed to study the variation in the crystalline phase by increasing the temperature by means of an XRD diffractometer (Malvern Panalytical, Empyrean Multicore, Detector PIXcel 3D) in the 25-400°C temperature range (HT stage Anton Paar HTK 1200N). During the experiment a vacuum level of 2x10⁻² mbar was reached and each pattern was acquired under isothermal condition.

Thermogravimetric analysis (TGA) was performed using a temperature ramp of 3°C min⁻¹ from 30 to 1000°C in N₂ atmosphere (100 ml min⁻¹ flows). The morphology, the elemental composition and the textural properties of the sample were

evaluated as described in Chapter 3. The Specific Surface Area was determined by using the BET method, over the range $P/P_0 = 0.05\text{--}0.2$ checking the Rouquerol consistency criteria. The cumulative pore volume and the pore size distribution were evaluated using the Non-Local Density Functional Theory (NL-DFT), using a cylindrical pore geometry and the “NL-DFT for Pillared Clays” model. Prior to the measurement the sample was activated at 80°C, 180°C or 400°C for 3 hours under vacuum.

The spectroscopic characterization was performed by means of Bruker Vertex using the parameters reported in Chapter 3. The sample was previously activated in vacuum for 3h at 80°C, 180°C or 400°C.

8.2 Catalytic tests and fundamental characterization

As mentioned above, the catalytic tests were carried out by Mr A. Allahverdiyev of Bielefeld University under the supervision of Prof. H. Gröger and are part of a recently submitted but not yet peer-reviewed paper. Since the catalytic tests were carried out by our colleagues, only the main results are quickly reported here, and a deeper focus is given to the characterisation part.

The sample was firstly tested for the dehydration of 1-hexanol performed under *in-situ* removal of formed hexene products at oil bath temperatures ranging between 150-180°C and catalyst loading of 2 mol%. This first test results in an alkene yield of 52%, which is surprisingly higher than the one shown by samples having stronger acidity such as Triflic acid (TfOH) ($pK_{a_{TfOH}} = -14$; $pK_{a_{FULCAT}} = -8$), in which alkene formation was found only to a negligible extent with a very low conversion of 8% when applying a catalyst loading of 2 mol%. This founding suggests that the pK_a is not the sole determining factor in the dehydration process of 1-alkanols for alkene formation. As the dehydration of a primary alcohol has been successfully conducted, also secondary and tertiary alcohols, requiring milder reaction conditions, have been investigated, yielding 88% and 91%, respectively (Table 8.1).

Table 8.1. Reaction conditions and alkene yield resulting from the dehydration of primary, secondary and tertiary alcohols using FULCAT-22F. The measurements were performed and kindly provided by Mr A. Allahverdiyev (Bielefeld University).

Reagent	Temperature	Time	Alkene yield

1-hexanol	150-180°C	6 h	52%
2-hexanol	150°C	3h	88%
2-methyl-2-hexanol	110°C	0.5	71%
		1h	91%

In case of tertiary alcohol, the measurement was repeated also at milder conditions to determine the lowest reaction temperature at which the tertiary alcohol could be dehydrated showing that at 80 °C an almost quantitative conversion was achieved after three hours while at 60°C a conversion of 40% was achieved in 6 h. Generally, an increase in alkene yield is observed with increasing temperature.

Since it was shown that the higher acidity of the catalyst was not the sole responsible for the alkene formation, a deeper insight into the structure of FULCAT-Here, under batch conditions, the conversion was determined at the end of the reaction using ¹H-NMR^{22F} became of particular interest. A detailed characterisation of this heterogeneous FULCAT-22F catalyst was therefore carried out to understand the origin of its high performances.

The synthesised sample and its behaviour on activation at increasing temperature were first studied by VT-XRD (Figure 8.2a), since, as mentioned above, the H₂O content can influence both the initial structural and acidic properties of the bentonite. The diffractogram of the as-synthesized material at 25 °C (black curve) evidenced the presence of the main reflections associated with the Montmorillonite (M) phase together with some impurities of Quartz (Q).¹¹ In particular, the main characteristic reflection of Montmorillonite at about 7°, corresponding to the (0 0 1) reflection, is evident at all the activation temperatures but it becomes broader with increasing temperature (from black to blue curves), giving rise to an additional peak at about 9°. This latter signal seems to persist even when the sample is cooled in vacuum to RT (dark gray curves). This behaviour, which was already observed in the literature,^{12,13} is caused by a change in the crystallographic parameters of the material during evacuation in the 25-500°C temperature range. Comparing the diffractogram of the as-synthesized sample collected at 25°C and the one activated at 400°C, the differences in the (0 0 1) reflection become particularly evident, suggesting a decrease in the basal spacing with the temperature caused by the dehydration of the sample.

Further information about the behavior of the material upon heating can be provided by TGA analysis (Figure 8.2b). Upon increasing the temperature three main

weight losses can be observed in the following ranges: i) from RT to 200°C; ii) from 450 to 650°C and iii) at around 900°C. The first is due to the removal of water which can be present in the sample as interparticle water, adsorbed water and interlayer water.^{12,14,15} The second weight loss in between 450 and 650°C is originated for the dihydroxylation of structural -OH group and the third one visible at around 900°C is due to the decomposition of clay minerals.^{14,15} These outcomes are in agreement with the VT-XRD where the splitting of the basal peak (0 0 1), ascribed to the loss of water, starts to occur at 50°C and becomes more evident at around 180°C.

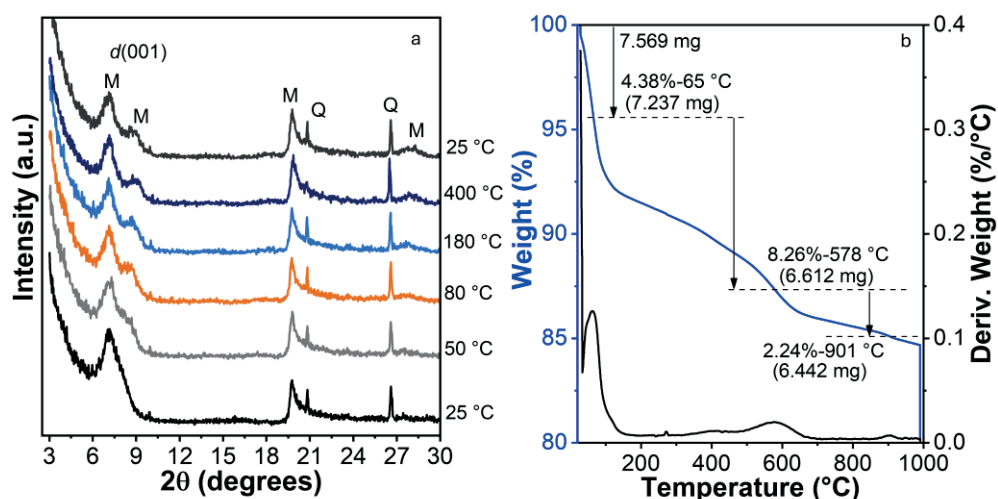


Figure 8.2. VT-XRD of FULCAT-22F heating the sample in vacuum in the temperature range from 25 to 400°C (from black to blue curves) and after cooling down to 25°C in vacuum (grey curve) (a) and TGA measurement of FULCAT-22F in the 25-1000°C range (b).

The specific surface area (SSA) and pore size distribution (PSD) of the sample activated at various temperatures were also evaluated. Three different temperatures (80°C, 180°C and 400°C) were chosen to see the effect of water removal on the textural properties of the material and will also be employed for the advanced characterisation (see below). All the three N₂ adsorption/desorption isotherms display a combination of type Ib and type IVa isotherm with a type H3 hysteresis loop (Figure 8.3a).¹⁶ As a matter of fact, clays exhibit three different types of porosity: (i) micropores due to the interlamellar pores localized in the interlayer span of the clay, (ii) mesopores due to intra-aggregate pores situated in between adjacent laminae piles and (iii) macropores due to inter-aggregate pores occupying space in-between aggregates of clay particles and non-clay particles (See Figure 8.4a for a schematic representation).¹⁷

The SSA of the material slightly decreased passing from 180°C to 400°C ($175 \text{ m}^2 \text{ g}^{-1}$ and $207 \text{ m}^2 \text{ g}^{-1}$ respectively), while an intermediate value was observed in the case of activation at 80°C ($200 \text{ m}^2 \text{ g}^{-1}$) (see Table 8.2). NL-DFT model highlights the presence of both micropores and mesopores (see Figure 8.3b, Table 8.2). In particular, the NL-DFT pores size distribution (PSD) of micropores showed the presence of a homogeneous family with a size of 1.5 nm for all the three activation temperatures while in the case of the samples activated at 80°C and 180°C, an additional smaller family centred at 1 nm can also be identified. A slight decrease of the micropore volume is also observed as the activation temperature is increased to 400°C (see Figure 8.3b). Concerning the mesoporous cavities, the PSD is characterized in the 2-10 nm range by the presence of a heterogeneous family of sites (Figure 8.3b and Table 8.2). In this case, the mesopore volume showed a slight decrease passing from 180°C to 400°C ($0.163 \text{ cm}^3 \text{ g}^{-1}$ and $0.161 \text{ cm}^3 \text{ g}^{-1}$, respectively) while a slightly lower volume is observed in case of the samples activated at the lowest temperature ($0.158 \text{ cm}^3 \text{ g}^{-1}$). The SSA and PSD values suggest that the interlamellar pores constantly decrease with increasing temperature, as shown by the reduction in SSA, micropores and mesopores volumes from 180°C to 400°C, in perfect agreement with VT-XRD and TGA analysis. However, for the sample activated at 80°C the presence of residual water is probably hindering the full accessibility of the surface leading to an underestimation of both SSA and mesopores volume of the material.

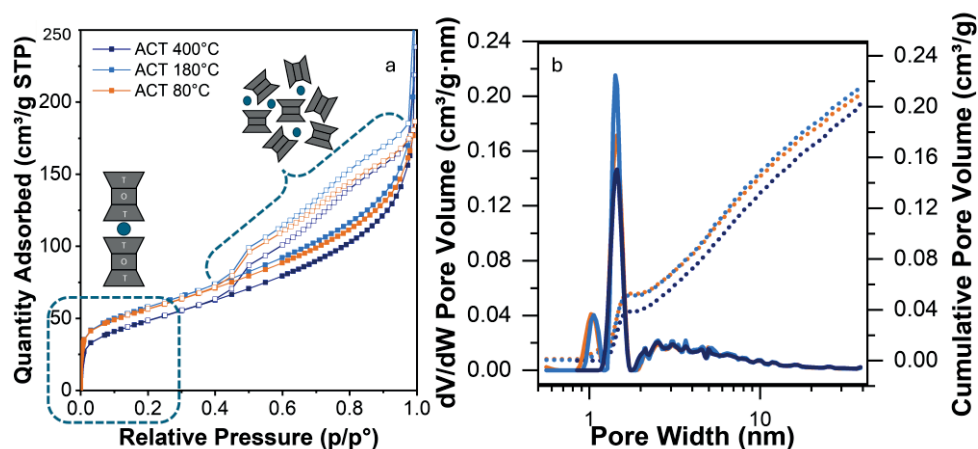


Figure 8.3. N_2 adsorption-desorption isotherms at 77 K of FULCAT 22-F activated at 400°C (in blue), 180°C (in light-blue) and 80°C (in orange) with a schematic representation of the porosity of the bentonite (the light-blue dots represent the location of pores) (a) and pore size distribution (solid curves) and cumulative pore volume (dotted curves). The data were obtained by using the NL-DFT method (b).

Table 8.2. Specific Surface Area as determined by the BET equation and porosity (determined by the NL-DFT method) for FULCAT-22F activated at 400°C, 180°C and 80°C. The mesopore volume was obtained by subtracting the micropore volume from the total pore volume.

	BET area (m ² g ⁻¹)	V total (cm ³ g ⁻¹)	V micro (cm ³ g ⁻¹)	V meso (cm ³ g ⁻¹)	Micropores size (nm)	Mesopores size (nm)
FULCAT-22F	175.1 ± 0.1	0.200	0.039	0.161	1.5	2-10
ACT 400°C						
FULCAT-22F	207.1 ± 0.3	0.218	0.055	0.163	1 / 1.5	2-10
ACT 180°C						
FULCAT-22F	200.8 ± 0.5	0.211	0.053	0.158	1 / 1.5	2-10
ACT 80°C						

Lastly, the main elements present in the sample were investigated by means of FESEM-EDX analysis (Figure 8.4).

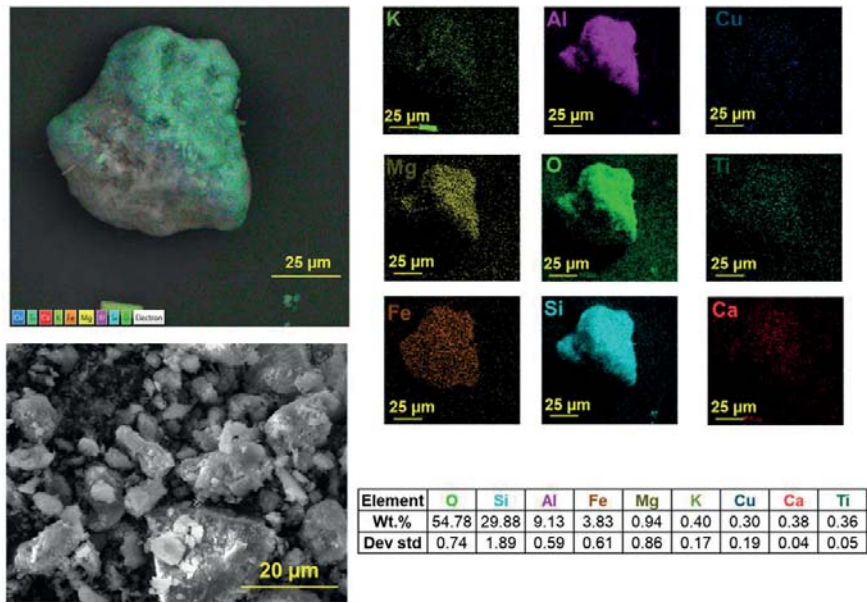


Figure 8.4. FESEM-EDX analysis of FULCAT-22F

The samples exhibited a leaf-like crystals which are organized in dense aggregate and all the elements result to be well dispersed (Figure 8.4). The sample has a large variety of elements with the prevalence of Si and Al followed by: Fe, Mg and K. Furthermore, Cu, Ca and Ti were also observed in a less extent. The elemental content is probably influenced by the acid treatment used to obtain the commercial sample which is probably also responsible for the higher Si/Al ratio of FULCAT-22F compared to that expected from the untreated montmorillonite structure (~2).

8.3 Advanced characterization

After having fundamentally characterized the sample, a detailed *in situ* IR characterization was performed to investigate the presence of acidic sites in the sample. Firstly, the sample was tentatively characterized trying to keep the conditions as close as possible to the catalytic test flowing liquid 1-hexanol onto FULCAT-22F previously deposited on the ATR crystal at 80°C (i.e the maximum temperature reachable with this HATR cell described in Chapter 3) The deposited sample initially shows the presence of bentonite but, after flowing hexanol at 80°C and keeping it in contact with the sample for 6h (i.e. minimum time for the catalytic reaction) only hexanol in liquid phase were detected (results not shown for sake of brevity). The absence of any significant result can be due to (i) the low Temperature reachable by the set-up and (ii) the probable detachment of the deposition from the crystal. Since no significant information were obtained from this experiment due to technical limitations, FULCAT 22-F was deeply studied by means of *FT-IR spectroscopy* using different molecular probes treating the sample at different temperatures. Firstly, a preliminary analysis of the as-synthesized and evacuated sample was carried out. The as-synthesised FULCAT-22F (black curve in Figure 8.5) shows the presence of an intense broad band in the high frequency region (3800-2600 cm^{-1}), which goes out of scale and, together with the 1640 cm^{-1} band, reveals the presence of significant interlayer and physisorbed water, preventing the identification of different contributions. By evacuating the sample in vacuum at increasing temperatures the presence of water drastically decreases till reaching the complete activation at 400°C (blue curve in Figure 8.5). During evacuation, two $\nu(\text{OH})$ bands appear at high wavenumbers: a small band at 3748 cm^{-1} and a broader

one centred at 3650 cm^{-1} , which are attributed to silanols and hydroxyl groups bridging Al, Fe and Mg ions in octahedral positions, respectively.⁴ On the other hand, the bending vibration of water (1640 cm^{-1}) completely disappeared at 400°C suggesting that both physisorbed and interlayer water were removed. Finally, the presence of Si-O stretching vibrations, HO-M-OH and M-OH lattice vibrations ($1200\text{--}600\text{ cm}^{-1}$) and overtones of bulk vibration modes ($2000\text{--}1665\text{ cm}^{-1}$) can be observed in all spectra.¹⁸

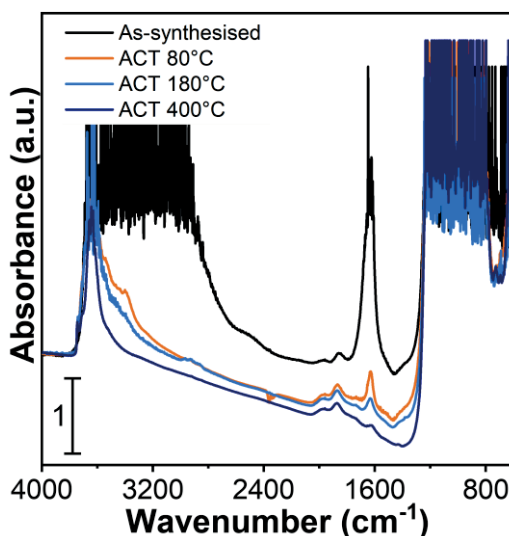


Figure 8.5. IR spectra of FULCAT-22F as-synthesised (black line) and evacuated at 80°C (orange), 180°C (light blue) and 400°C (blue).

In IR spectroscopy, it is common practice to completely evacuate the sample prior to adsorption of various probe molecules.¹⁹ However, as mentioned above, the variable water content in montmorillonite can affect both the structural and acidic properties of the material, and therefore the activation temperature should be chosen carefully. In this regard, three different temperatures were selected for the activation: 80°C , 180°C and 400°C . At the first two temperatures some interlayer water molecules remain in the structure. These conditions result quite close to those one of the catalytic tests. On the other hand, the temperature of 400°C , at which molecular water has been completely removed from the sample, represents the best activation temperature for spectroscopy, although it is not achievable during catalyst testing. Different probe molecules with different basicity were dosed on the sample, previously activated at 80°C and 180°C , to study the presence and the variations of Lewis acid sites (LAS) and Brønsted acid sites (BAS) and try to correlate them with the catalytic activity of the sample. The sample activated at

400°C, which is an ideal working condition for IR spectroscopy, was also studied in the same way for comparison.

The interaction of CO with the sample activated at the three temperatures was firstly studied by dosing a proper amount of gas (~60 mbar) into the cell and cooling down to -196 °C with liquid nitrogen (Figure 8.6).

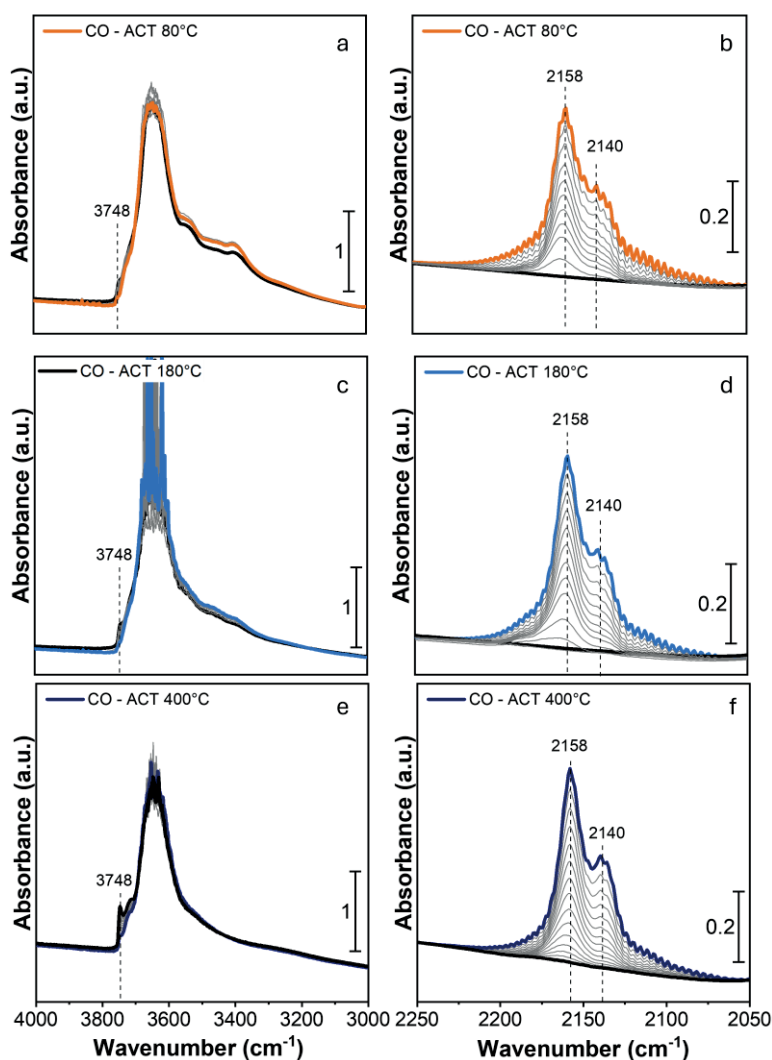


Figure 8.6. IR spectra of FULCAT-22F after adsorption of 60 mbar CO on the previously evacuated sample at 80°C (a, b), 180°C (c, d) and 400°C (e, f) reported in the 4000-3000 cm^{-1} (a, c, e) and in the 2250-2050 cm^{-1} (b, d, f) spectral range. Coloured, grey and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively. The spectra were normalised by means of the overtone (1860 cm^{-1}) intensity.

In all the three cases two main bands appear due to the interaction with CO: one more intense band at 2158 cm^{-1} and a broader weaker one at 2140 cm^{-1} (Figure 8.6 b, d, f). These two signals can be assigned to CO interacting with weakly acidic silanols present in the tetrahedral silica sheets and liquid-like CO, respectively. A further proof of this assignment is the erosion of the sharp OH stretching band at 3748 cm^{-1} when interacting with the probe molecules (Figure 8.6 a, b, c). The eroded 3748 cm^{-1} band is expected to be shifted about -90 cm^{-1} but the presence of the broad and intense 3650 cm^{-1} hydroxyl band probably covers the growth.¹⁹ Lastly, in particular in case of the sample activated at 180°C a small broad band between 2200 and 2172 cm^{-1} starts to appear at low CO pressures. Due to the broadness and low intensity of the band, it is difficult to clearly identify the maxima and make an exact assignment.

To better identify the presence of BAS and LAS in the material other stronger basic molecular probes as CD_3CN and Pyridine were employed (Figures 8.7 and 8.8)

The interaction of CD_3CN with the sample activated at 80°C , 180°C and 400°C is shown in Figure 8.7. CD_3CN , a strong Lewis base, can interact with acidic sites via its nitrogen atom, resulting in a perturbation of the original C-N stretching mode of free CD_3CN (2263 cm^{-1}), whose upward shift is proportional to the strength of the acidic sites.²⁰ The adsorption of CD_3CN at RT on the FULCAT-22F samples resulted in the appearance of numerous bands with different shifts, indicating the presence of several sites having different acidity.

In both samples two sharp bands are observed at 2286 cm^{-1} and 2264 cm^{-1} whose intensity varies according to the activation: in the sample activated at 180°C the two bands reach similar intensities, whereas in the sample activated at 80°C the one at 2286 cm^{-1} is more intense. Additionally, at 180°C , the 2286 cm^{-1} band is broader, suggesting the presence of an additional signal at lower wavenumbers ($\sim 2274\text{ cm}^{-1}$) which is easily desorbed during outgassing. As the pressure decreases, the 2264 cm^{-1} band quickly disappears, while the 2286 cm^{-1} signal is more resistant and shifts slightly towards 2290 cm^{-1} , a contribute that persists even when the sample is reheated (see the dotted lines in Figure 8.7 b and d). Considering the evolution and position of 2264 cm^{-1} and 2286 cm^{-1} bands, the former is assigned to the liquid-like CD_3CN , while the latter is tentatively attributed to the interaction of the molecular probe with the BAS of the material, which can be both structural and/or due to the water polarisation. Differently, the shoulder visible in the 180°C activated spectra at 2274 cm^{-1} is due to the interaction with silanols. In fact, in the OH stretching region

(Figure 8.7 a, c and e) the 3748 cm^{-1} band is consumed and shifted to a broader signal at 3425 cm^{-1} . It is worth noting that as expected the negative shift of $\nu(\text{OH})$ band increases with increasing the proton affinity of the base used as molecular probe.¹⁹

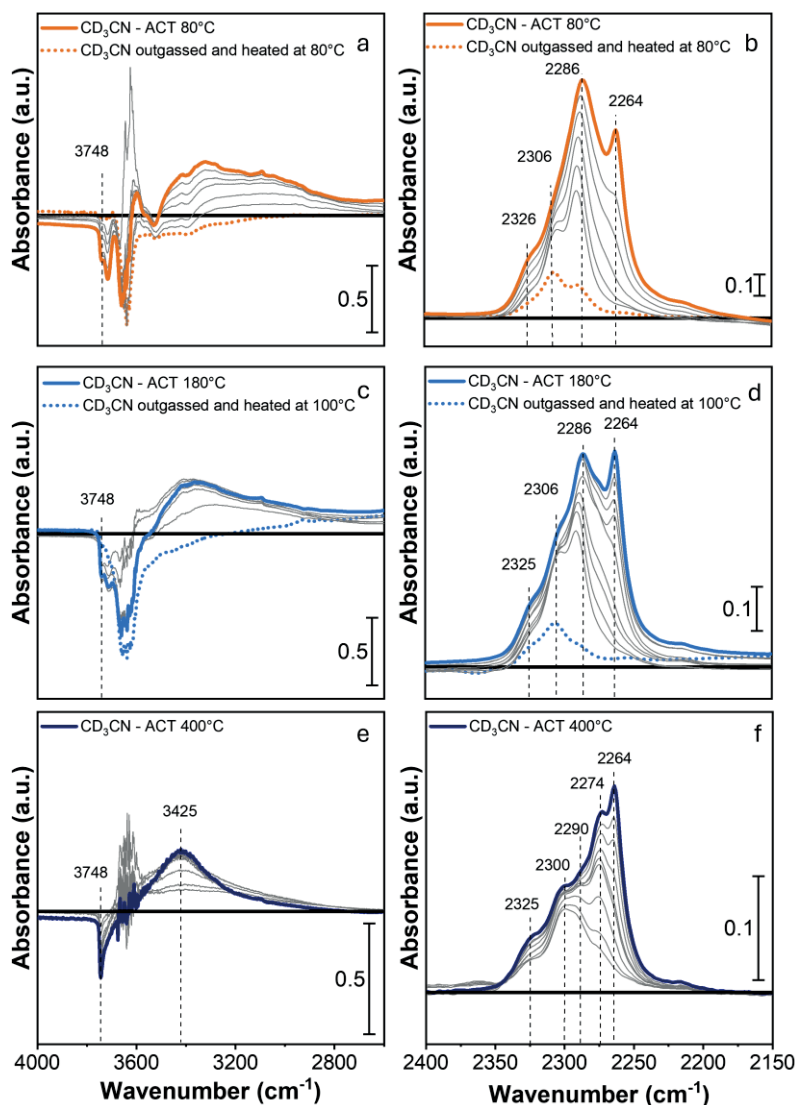


Figure 8.7. IR spectra of FULCAT-22F after adsorption of 15 mbar CD_3CN on the previously evacuated sample at 80°C (a, b), 180°C (c, d) and 400°C (e, f) reported in the $4000\text{--}2600\text{ cm}^{-1}$ (a, c, e) and in the $2400\text{--}2150\text{ cm}^{-1}$ (b, d, f) spectral range. Coloured, grey and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively. Dotted coloured lines represent the sample evacuated at 100°C and 80°C . The spectra were normalised by means of the overtone (1860 cm^{-1}) intensity.

At wavenumbers higher than 2286 cm^{-1} , both the samples display the presence of one main signal at 2306 cm^{-1} and a lower and broader one having the apparent maximum at around 2325 cm^{-1} . Again, the broadness of the bands suggests the presence of multiple sites. In addition, unlike what has been observed previously, these two signals are stable during outgassing and only by reheating the sample the intensity decrease visibly. Taking into consideration the large shift to higher frequencies of those bands (respectively $\Delta\nu=+43$ and $\Delta\nu=+62\text{ cm}^{-1}$ with respect to 2263 cm^{-1}) and the high stability to evacuation, those signals could be assigned to the interaction of CD_3CN with LAS. Although a precise assignment is not straightforward the 2306 cm^{-1} and 2325 cm^{-1} signals can be further examined. Considering the moderate resistance of Al to the acid treatment, as confirmed by EDX analysis, and the stronger acidity with respect to the other residual elements, we can tentatively assign the band at 2325 cm^{-1} to the interaction of CD_3CN with Al^{3+} . As a matter of fact, in case of zeolites where strong Lewis species such as uncoordinated Al^{3+} or extra-framework Al^{3+} species are present, some components at 2315 cm^{-1} and 2327 cm^{-1} , respectively, were observed.^{21,22} Similarly, in case of Fe-ZSM5 a band at 2300 cm^{-1} due to Fe^{3+} LAS was observed, which might, again tentatively, suggest the assignment of the 2306 cm^{-1} signal to Fe due to its relative abundance in the sample and the relatively high acidity.²³ However, the possibility that the 2306 cm^{-1} band is due to a stronger BAS present in the sample cannot be excluded, indeed a signal at 2302 cm^{-1} was previously attributed by Haffad et al. to BAS forming strongly hydrogen-bonded species.⁴

Considering the assigned BAS and LAS species, some differences can be observed when the sample is activated at different temperatures. As a matter of fact, when the sample is activated at 80°C the relative intensity of BAS seems to prevail with respect to both silanols and Lewis ones. However, upon increasing the activation temperature to 180°C , the prevalence of BAS slowly decreases as underlined by the appearance of 2274 cm^{-1} silanols band and by the lower intensity of the 2286 cm^{-1} signal. This tendency is confirmed by repeating the experiment on the sample activate at 400°C (Figure 8.7 e and f). In this case silanols and liquid-like bands (2274 and 2264 cm^{-1} respectively) predominate, while the band relative to BAS decreases and slightly shifts to 2290 cm^{-1} . A possible explanation of this behaviour is due to the different water content of the sample activated at the three temperatures. As previously explained, it is well known that part of the BASs in Montmorillonite comes from the polarization of the H_2O molecule and therefore prevails at low activation temperature.⁴ When the activation temperature reaches 400°C , the

residual BAS signal at 2290 cm^{-1} is likely to be due to some structural BAS sites rather than to the one coming from the polarization of H_2O , which are expected to be almost completely outgassed.

The acid sites present in FULCAT-22F were then further studied by dosing Pyridine (Py) on the sample activated at the three temperatures (Figure 8.8).

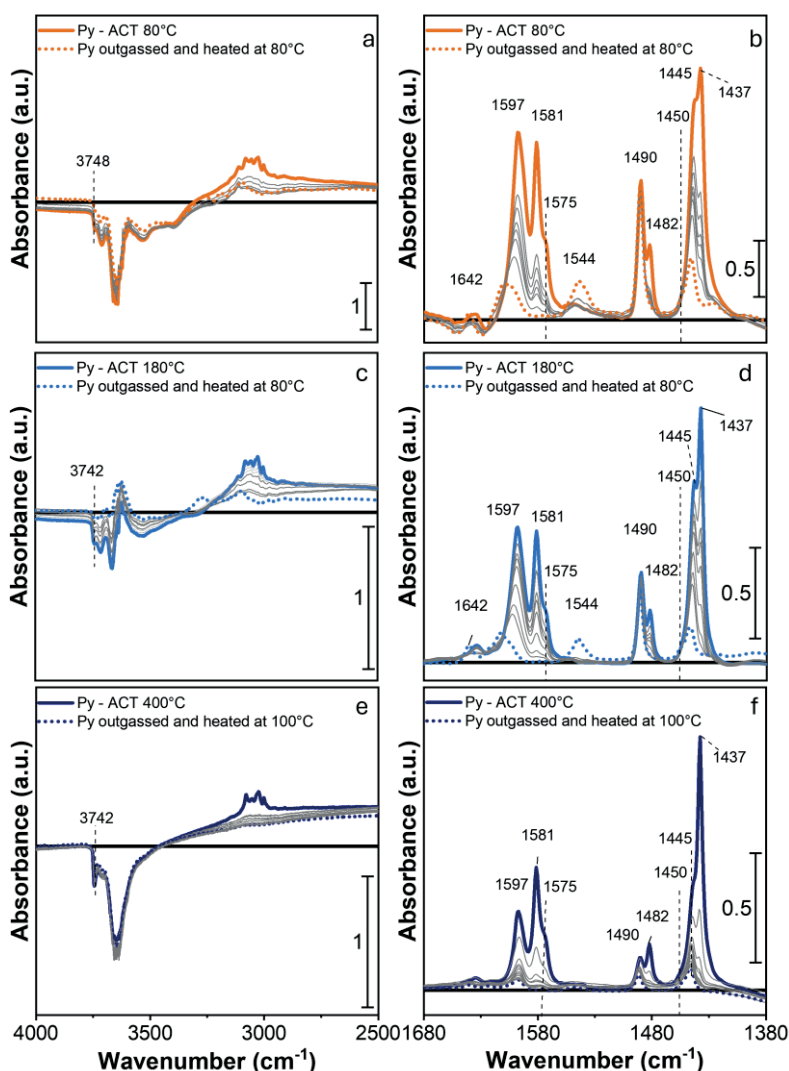


Figure 8.8. IR spectra of FULCAT-22F after adsorption of 26 mbar Pyridine on the previously evacuated sample at 80°C (a, b), 180°C (c, d) and 400°C (e, f) reported in the $4000\text{--}2500\text{ cm}^{-1}$ (a, c, e) and in the $1680\text{--}1380\text{ cm}^{-1}$ (b, d, f) spectral range. Dark coloured, grey and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively. Dotted coloured lines represent the sample evacuated at 100°C and 80°C . The spectra were normalised by means of the overtone (1860 cm^{-1}) intensity.

The interaction of Pyridine with the samples led to the appearance of numerous signals in the 1680-1380 cm^{-1} spectral range representative of the 8a, 8b, 19a and 19b ring-stretching modes of Py.^{21,24} Within this spectral range all the samples show the presence of bands at 1581, 1482 and 1437 cm^{-1} which are easily desorbed during the outgassing and can be reasonably assigned to modes 8a, 19a and 19b of physisorbed Py.^{21,25,26} Additionally, the hydrogen-bonded Py to weakly acidic silanols, which is more stable during the outgassing compared to the physisorbed Py, is observed at 1597 (8a) and 1445 cm^{-1} (19a).^{4,21,25} At the same time, in the OH stretching region (Figure 8.8 a, c and e) the interaction with silanols caused the erosion of 3748 cm^{-1} bands and the formation of a strong and broad absorption centred at about 3000 cm^{-1} ($\Delta\nu \sim 700 \text{ cm}^{-1}$).²⁶ In addition, in the high frequency region, the appearance in the 3200-3000 cm^{-1} spectral range of different CH stretching bands is also observed. In all the three samples two weak signals at 1575 and 1450 cm^{-1} present as shoulders of the more intense bands at 1581 and 1445 cm^{-1} can be distinguished and can be attributed to the interaction with LAS (L-Py) (8b and 19b modes respectively).^{21,25} In addition, 1490 cm^{-1} signal can be due to the 19a mode of L-Py, although it is also attributed to the interaction with both LAS and BAS.^{4,21,27}

By reactivating the samples (dotted curves in Figures 8.8), the silanols bands at 1597 and 1445 cm^{-1} decrease drastically, while 1490 cm^{-1} band seems to remain almost unchanged. However, the most interesting phenomenon is the appearance in case of sample activated at 80°C and 180°C of a band at 1544 cm^{-1} , which was (almost) completely absent when Py starts to be dosed on the two activated samples. The appearance of this band is characteristic of the formation of pyridinium ion generated by the interaction with BAS.^{4,28} Also, one additional band at 1642 cm^{-1} , due to 8a or 8b mode of BAS, appeared.²⁴ The appearance of BAS only during the outgassing or the re-activation of the sample seems to be a rather unusual phenomenon. A possible explanation could be that the pyridine molecules firstly interact with residual physisorbed or interlayer water molecules present in the clay through the formation of a bond between the nitrogen atom of pyridine and one of the hydrogen atoms of water.²⁹ During the outgassing those water molecules start to be evacuated facilitating the interaction with the structural BAS of the samples. However, this pyridine "washing" alters the amount of H_2O present in the sample, which is responsible for the formation of the H^+ BAS through the polarization of interlayer cations, making impossible to study the true nature of the sample. For this reason, pyridine probably is not the most suitable molecular probe to detect

differences in BAS present in the samples activated at different temperatures. Interestingly, the sample activated at 400°C (Figure 8.8 f) did not show the appearance of the 1544 cm⁻¹ signal probably due to the low water content, and consequently low concentration of BAS present in the sample which can be further reduced by the “pyridine washing”.

The low concentration of BAS sites, the partial loss of structure due to thermal treatment and the hindrance of the pyridine molecule probably prevent the appearance of any bands relative to BAS, which was otherwise observed for CD₃CN on the 400°C activated sample (Figure 8.7 f). Only the interaction with a strong and smaller molecule as NH₃ (kinetic diameter 5.7 Å and 2.6 Å for pyridine and NH₃ respectively)^{30,31} reveals the presence of some residual more easily accessible structural BAS (Figure 8.9)

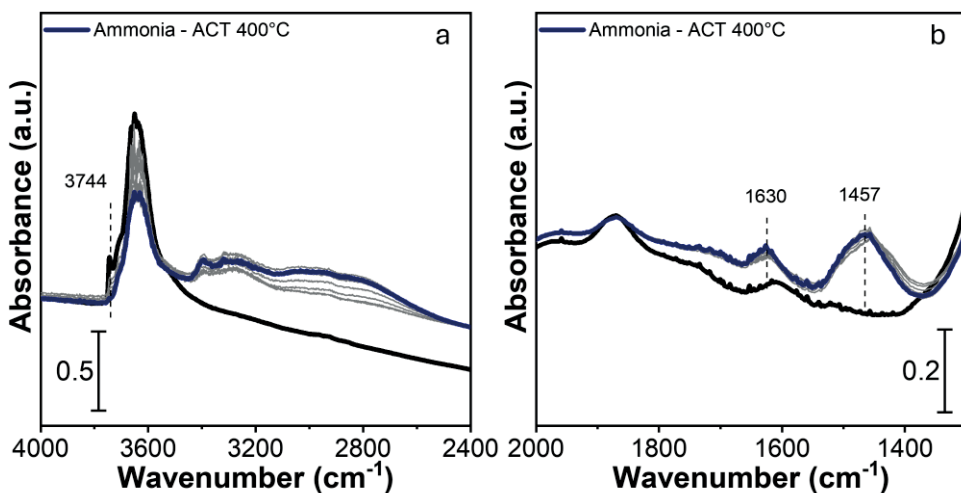


Figure 8.9. IR spectra of FULCAT-22F after adsorption of 30 mbar ammonia on the previously evacuated sample at 400°C reported in the 4000-2400 cm⁻¹ (a) and in the 2000-1300 cm⁻¹ spectral range (b). Blue, grey and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated sample at 400°C. The spectra were normalised by means of the overtone (1860 cm⁻¹) intensity.

As a matter of fact, the interaction of ammonia with the sample activated at 400°C (Figure 8.9 b) caused the appearance in the low frequency region of one intense band at 1457 cm⁻¹ which is related to the deformation mode of the ammonium ion generated by the interaction of NH₃ with BAS.^{32,33} One additional band at 1630 cm⁻¹ of deformation mode ν_4 (NH₃) can also be observed. At high wavenumbers (Figure

8.9 a) the O-H stretching bands at 3744 cm^{-1} and 3645 cm^{-1} were consumed in favour of the growth of a broad signal in the $3400\text{--}2500\text{ cm}^{-1}$ range underlining their interaction with ammonia. Lastly, also the $\nu_{\text{asym}}(\text{NH}_3)$ and $\nu_{\text{sym}}(\text{NH}_3)$ bands results to be downward shifted at 3396 cm^{-1} and 3319 cm^{-1} respectively due to the interaction with silanols or other acids sites present in the sample (Figure 8.9a).³²

Lastly, in order to study the accessibility of the different acid sites to 1-hexanol and to simulate a situation closer to the catalytic conditions, heptanenitrile ($\text{C}_7\text{H}_{13}\text{N}$) was dosed to the sample activated at 180°C (Figure 8.10).

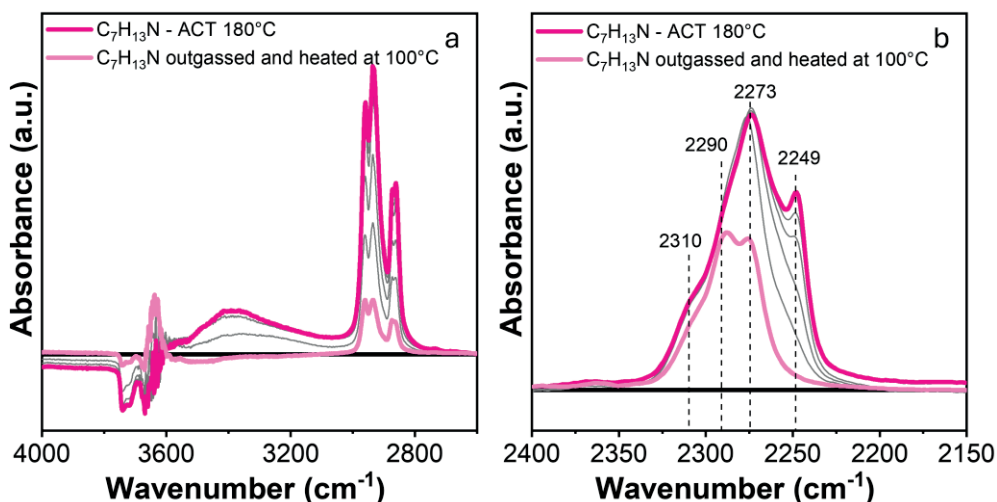


Figure 8.10. IR spectra of FULCAT-22F after adsorption of 2 mbar $\text{C}_7\text{H}_{13}\text{N}$ on the previously evacuated sample at 180°C reported in the $4000\text{--}2600\text{ cm}^{-1}$ (a) and in the $2400\text{--}2150\text{ cm}^{-1}$ (b) spectral range. Dark coloured, grey and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively. Light-pink lines represent the sample evacuated at 100°C . The spectra were normalised by means of the overtone (1860 cm^{-1}) intensity.

Upon interaction with $\text{C}_7\text{H}_{13}\text{N}$ one main band at 2273 cm^{-1} together with two shoulders at around 2290 and 2310 cm^{-1} appear. Additionally, a sharp signal at lower wavenumber (2249 cm^{-1}) can be detected. In the gas phase spectrum of $\text{C}_7\text{H}_{13}\text{N}$, the C-N stretching mode is shifted downwards of -15 cm^{-1} with respect to CD_3CN . This evidence leads us to assign the 2249 cm^{-1} band to liquid-like heptanenitrile.³⁴ By comparing the adsorption of $\text{C}_7\text{H}_{13}\text{N}$ with the one of CD_3CN (Figure 8.11) similar bands with different intensities can be easily detected. Interestingly, also the signals at 2310 , 2290 and 2273 cm^{-1} result to be shifted of 15 cm^{-1} with respect to the 2325 , 2306 and 2286 cm^{-1} bands of CD_3CN , suggesting that the former two can be assigned to the interaction with LAS while the latter one to BAS. The presence of the same bands having very similar relative intensities highlighted that the different acid sites

are all available to hexanol, used for the catalytic test, and the hindrance of the molecule is not playing a role in their accessibility.

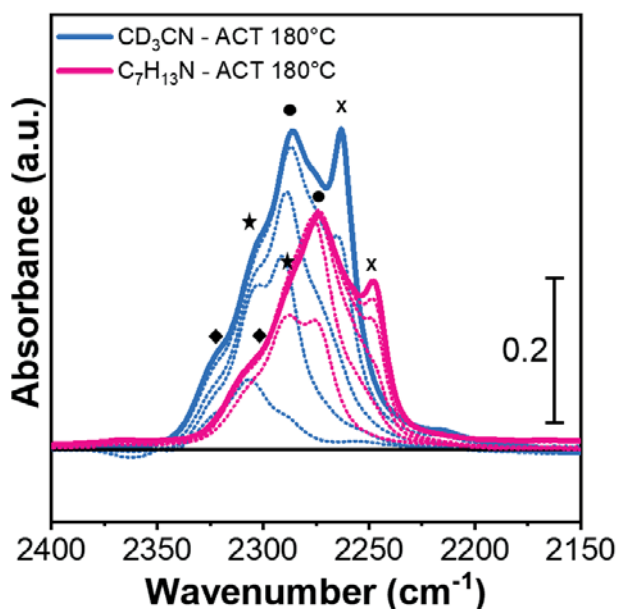


Figure 8.11. Comparison of IR spectra of FULCAT-22F activated at 180°C after adsorption of $C_7H_{13}N$ (pink curves) and CD_3CN (light-blue curves). Coloured solid, dotted and black lines represent the maximum adsorption, the progressive outgassing and the fully evacuated samples, respectively. The spectra were normalised by means of the overtone (1860 cm^{-1}) intensity.

In conclusion, the use of different probe molecules reveals a modification of the BAS and LAS present in the samples, changing the activation conditions, with a prevalence of BAS over LAS at low temperature (80°C). Those BAS are probably mainly due to H^+ sites coming from water polarised by the cations in the interlayer.

Although it is difficult to make a direct correlation between in situ IR characterisation and the catalytic tests, we can hypothesise that the presence of the evidenced acidic (and basic) sites and its synergistic interaction are the key reasons for the observed high reaction yield of this heterogeneous clay-type catalyst FULCAT-22F. Additionally the ratio of BAS to LAS present in the material at different temperatures drive the reaction to different yields in agreement with what previously proposed by Haffad et al. in the case of propane-2-ol.⁴ At low temperature, where the BAS predominate, the catalytic reaction is more selective

towards ether formation, while increasing the temperature and decreasing the BAS content in favour of LAS, a higher selectivity towards alkene is observed. A final scheme of the main findings of this chapter is presented in Figure 8.12).

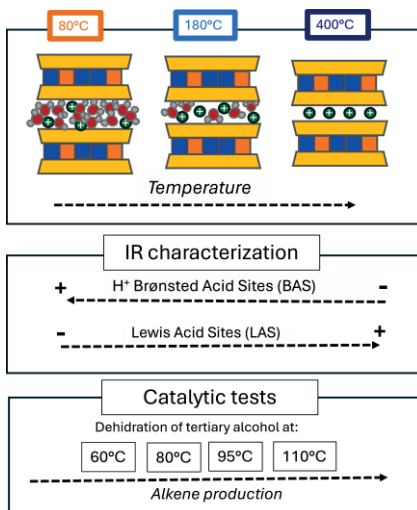


Figure 8.12. Schematic and pictorial representation of the main changes that occur in the structure with increasing temperature in relation to the results obtained from IR characterisation and catalytic tests.

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9. CONCLUSIONS

Among the various mitigation strategies aiming to counter the greenhouse effect, Carbon Capture Utilization and Storage (CCUS) technologies were expected to reduce for almost 15% the actual cumulative CO₂ emissions. The aim of this work was to investigate and characterise different materials as potential candidates for CCUS technologies, which are among the promising approaches currently being extensively investigated for the reduction of anthropogenic emissions.

Specifically, three different solid adsorbents for CO₂ capture and various catalysts for the conversion of CO₂ into liquid jet fuels have been tested and/or fully characterised, in an attempt to study the different steps of the anthropogenic CO₂ cycle.

For what concerns CO₂ capture, nine different criteria must be considered for a real application of the material: adsorption capacity, selectivity, fast kinetics, easy of regeneration, stability over cyclability, mechanical and thermal stability, low costs, tolerance to moisture and to other impurities and possibility of shaping.

Zeolite, MOFs and hydrotalcites were selected because each offer specific and unique characteristics as potential solid adsorbents for CO₂ capture and separation technologies. For each class of adsorbents, a specific material (i.e. LTA, F4 MIL-140A(Ce) and Mg-Al 3:1 LDH) has been identified and thoroughly characterised, highlighting their potentialities and weaknesses considering the above-mentioned criteria. Even though a specific characterisation procedure was carried out for each sample, for all three classes, the materials were previously analysed in powder form and then 3D monoliths synthesised by the Direct Ink Writing technique were investigated. This allows a comparison between the different samples and enables the formulation of some general conclusions.

The LTA zeolite showed the highest CO₂ capture capacity, ranging in between 4.1 to 3.0 mmol/g at 1 bar in the 25°C ≤ T ≤ 90°C range. The F4 MIL-140A(Ce) exhibited an overall lower CO₂ uptake, between 2.6 and 2.2 mmol/g at 5 bar in the 25°C ≤ T ≤ 70°C range, but the peculiar S shaped isotherm characterized by a step at low pressures (between 200 mbar and 1 bar as the temperature increases) allowed to

reach higher working capacity and selectivity. On the other hand, the adsorption capacity of Mg-Al 3:1 LDH appeared to be modest (0.53 mmol/g at 1 bar and 300°C), but not in view of the considerable high temperature employed, at which the majority of solid sorbents, including the previously mentioned LTA and F4 MIL-140A(Ce), show almost negligible uptake.

For both LTA and F4 MIL-140A(Ce), easy regeneration conditions (outgassing at room temperature) were observed suggesting a considerable stability upon cyclability, while for LDH samples the simple evacuation was not able to completely recover the initial CO₂ uptake. In fact, for the latter sample, the activation temperature (400°C) was responsible for the transformation into a Layered Double Oxide (LDO) or Mixed Metal Oxide (MMO) structure, which did not show fully reversible adsorption. However, for this sample, in powder form, both the structural and the adsorption capacity were completely recovered by simply exposing it to H₂O solutions. These results suggested a peculiar and beneficial effect of H₂O in adsorption, at least for improving the cyclability. In this regard, while for both LDH and LTA zeolite the competitive H₂O/CO₂ adsorption should be investigated in the future, for F4 MIL-140A(Ce), its peculiar mechanism of CO₂ interaction was investigated in both dry and humid conditions. In particular, under dry conditions the adsorption occurred through cooperative pathway, involving a first rotation of the fluorinated rings happening at low pressures which leads, at higher coverages ($P > 200$ mbar depending on the temperature), to the opening of tight pockets where the simultaneous interaction of CO₂ with Ce⁴⁺ open metal sites and three F atoms of the linker took place. In partially hydrated sample this mechanism can still occur, even if shifted to higher pressures, since the presence of H₂O coordinated to Ce⁴⁺ sites delayed the access of CO₂ and the concerted rotation of the rings.

For what concerns the 3D monoliths, only for NaLTA zeolite it was currently possible to synthesise a mechanically robust and binderless monolith, having both static and dynamic CO₂ adsorption capacities comparable to the powder sample. For both the MOF and the hydrotalcite, other components (binders and additives) were added to the ink to make it printable and able to maintain structure and shape. The 3D monolith of MOF exhibited the peculiar S shaped isotherm in the same pressure range of the pure MOF and a perfect agreement between the experimentally measured CO₂ uptake (1.16 mmol/g at 25°C and 1 bar) and the theoretical CO₂ adsorption calculated by summing the adsorbed amount weighted by the percentage of the different components present in the 3D sample. On the other hand, a LDH monolith having 40% of active phase (57 wt% of binder NaGP, 3% of

heology modifier NaBT) was prepared for CO₂ capture at high temperature. Unfortunately, although at the beginning the sample showed a CO₂ capture capacity even higher than the theoretical one, a decrease in performance was observed due to a prolonged exposure to high temperatures. This loss can only be partially recovered by exposure to H₂O solutions leading to only modest capture capacities (in the 0.24-0.16 mmol/g range at 300°C and 1 bar).

Although additional work must be carried out on all the three adsorbents in the future, both in terms of further characterisation and synthesis optimization, as well as the evaluation of properties such as kinetics or selectivity, this thesis has contributed to understanding key properties that lay the foundation for further improvements of these materials.

After considering the CO₂ capture step, the thesis focused on its possible use for the synthesis of e-fuels, following the approach proposed by “4AirCRAFT” (Grant Agreement Number JPMJSC2102), an European project whose main goal is the direct conversion of captured CO₂ into C₈-C₁₆ liquid jet fuels under low temperature and pressure conditions. In order to reach this goal, the project aims to develop a single cascade reactor working through three-step reactions including: (i) a first electrocatalytic reduction of CO₂ into CO ($\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$), followed by (ii) hydrogenation of the produced CO to short chain hydrocarbons and (iii) a final transformation into C₈-C₁₆ products thanks to an oligomerization process. Among the different catalysts involved in the various reactions, my research activity focused on the characterization of electrocatalysts working in the first step of the reaction (from CO₂ to CO) and of catalysts involved in the second stage (from 1-alkanols to 1-alkenes).

For what concerns the electrochemical reduction of CO₂, different LDHs were deeply characterized to explore the active sites present in the materials and to understand the reason of their different electrocatalytic performances. Firstly, the study was focused on catalysts having different elemental compositions: Zn-Al, Ni-Al, Ni-Fe LDH. After that, the attention was shifted to Zn-Al LDHs, in which a higher Faradaic Efficiency (FE) was observed. Zn-Al LDHs having different stoichiometries (2:1, 1:1 and 1:2) were studied by means of ATR-IR spectroscopy disclosing the presence of different carbonates families in the three samples. In particular, looking at the ratio between monodentate and bidentate carbonates, the Zn-Al 1:2 LDH, which is also the most electrochemical active sample, showed a greater contribution of monodentate species with respect to the others. Since the differences observed in

the carbonate families provides a powerful tool to discriminate among materials with different basic sites in the Zn-Al 1:2 LDH, a higher content of low coordination oxygen anions with strong basic character is expected. On the other hand, increasing the $\text{Zn}^{2+}/\text{Al}^{3+}$ ratio, the samples were characterized by a higher content of acid-base pairs with intermediate basic strength. Since CO_2 adsorption is the first step of the CO_2 reduction reaction (CO₂RR), differences in the basic character and consequently in the carbonate formation are expected to play a crucial role in the overall reaction, but to clearly understand the reaction mechanism, an *operando* characterisation should be performed. In the last part of the thesis, initial studies were carried out using a recently acquired cell capable of combining electrochemical measurements with ATR spectroscopy showing promising results. Lastly, by comparing the different experiments, it was observed a change in the electrochemical performances by changing the grinding time at which the sample was subjected. In particular Zn-Al 2:1 ground for increasing times showed a gradual decrease in the crystallinity. Preliminary analysis by IR spectroscopy suggested that the grinding of the sample could be responsible for an initial reduction of active sites becoming unavailable and/or inaccessible to CO_2 . However, upon contact with H_2O , the LDH structure seems to be regenerated and a high content of carbonates was observed. These considerations suggested that the electrochemical activity of LDH might be influenced by changes in the physico-chemical properties of the original material due to grinding.

Finally, after the electrochemical reduction of CO_2 to CO, it reacts with renewable H_2 to produce 1-alkanols, through the microbial transformation developed by Siemens and Evonik Industries and already available in industry, and then undergoes a dehydration reaction to produce 1-alkenes. The catalysts employed for the latter reaction was a commercial acid-leached bentonite, FULCAT-22F. Indeed, this catalyst firstly tested for the dehydration of 1-hexanol resulted in an alkene yield of 52%, even higher than the one displayed by more acidic samples such as Triflic acid. Subsequently, FULCAT-22F was tested with secondary and tertiary alcohols under milder reaction conditions, achieving yields of 88% and 91%, respectively. For tertiary alcohols, a general increase in alkene yield was observed with rising the temperature. In order to explain this high catalytic activity, the catalyst was deeply characterized using both fundamental and advanced spectroscopic techniques. The fundamental characterization evidenced that the evacuation of the water present in the structure leads to changes in both the crystallographic and the textural property of the sample. The deep spectroscopic analysis, carried out with different

molecular probes of variable basicity (CO, CD₃CN, Py and NH₃), revealed a modification of the Lewis Acid Sites (LAS) and Brønsted Acid Sites (BAS) present in the samples activated at different temperatures with a prevalence of BAS over LAS at low temperature (80°C) and an opposite trend at higher temperature. Merging the catalytic results and the spectroscopic characterisation, we hypothesised that the ratio of BAS to LAS sites present in the material at different temperatures drives the reaction to different product yields. At low temperature, where the BAS predominated, a low yield of reaction was observed for all the three types of alcohols, while by increasing the temperature (so decreasing the BAS content in favour of LAS), a raise in the productivity of the alkene was achieved.

Concerning the CO₂-to-fuels conversion, the characterisation step allowed catalysts improvement and the understanding of the reaction mechanism. Again, the experimental work provided the basis for some further investigations and the development of cutting-edge characterisation techniques, such as spectroelectrochemistry.

Acknowledgements

As the thesis focuses mainly on characterisation, I would like to explicitly thank all those who worked with me on the various sections of the thesis, without whom I would not have been able to do much of this work.

For the part of the thesis concerning “Materials for CO₂ capture” I would like to thank:

Dr Marco D'Agostini, Prof. Giorgia Franchin and Prof. Paolo Colombo of the Advanced Ceramics and Glasses Group of the University of Padova, who worked on the synthesis of the LTA, MOF and LDHs monoliths using the direct ink writing technique.

Prof. Marco Taddei of the University of Pisa, who synthesised and involved me in the study of F4_MIL-140A(Ce) and others interesting materials not discussed in the present thesis.

Dr. Melodj Dosa, Mr. Andrea Rizzetto and Prof. Marco Piumetti of the Politecnico di Torino for their collaboration in the study of both beads and monolithic LTA.

I would also like to thank Dr. Cesare Atzori who started the study of F4_MIL-140A(Ce) and Dr. Matteo Signorile who helped me in many of these activities.

For the part of the thesis concerning “Materials for CO₂ conversion” I would like to thank:

Prof. Kiyoharu Tadanaga, Dr. Ryosuke Nakazato of Hokkaido University for synthesising and testing the various LDHs for CO₂RR.

Mr. Elías Rodríguez-Jara, Prof. Nataly Carolina Rosero-Navarro, Prof. Jadra Mosa, Prof. Mario Aparicio of the CSIC-ICV Centre of Madrid, who hosted me and introduced me to the world of electrochemistry.

Mr. Matthias Quintelier, Prof. Joke Hadermann of the University of Antwerp for performing SEM and TEM images

Mr. Adil Allahverdiyev, Ms. Jianing Yang and Prof. Harald Gröger, Bielefeld University, for providing the FULCAT sample and performing the catalytic tests for dehydration of alcohols to alkenes.

I would also like to thank Dr. Vanesa Gil for coordinating the 4AirCRAFT project and helping us in many situations.

I thank the 4AirCRAFT project for founding my PhD. 4AirCRAFT has received funding from the European Union's Horizon 2020 research and innovation programme (No 101022633) and Japan Science and Technology Agency (JST) (No JPMJSC2102). Lastly, I acknowledge support from the Project CH4.0 under the MUR program "Dipartimenti D13C22003520001).

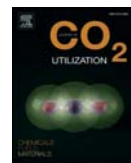
Finally, I would like to thank my supervisors Prof. Francesca Bonino and Valentina Crocellà for their help and support during these years.

APPENDIX A

Appendix A contains the papers published during my PhD, related to the topic of the project and discussed in the thesis.

In particular:

- “Cavallo, M.; Dosa, M.; Porcaro, N. G.; Bonino, F.; Piumetti, M.; Crocellà, V. Shaped Natural and Synthetic Zeolites for CO₂ Capture in a Wide Temperature Range. *J. CO₂ Util.* 2023, 67, 102335” was discussed in Chapter 4 “LTA ZEOLITE FOR CO₂ CAPTURE: FROM POWDER TO 3D PRINTED MONOLITHS”
- “Cavallo, M.; Atzori, C.; Signorile, M.; Costantino, F.; Venturi, D. M.; Koutsianos, A.; Lomachenko, K. A.; Calucci, L.; Martini, F.; Giovanelli, A.; Geppi, M.; Crocellà, V.; Taddei, M. Cooperative CO₂ Adsorption Mechanism in a Perfluorinated CeIV -Based Metal Organic Framework. *J. Mater. Chem. A* 2023, 11 (11), 5568–5583” was discussed in Chapter 5 “CO₂ CAPTURE IN MOFs: THE CASE OF F4 MIL-140A (Ce)”
- “Nakazato, R.; Matsumoto, K.; Yamaguchi, N.; Cavallo, M.; Crocellà, V.; Bonino, F.; Quintelier, M.; Hadermann, J.; Rosero-Navarro, N. C.; Miura, A.; Tadanaga, K. CO₂ Electrochemical Reduction with Zn-Al Layered Double Hydroxide-Loaded Gas-Diffusion Electrode. *Electrochemistry* 2023, 91 (9), 23–00080” was discussed in Chapter 7 “ELECTROCATALYSTS FOR CO₂ REDUCTION REACTION” paragraph 7.2 “LDHs with different elemental composition: Zn-Al, Ni-Al, Ni-Fe LDH”
- “Cavallo, M.; Dosa, M.; Nakazato, R.; Porcaro, N. G.; Signorile, M.; Quintelier, M.; Hadermann, J.; Bordiga, S.; Rosero-Navarro, N. C.; Tadanaga, K.; Crocellà, V.; Bonino, F. Insight on Zn-Al LDH as Electrocatalyst for CO₂ Reduction Reaction: An in-Situ ATR-IR Study. *J. CO₂ Util.* 2024, 83, 102804” was discussed in Chapter 7 “ELECTROCATALYSTS FOR CO₂ REDUCTION REACTION” paragraph 7.3 “Zn-Al LDH with different M²⁺/M³⁺ molar ratio”



Shaped natural and synthetic zeolites for CO₂ capture in a wide temperature range

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ARTICLE INFO

Keywords:

CO₂ adsorption
Breakthrough measurements
Clinoptilolite
Linde-Type A zeolite
Natural zeolites

ABSTRACT

The CO₂ adsorption performances of a Linde-Type A (LTA) zeolite and a natural Clinoptilolite (Clino) zeolite, both in shaped form, were investigated as such or after an ion-exchange procedure and compared to assess their potential application as solid adsorbents for Carbon Capture and Storage (CCS). The samples were characterized following a multi-technique approach. Their structural and textural properties were evaluated to investigate the accessibility of the different ions present inside the microporous structure and the strength of their interaction with the adsorbates. The CO₂ adsorption tests were carried out performing pure CO₂ adsorption/desorption isotherms and dynamic breakthrough measurements in a wide range of temperature (298–423 K). The ion-exchange enhanced the adsorption capacity of the synthetic zeolite, while no significant increment in the CO₂ adsorption performances is observed for the natural one. Nonetheless, the CO₂ adsorption reversibility is affected by the cation exchange process in both synthetic and natural zeolites. The CO₂ adsorption capacities of LTA zeolites are higher at lower temperatures, whereas the CO₂ adsorption performances of natural Clino are interesting also at medium-high temperature, being the most performant material at 423 K. By performing IR experiments with specific probe molecules, the presence of a consistent number of Fe²⁺ ions in the framework of natural Clino, responsible for the capacity of this material to strongly interact with CO₂ also at medium-high temperatures, was proved. The peculiar adsorption behavior of natural Clino, its low cost and availability in shaped form are some of the essential features for its possible implementation in real CCS technologies.

1. Introduction

Carbon dioxide (CO₂) is naturally occurring in the Earth's carbon cycle, and it is exchanged among plants, animals, soils and oceans in the biosphere. However, the CO₂ amount in the atmosphere has significantly increased during the last decades, due to the human activities that have irreversibly altered the atmospheric CO₂ concentration, by modifying the capture capacity of forests and soils and by directly releasing huge amount of CO₂. The combustion of fossil fuels (i.e., coal, oil, and natural gas) is the main responsible of the CO₂ emissions in the atmosphere. In particular, the following emission percentages by field were reported: 35 % transportation, 31 % electricity production, 16 % industry, 10 % residential and commercial and 8 % non-fossil fuel combustion [1]. In 2019, the amount of CO₂ in the atmosphere was about 80 % of all greenhouse gasses emissions, while the contribution of the other stood at 10 % for methane (CH₄), 7 % for nitrous oxide (NO_x) and 3 % for

fluorinated gases [1]. Due to the huge amount of CO₂ emissions, this molecule remains the major responsible for the greenhouse effect, even if its global warming potential is lower than the one estimated for other GHGs [1,2]. In the last decades, several strategies have been developed to decrease the amount of CO₂ in the atmosphere. The attention of the scientific community has mainly focused on the development of technologies aimed at reducing the emissions of CO₂ deriving from electricity and industrial productions, which account together for about 47 % of the total emissions. Nowadays, the main Carbon Capture and Storage (CCS) technologies employed in the post-combustion CO₂ capture are chemical and physical absorption, adsorption-based solid materials, cryogenics methods, membranes, microbial/Algal systems and solvent scrubbing [3–7]. The CO₂ capture by solid adsorbents has gained particular interest thanks to several advantages, as low energy costs, mild regeneration conditions and low volatility of the captured CO₂ [7]. Among the possible adsorbents for the CO₂ capture, zeolites possess

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<https://doi.org/10.1016/j.jcou.2022.102335>

Received 5 September 2022; Received in revised form 26 October 2022; Accepted 17 November 2022

Available online 24 November 2022

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some interesting features due to their textural, structural and chemical properties, as far as for their high cation exchange potential and polarity properties [7–15]. For this reason different synthetic and natural zeolites have been widely studied in academia for CO₂ capture over the years [16].

In this scenario, Clinoptilolite, a natural zeolite, has received interest for CO₂ capture due to the low-cost comparing to commercial (synthetic) zeolites (vide infra), which depends on its chemical composition and geographical origin [17–20]. This natural material, which belongs to the heulandite (HEU) framework-type group, exhibits a (NaKCa)₄(Al₆Si₃₀O₇₂)·24H₂O unit cell formula and is characterized by two parallel channels (0.30 × 0.76 nm and 0.33 × 0.46 nm) connected with a third one (0.26 × 0.47 nm) [21].

Among the synthetic zeolites, LTA (Lynde-Type A), generally applied as an industrial desiccant, has been recently studied for the adsorption of other molecules, including CO₂ [22,23]. The general formula of this zeolite is $[\text{Na}^+_{12}(\text{H}_2\text{O})_{27}]_8[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]_8$ and is commonly available with Na⁺ as extra-framework cations balancing the negative charge given by the presence of aluminum atoms. The lowest possible Si/Al ratio of this zeolite (Si/Al = 1) leads to a higher cations exchange capacity, with possible positive effects on the CO₂ uptake of the material [24]. In LTA, tetrahedra are organized to form a structure composed by 8 beta cages (sodalite cages) connected each other with cubic structures (d4r), creating a central alpha cage (made by 48 T structures). The dimension of the diameter of the central alpha cage is 1.1 nm, while the external 8-member ring aperture is about 0.4 nm [25].

Both the Clinoptilolite and the LTA zeolites can adsorb CO₂ by Van der Waals forces and the modification of their chemical composition (i. e., by varying the nature of cations present in the framework) may increase the CO₂ adsorption capacity [26]. However, beside the great interest of zeolites as CO₂ adsorbents, for an actual application in the industrial sector, adsorptive flue gases should be dehydrated due to their well-known strong affinity for water. [27].

This aspect affects the energy consumption, increasing the final cost of the entire process. [28,29] For this reason, to be compatible with other established or emerging technologies and to be considered worthy of industrial potential, those adsorbent materials must at least comply with other specific requirements, such as low costs, regeneration capacity, cyclability, selectivity and availability into mm-scale shaped particles.

In the present work, both Clinoptilolite and LTA zeolites were studied in an already shaped form and compared to evaluate their CO₂ adsorption capacity at various temperatures (in the 298–423 K range) to assess their potential application as CCS adsorbents in different capture conditions. Moreover, to possibly enhance their adsorption capacity, both samples were ion-exchanged with different cations. The materials were deeply characterized by using different complementary techniques and their CO₂ capture capacity were investigated in both static ideal and flow conditions by collecting CO₂ adsorption experiments with pure CO₂ and under a N₂/CO₂ flow.

2. Experimental methods

2.1. Materials preparation

The natural zeolite Clinoptilolite (herein labeled as “Clino”) was provided by Zeolado (Greece), while the synthetic LTA (hereafter referred to as “NaLTA”) was purchased in sodic form from Sigma Aldrich. Usually for research purposes, the samples are supplied in powder form, whereas for practical and industrial applications the use of already shaped materials into mm-scale particles is required [30]. For this reason, a LTA in spherical beads (ø 3–5 mm) and a Clino in natural rock fragments (ø 0.15 mm) were used in the present work.

Due to its natural origin, Clino contains many different cations (Fe, K, Ca, Na, Mg). To homogenize its composition and discriminate the effect

of different cations, NaClino and CaClino were prepared starting from the pristine Clino. Similarly, CaLTA was generated from pristine NaLTA, using a similar ion-exchange procedure as graphically described in Scheme1.

The difference in the two ion-exchange procedures consists in a previous de-cationization process needed for natural Clino. The cations substitution in this framework is usually hard if compared to other types of zeolites, due to the stronger interaction of Clino cations with the structure [31,32]. In order to increase their exchange capacity, a previous substitution with NH₄⁺ ions is commonly performed, exploiting the high selectivity of Clino for these cations [33].

The exchange method employed for Clino was adapted from the procedure reported by Valdés et al. [33]. A preliminary washing procedure was performed on the starting Clino: the material was washed in ultra-pure water at room temperature under stirring for 10 min, centrifuged and oven-dried at 348 K for 12 h. The washed Clino was first exchanged with NH₄⁺ ions by immersing for 2 h the sample in a 0.1 M solution of (NH₄)₂SO₄ (30 mL solution/g sample) under stirring at 363 K. The sample was washed by replacing the solution with ultra-pure water and stirred at 363 K overnight. This procedure was repeated twice to improve the exchange ratio and finally the sample was oven-dried at 398 K overnight. After this step, the NH₄⁺ ions were exchanged with Na⁺ and Ca²⁺ to obtain a fully exchanged Na-Clino (NaClino) and Ca-Clino (CaClino) respectively. The sample in ammoniac form was immersed for 18 h in a 0.5 M solution of NaNO₃ (for NaClino) or Ca(NO₃)₂ (for CaClino) under stirring at 333 K (20 mL solution/g sample). The procedure was repeated a second time by replacing the solution with a fresh one. The sample was eventually dried at 373 K overnight and stored in a desiccator until further use.

In contrast to Clino, the NaLTA can be easily exchanged with a simple ion exchange procedure [34]. Therefore, an LTA sample exchanged with Ca²⁺ ions (CaLTA) was prepared by immersing the original NaLTA sample in a 0.5 M solution of Ca(NO₃)₂ (20 mL solution/g sample), following the same conditions used for CaClino. Also in this case, the procedure was repeated twice.

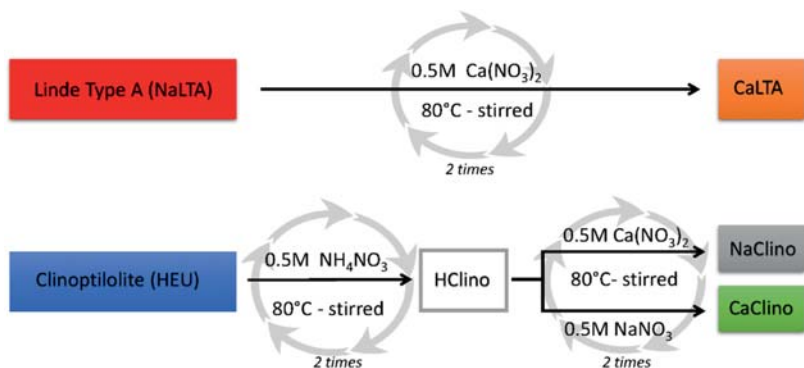
2.2. Characterization methods

The EDX analysis were performed on a FESEM TESCAN S9000G. The voltage used for electron acceleration is 15 kV and the probe current 300 pA, the software AZTEC was used for the microanalysis.

FT-IR spectroscopy was employed to follow the CO adsorption at 77 K by using a Bruker Invenio spectrophotometer equipped with a MCT (mercury cadmium tellurium) cryo-detector. All the spectra were collected in the 4000–650 cm^{−1} spectral range with a resolution of 2 cm^{−1} and an average of 32 scans. Before the analysis all the samples, in form of self-supported pellets protected by a gold envelope, were inserted in a special home-made quartz cell and activated in vacuum at 673 K for 4 h. Then, they were cooled down to Room Temperature (RT) and approximately 60 mbar of CO were dosed to the sample. The cell was cooled down with liquid nitrogen until reaching a nominal temperature of 77 K, at which the interaction of CO with the cationic acid sites of the zeolite are well visible. Finally, different spectra were collected during gas expansions until all CO was desorbed.

The powder X-ray diffractograms of the materials were collected on a PANalytical X'Pert diffractometer using Cu Kα radiation and a power of 45 kV 40 mA in Capillary configuration (2θ range = 5–65°).

Volumetric measurements were performed by means of a Micro-meritics ASAP2020 sorption analyser, by collecting adsorption/desorption isotherms of both N₂ at 77 K and CO₂ at 273 K up to 1000 mbar. For CO₂ adsorption, the temperature was kept constant thanks to a special home-made patented apparatus coupled with the Micro-meritics ASAP 2020 volumetric instrument, consisting of a glass buret inserted in a concentric jacket, in which a coolant or heating fluid circulates through a JULABO CD-200F [35]. The system ensures precise temperature control during the measurement in terms of homogeneity



Scheme 1. Schematic representation of ion-exchange procedure for the two samples.

and stability over time, allowing isotherms collection with a very low temperature resolution. Before the measurement, the samples were activated at 673 K for 4 h in vacuum.

The CO₂ adsorption/desorption isotherms were measured at other four different temperatures (298, 333, 363 and 423 K) using the same volumetric set-up and following the same activation procedure. The specific surface area was determined by both N₂ and CO₂ adsorption isotherms, applying the Brunauer–Emmett–Teller (BET) equation in the $0.05 < p/p_0 < 0.3$ and $0.003 < p/p_0 < 0.03$ range respectively.

An evaluation of the isosteric heat of adsorption was also performed by applying the Clausius–Clapeyron equation to the isotherms measured at the first three temperatures (298, 333, 363 K) [36]:

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \quad (1)$$

Different isosteric curves can be obtained plotting the natural logarithm of the pressure at constant loading as a function of $1/T$. Multiplying the slope of this curve by the gas constant the isosteric heat for different quantities adsorbed was obtained [37]. Data elaboration was performed by using the Micromeritics' data analysis software (Micro-Active version 5.02.01).

Breakthrough CO₂ adsorption tests were performed in an experimental set-up characterized by the following equipment: a quartz-U reactor (inner diameter 1 cm, height 3 cm) with a fixed bed, a furnace and a paramagnetic gas analyzer (Emerson XStream X2GP). In this set-up, the adsorbent material (300 mg) was placed into the quartz-U reactor. The reactor was positioned into the furnace and connected to the mass-flow controllers. A K-type thermocouple, placed in the quartz-U reactor chamber on the top of the adsorbent material (at around 1 mm distance), was used for the temperature control. The flow-out from the reactor was monitored by the gas analyzer every 10 s, monitoring the CO₂ volume fraction (ppm). Before the adsorption tests, a pretreatment was carried out to eliminate impurities on the adsorbent material (i.e., carbonates and humidity). The pretreatment was performed by using N₂ (total flow = 40 mL min⁻¹) at 673 K for 2 h. Then, the temperature was cooled down and the adsorption tests were performed: the total flow was 40 mL min⁻¹ comprised by 10 vol% CO₂ volume balanced with N₂. The temperatures chosen for the CO₂ adsorption tests were 298, 333, 363 and 423 K, according to the volumetric measurements. In each adsorption test, the CO₂ volume fraction was recorded until the concentration reaches the initial value (10 vol%). The amount of CO₂ was evaluated by the integration of the breakthrough curves, as reported in the [Supplementary material](#).

Furthermore, the adsorption loading capacities of the adsorbent materials were evaluated by the following equation:

$$\alpha_{zeolite} = \frac{n_{CO_2,adsorbed}}{m_{sorbent}} \quad (2)$$

where:

$n_{CO_2,adsorbed}$ is the total amount of CO₂ (moles) adsorbed by the material.
 $m_{sorbent}$ is the total amount (mass - g) of adsorbent material used for the test.

3. Results and discussions

3.1. Physico-chemical characterization

A first proof of the efficacy of the ion-exchange procedure was verified by means of EDX analysis, which provides the elemental composition of the zeolites. Results are summarized in [Table 1](#) for all samples. The resulting values are an average obtained analyzing five points located in different regions of the samples.

The pristine Clino is characterized by the presence of different cations inside the HEU framework, the most abundant being Fe, followed (in order of abundance) by K⁺, Ca²⁺, Mg²⁺, and Na⁺. Fe can be present as Fe²⁺ and Fe³⁺ in different ratio, depending on the geographical origin of the clinoptilolite [38]. In NaClino exchanged sample, Na⁺ has the highest atomic and weight percentage, underlining that the ion exchange procedure probably succeeded mainly at the expense of Fe^{2+/3+} and Ca²⁺ cations, leaving small amounts of Mg²⁺ and K⁺ inside the framework. Similarly, Fe^{2+/3+}, Mg²⁺ and Na⁺ were entirely substituted by Ca in CaClino, whereas a small fraction of K⁺ ions remain in the zeolite framework. For all the Clino samples the Si/Al ratio is around the theoretical value (~5), with a slight increase in the exchanged sample probably due to a partial dealumination [39]. As expected for a synthetic zeolite, in the starting NaLTA sample the main cation present in the zeolite framework is Na⁺, with some Ca²⁺ and Mg²⁺ impurities. Na⁺ ions are mostly substituted by Ca²⁺ in the CaLTA sample, proving that a milder ion exchange procedure, without a decationization step, is sufficient to replace the cations of the LTA zeolite beads. Both NaLTA and CaLTA exhibit a Si/Al ratio around the theoretical value (~1), proving that the exchange procedure does not modify the Al content of the sample.

XRD patterns were collected to prove that the crystalline structure of the zeolites was not affected by the ion-exchange procedure. As reported in [Fig. 1](#), Clino, NaClino and CaClino samples exhibit the main reflections of the HEU framework, [40,41] whereas NaLTA and CaLTA samples show the characteristic diffraction pattern of the LTA topology. [42] The broader peaks of Clino sample could be associated with the presence of smaller crystals compared to LTA. Both the zeolites display no changes in the position of the main peaks, confirming that the zeolite structure has been preserved after the ion-exchange process.

Table 1
Elemental composition of the samples obtained by EDX analysis.

Sample	Weight (%)					Atomic (%)					Si/Al atomic ratio
	Fe	K	Na	Ca	Mg	Fe	K	Na	Ca	Mg	
Clino	4.65	2.60	0.25	1.45	0.80	1.75	1.40	0.22	0.76	0.71	4.62
NaClino	–	0.85	2.70	–	0.35	–	0.44	2.38	–	0.29	4.95
CaClino	–	0.70	–	3.50	–	–	0.36	–	1.76	–	4.97
NaLTA	–	–	12.45	0.30	2.10	–	–	10.99	0.29	1.75	1.28
CaLTA	–	–	1.35	13.00	1.55	–	–	1.26	6.92	1.36	1.29

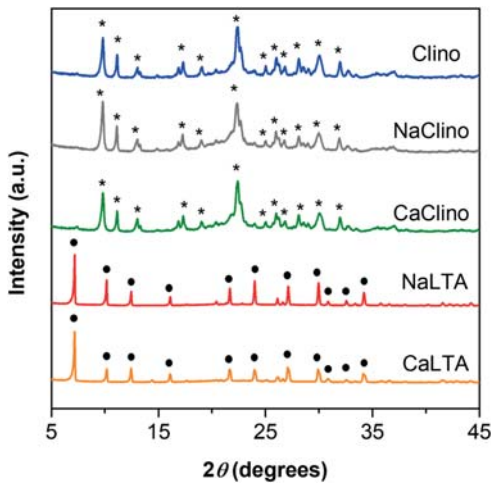


Fig. 1. X-ray diffraction patterns of the starting (Clino and NaLTA) and ion-exchanged (NaClino, CaClino and CaLTA) samples. Asterisks: main reflections of HEU framework. Circles: main reflections of LTA framework.

The elemental analysis suggests the ion exchange process occurred successfully. The semi-quantitative information about the composition of the samples can be further valorized by performing IR spectroscopy using carbon monoxide (CO) as molecular probe. CO is commonly used in IR spectroscopy in zeolites characterization, for studying the presence of isolated ions located in the structure [43,44]. Indeed, being a weak basic probe and not having steric limitations, CO possesses the subtle ability to discriminate between sites of slightly different acidity located inside the microcavities of the zeolitic structure. Thanks to its Lewis basic character, CO can interact with Lewis acids sites, like cations, forming carbonyl complexes.

This molecular probe has a small dipole moment but a rather high polarizability. Therefore, the stretching frequency of CO adsorbed on alkaline/alkaline earth cations (through the carbon atom) exhibits a hypsochromic shift with respect to the stretching frequency of the free gaseous molecule (2143 cm^{-1}), resulting from polarization and from the consequent increase in the force constant of the C–O bond. The C-bonded carbonyls show an upward shift proportional to the strength of the Lewis acidity of the cations involved in the interaction, allowing the exact determination of the actually accessible ions present in the structure [45,46].

Fig. 2A–F reports the IR spectra of CO adsorbed on the different zeolites, after activation in vacuum at 673 K, in the spectral region of C≡O vibrational modes between 2250 and 2050 cm^{-1} . The spectra of the materials, showing the full mid-IR spectral region before CO contact, are provided in Fig. S1. Concerning the natural Clino (Fig. 2A) the different types of cations present in the sample are responsible for the complex envelope of bands observable at the maximum CO coverage (see blue spectrum). Indeed, as previously pointed out, the composition

of natural zeolites is closely related to their origin, but the major cations present inside the Clinoptilolite framework are usually $\text{Fe}^{2+/3+}$, K^+ , Na^+ , Ca^{2+} and Mg^{2+} , as confirmed by EDX analysis [47]. For some of them, the interaction with CO causes the appearance of vibrational bands in the same spectral range, making the assignment of the different IR signals not straightforward. For pristine Clino, five main components can be distinguished in the $2250\text{--}2050\text{ cm}^{-1}$ spectral range at 2197, 2183, 2163, 2155 and 2148 cm^{-1} , with a different spectral behavior by varying the CO coverage. The signals at 2197 and 2183 cm^{-1} are the most stable (i.e. less reversible upon CO outgassing) and could be associated to the interaction of CO with Fe^{2+} and with Ca^{2+} cations respectively [48–51]. The assignment of these bands is not unambiguous due to the existence in the same spectral region of the signals generated by CO adsorption on Mg^{2+} ions [52]. However, the high amount of Fe detected by EDX together with the intensity and persistence of the 2197 cm^{-1} band, would be inclined to assign this component to Fe^{2+} ions. The less persistent signal at 2163 cm^{-1} can be ascribed, also considering the elemental analysis obtained by EDX, to the CO- K^+ adducts, nevertheless a possible overlap of signals can occur also in the present case, because the components due to the interaction of CO with Na^+ ions fall in the same spectral range ($2162\text{--}2172\text{ cm}^{-1}$) [53,54]. The band with apparent maximum at 2155 cm^{-1} , which readily disappears upon CO outgassing, is probably due to the interaction of CO with the OH groups of the zeolite, as testified by the IR spectra reported in the extended IR region of Fig. S1A where a clear perturbation of the OH stretching modes between 3800 and 3500 cm^{-1} is evident when CO interacts with the sample. The band at 2148 cm^{-1} , visible in the spectra at high CO coverage as a shoulder, reveals its actual profile and persistent nature just upon CO desorption: it should be ascribed to CO molecules bridging two K^+ cations. Finally, the weak and labile band located at around 2130 cm^{-1} is due to a small fraction of liquid-like CO phase, which forms inside the zeolite micropores [55].

The IR spectra of Clino sample exchanged with Na^+ ions (NaClino), collected at 77 K are reported in Fig. 2B. The envelope of bands generated by the CO interaction with the sample is definitely less complex compared to pristine Clino, with only two intense and well-defined components at 2163 and 2175 cm^{-1} exhibiting a similar behavior upon CO outgassing. These bands can be attributed to CO- K^+ and CO- Na^+ adducts respectively. At low CO coverage, a weak band at 2197 cm^{-1} , ascribed to Mg^{2+} ions, is also visible upon magnification. The species detected by CO are perfectly in agreement with the results of the EDX analysis, highlighting the difficulty to totally exchange the K^+ ions with Na^+ cations in the natural zeolite. [56].

The adsorption of CO onto CaClino (Fig. 2C) result in the formation, at the highest CO coverages, of an intense signal at 2183 cm^{-1} which readily undergoes an upward shift at $\sim 2200\text{ cm}^{-1}$ upon outgassing. This behavior is due to the gradual conversion of $\text{Ca}^{2+}(\text{CO})_2$ dicarbonyls into monocarbonyls species [56]. At high CO coverage, a labile shoulder at around 2170 cm^{-1} is probably ascribed to the presence of residual K^+ ions, as already proved by the EDX analysis. In the ion exchanged CaClino sample, the band of liquid-like CO at 2139 cm^{-1} is more evident than in the other Clino samples, due probably to a larger fraction of void volume inside the zeolite microchannels, left by the exchange of monovalent ions with divalent ones.

A comparison of IR spectra of Clino, NaClino and CaClino are

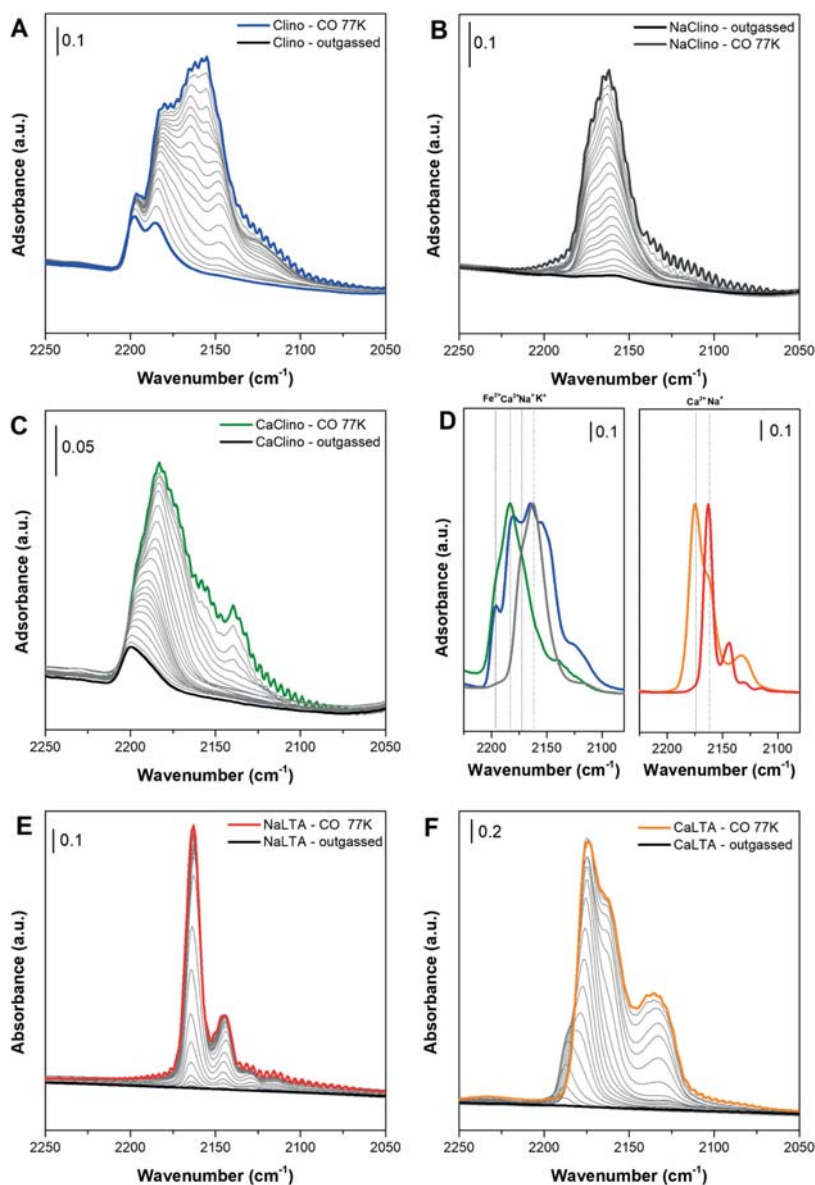


Fig. 2. IR spectra of CO adsorption at 77 K on activated samples, recorded at different CO coverages and reported in the CO vibrational modes region: A) Clino, B) NaClino C) CaClino, E) NaLTA and F) CaLTA. D) Comparison of normalized spectra of LTA (right) and Clino (left) samples at the same CO pressure (0.1 and 0.5 mbar respectively). Colored spectra: maximum CO coverage (60 mbar). Light grey spectra: decreasing pressure steps. Black spectra: outgassing in vacuum until 10^{-3} mbar. Dotted lines represent the position of the main cations expected in the different ion-exchanged samples.

reported in Fig. 2D (left side) at the same CO coverage, to better appreciate the spectroscopic differences among the various samples. The spectrum of pristine Clino (blue curve) exhibits a complex profile, testifying the formation of different adducts with CO, whereas the predominance of Na^+ and Ca^{2+} cations is clear in NaClino and CaClino spectra (gray and green curves respectively). In both cases, the CO- K^+ adducts are also evident, proving the difficulty in totally replacing the K^+ monovalent ions, whereas the signal ascribable to Fe^{2+} cations is totally absent, confirming the complete exchange of this cations with Na^+ or Ca^{2+} .

The interaction of CO with the LTA zeolite is reported in Figs. 2E and 2F. Spectra of CO adsorption at 77 K on the commercial LTA sample in sodic form (NaLTA) are reported in Fig. 2E. The CO stretching region

displays the presence of two well-resolved signals. The sharp band at 2163 cm^{-1} is assigned to Na^+ -CO adducts, whereas the component at 2145 cm^{-1} is due to the C-O stretching mode of CO molecules bridging two Na^+ ions [57]. Finally, the weak band at around 2130 cm^{-1} is due to a small fraction of liquid-like CO phase.

The interaction of CO with CaLTA (Fig. 2F) shows a band at $\sim 2174\text{ cm}^{-1}$ which exhibits an upward shift till $\sim 2186\text{ cm}^{-1}$ upon outgassing. According to Montanari et al. [58] the signal at 2174 cm^{-1} can be associated to $\text{Ca}^{2+}(\text{CO})_2$ dicarbonyls (less energetically stable) which decompose during outgassing to give Ca^{2+}CO monocarbonyls, more energetically stable and shifted at higher wavenumbers. The component located at 2163 cm^{-1} , which readily disappears by decreasing CO pressure, can be assigned to Na^+ carbonyls, in accordance

with the atomic percentages of the EDX elemental analysis (Table 1). The broad and labile band detectable at $\sim 2135\text{ cm}^{-1}$ can be confidently associated to the liquid-like CO. It is worth noting that the signal associated to liquid like CO is particularly intense for CaLTA, as already observed for the CaClino sample. This consideration suggests the presence of a lower limitation in the probe molecule diffusion and adsorption inside the CaLTA cages.

The comparison between NaLTA and CaLTA spectra (Fig. 2D right side), at the same CO coverage, points out the successful exchange procedure in the Ca containing sample.

Considering the results of CO adsorption, it is clear that the ion exchange process has modified the relative content of the cations present in both Clino and LTA frameworks (enhancing the presence of the desired ion), even if, as already highlighted by the EDX analysis, the ion exchange is not complete. This behavior is particularly evident for the natural zeolite, containing a significant fraction of K^+ ions.

More in general, the detailed study of CO adsorption fully confirmed the results obtained by EDX analysis and, at the same time, allowed the evaluation of the actual accessibility of the cations present inside the zeolitic framework to a small molecule in the gas phase.

The Specific Surface Area (SSA) of the samples, computed applying the BET equation, are reported in Table 2. It is well known that the narrow micropores of a type A zeolite cannot be assessed by N_2 adsorption at 77 K due to its slow kinetic of diffusion at cryogenic temperature [59]. Indeed, the restricted diffusion prevents nitrogen molecules from entering the microcavities of this zeolite, hindered by the presence of a huge number of cations. However, N_2 adsorption at 77 K was anyhow carried out on both LTA and Clino series to evaluate the effect of the presence of different cations inside the microporous cavities on the textural properties of the materials [60,61]. The adsorption/desorption isotherms of N_2 at 77 K are reported in Fig. S2 of the Supplementary material. Among the different substituted zeolites, the CaLTA sample exhibits a reasonable SSA computed with N_2 at low temperature. In LTA framework, the substitution of Na^+ ions located near the aperture of the pores with Ca^{2+} cations, having a lower ionic radius, facilitates the diffusion of N_2 inside the microporous structure [62,63]. The high content of liquid like CO phase detected during IR adsorption experiments in the CaLTA compared to NaLTA sample (Fig. 2F) further testifies the presence of a larger fraction of void volume accessible to the probe molecule. N_2 adsorption at 77 K in the HEU framework exhibits the same diffusional problems observed for the synthetic zeolite (see N_2 isotherms reported in Fig. S2 and SSA values listed in Table 2), due to the presence of a huge number of cations needed for compensating the negative charge induced by the high Al content of this zeolite. In contrast to the synthetic zeolite, the Ca-exchanged Clino sample (CaClino) did not show an increment in SSA, probably due to the different location of the ions inside the Clino framework and to the presence of different residual cations hindering the pores filling. The results obtained with N_2 for the Clino samples are compatible with those reported in the literature, however small variations could be due to the different origin of this natural zeolite [64].

Table 2

BET specific surface area of Clino, NaClino, CaClino, NaLTA and CaLTA derived from N_2 and CO_2 adsorption isotherms at 77 and 273 K respectively.

Sample	N_2 adsorption, 77 K S_{BET} ($\text{m}^2\text{ g}^{-1}$) ^a	CO_2 adsorption, 273 K S_{BET} ($\text{m}^2\text{ g}^{-1}$) ^b
Clino	22 ± 1	240 ± 1
NaClino	43 ± 1	233 ± 1
CaClino	48 ± 1	201 ± 2
NaLTA	26 ± 1	378 ± 2
CaLTA	438 ± 9	447 ± 1

^a Computed applying the BET equation to the N_2 adsorption isotherm at 77 K in the 0.05–0.3 p/p₀ range.

^b Computed applying the BET equation to the CO_2 adsorption isotherm at 273 K in the 0.003–0.03 p/p₀ range.

A valuable adsorptive for a correct assessment of the porosity of ultramicroporous materials is CO_2 , which is usually measured at 273 K (see CO_2 isotherms reported in Fig. S3 and SSA values listed in Table 2) [65]. Even if the CO_2 , with its large quadrupole moment could be responsible for specific interactions with the cations of the zeolites, this measurement can still be useful to evaluate the specific surface area of materials which cannot be assessed by nitrogen or argon adsorption at cryogenic temperature, as reported elsewhere [66–69]. In this case, the synergistic effect of its slightly lower kinetic diameter (3.3 Å) [70] and the higher temperature of adsorption results in an easier entrance and diffusion into the ultramicropores of the zeolite [71]. Indeed, a steep increment in SSA value can be observed in all the samples previously unable to adsorb N_2 molecules at 77 K. The difference in SSA values between CO_2 and N_2 displayed by all the samples (except for CaLTA) suggests a great selectivity of those materials toward CO_2 . The specific surface area of Clino samples computed by CO_2 is around 200–240 m^2/g ; variations among samples are due to the different cations population. The SSA values computed for LTA samples in spherical beads are definitely higher compared to Clino series. The specific surface area of CaLTA obtained by CO_2 adsorption at 273 K (447 m^2/g) is totally comparable to the value computed by N_2 adsorption at 77 K (438 m^2/g). Moreover, the SSA of this sample is higher compared to the pristine NaLTA beads (378 m^2/g) due to the lower concentration of divalent Ca^{2+} cations required in the zeolite framework to compensate the negative charge and, at the same time, to their smaller ionic radius.

3.2. Evaluation of CO_2 adsorption capacity: volumetric measurements

The pure CO_2 adsorption capacity was evaluated for all samples by collecting isotherms at different temperatures (298, 333, 363, 423 K), until 1100 mbar, as reported in Fig. 3A, D, 3G and 3L. Their adsorption capacities at 100 and 1000 mbar were reported in the respective histograms (middle and right frames of Fig. 3) and in Table S1 (Section S4 of SI) to better highlight the adsorption trend at different temperatures. The pressure of 1000 mbar was chosen to evaluate the adsorption capacity at atmospheric pressure, while 100 mbar is the CO_2 pressure employed in breakthrough curves since the CO_2 adsorption tests were performed with 10 vol% CO_2 (total pressure during the tests = 1000 mbar, partial CO_2 pressure during the tests = 100 mbar). As pointed out by the histograms, despite the absolute values, the CO_2 uptake capacity of the samples at 298 and 333 K has the same trend at the two selected pressures, with the LTA zeolite prevailing over the Clino. In contrast, a different adsorption trend between the two pressures can be detected at 363 K, becoming even more evident at 423 K.

For all the samples, the isotherms in Figs. 3A, 3D, 3G and 3L exhibit a general predictable decrease of the CO_2 uptake by increasing the temperature. At 298, 333 and 363 K, CaLTA seems to have the highest CO_2 adsorption capacity at high pressures (orange curves) followed by NaLTA (red curves). At 363 K, the capture capacity of both NaLTA and CaLTA is drastically reduced in the low-pressure range (see Figs. 3G and 3H), whereas it prevails at higher pressures (see Figs. 3G and 3I). By further increasing the temperature, the distance between the two isotherms drops, until their partial overlapping at 423 K, where NaLTA slightly overcomes the CaLTA capture capacity at 1000 mbar. The CO_2 capture capacity decrease of LTA samples is especially evident at low pressures (100 mbar), where the CO_2 adsorption of CaLTA and NaLTA reduces of around 90 % and 87 % respectively, from 298 to 423 K. The adsorption behavior agrees with the literature data reporting the CO_2 adsorption capacity at low temperature of both 4 A and 5 A (mix of sodium and calcium) zeolites in comparison with $13 \times$ zeolite [72–74].

The pristine Clino sample always exhibits a higher CO_2 adsorption capacity (blue curves and histograms) compared to exchanged NaClino (grey curves and histograms) and CaClino (green curves and histograms) samples. In contrast to LTA zeolite, the ion exchange seems not to enhance the CO_2 uptake. It appears that the heterogenous mix of cations present in the pristine natural zeolite is responsible for a stronger

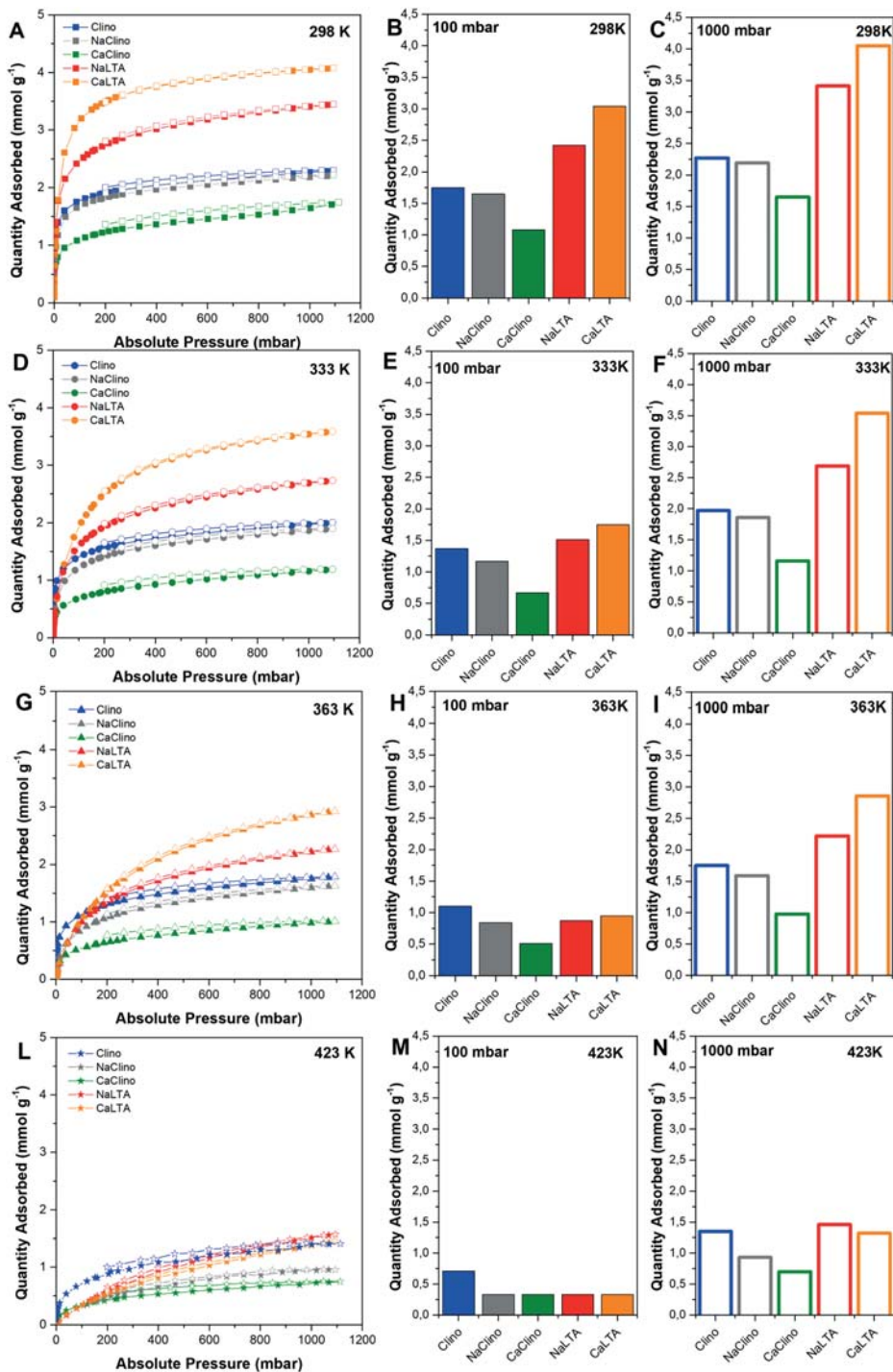


Fig. 3. CO₂ adsorption/desorption isotherms at: A) 298, D) 333, G) 363 and L) 423 K. Quantity adsorbed in mmol_{CO₂} g_{adsorbent}⁻¹ at 100 mbar absolute pressure at: B) 298, E) 333, H) 363 and M) 423 K. Quantity adsorbed in mmol_{CO₂} g_{adsorbent}⁻¹ at 1000 mbar absolute pressure at: C) 298, F) 333, I) 363 and N) 423 K.

electrostatic interaction which leads to a higher CO₂ adsorption capacity compared to the exchanged samples [75]. This stronger interaction is preserved especially at higher temperatures (333 and 423 K), where the adsorption capacity of pure Clino in the low-pressure range overcomes the one of LTA. Moreover, at 423 K pristine Clino exhibits the best adsorption performances for nearly all the pressure range (until 800 mbar). The above reported results prove that pure Clino maintains a better CO₂ adsorption capacity at higher temperature compared to LTA samples, losing only the 61 % of its adsorption capacity at 100 mbar, by increasing the temperature from 298 to 423 K.

In general, at low temperature all the samples show a steep CO₂ uptake in the low-pressure region, whereas at higher temperature the adsorption capacity at the same pressure drastically decreases, except for pure Clino, which maintains discrete uptake capacity below 300 mbar. Moreover, both the exchanged Clino samples (NaClino and CaClino) show a reduced CO₂ adsorption at 423 K in the whole pressure range compared to raw Clino, proving that the CO₂ capture capacity at this temperature does not depend on the presence of Ca²⁺ or Na⁺ ions, but it is probably related to the strong interaction with Fe²⁺ cations present only in the starting natural zeolite.

The CO₂ capture capacity of the materials was also investigated by performing a secondary adsorption run at 298 K, as explained in Section 5 of the SM, to study the reversibility of the adsorption process and evaluate the possible real use in cyclic adsorption/desorption experiments. The reversibility data clearly highlight that, although the ion-exchanged Clino samples do not exhibit enhanced CO₂ adsorption performances, they possess a higher CO₂ adsorption reversibility compared to raw Clino (see Fig. S4A–C and Table S2). The cyclic adsorption capacity is strictly related to the possible regeneration conditions of the material and, therefore, it must be considered for the use in real capture applications. For what concerns the LTA samples, the ion exchange procedure with Ca²⁺ affects the overall adsorption capacity at 298 K and, in parallel, provides a full reversibility of the material (see Fig. S4D and S4E).

The isosteric heat of adsorption was evaluated for the samples with the best CO₂ adsorption performances at 1000 mbar (i.e. NaLTA, CaLTA and Clino), by applying Eq. 1 on the isotherms collected at 298, 333 and 363 K, in the 0.2–2 mmol g^{−1} range of quantity adsorbed (Fig. 4). The isosteric heat value at vanishing coverage was extrapolated by considering the y-axis intercept and is reported in Table S3 (Section S6 of SI).

This isosteric heat of adsorption (Q_{st}), also reported as the opposite of the isosteric enthalpy of adsorption ($-\Delta H_{ads}$), is the heat released when

an adsorptive molecule interacts with a surface site [76]. The Q_{st} curves of NaLTA and CaLTA (see red and orange curves in Fig. 4) show a quite flat and constant trend, between 54 and 50 kJ/mol and 44–40 kJ/mol respectively. The lower isosteric heat of CaLTA sample testifies the weaker interaction between CO₂ and the Ca²⁺ cations compared to Na⁺, fully compatible with the total reversibility displayed by this material upon a secondary CO₂ adsorption (Fig. S4E).

The isosteric heat of CO₂ adsorption of Clino is clearly distributed in a broader range, from 60 to 35 kJ/mol, confirming the great heterogeneity of cations present in the microchannels of the HEU framework, as already pointed out by EDX analysis and IR spectroscopy.

3.3. Evaluation of CO₂ adsorption capacity: breakthrough measurements

All the previously reported data were collected with pure CO₂ in static environment. However, the possible applications of those materials as adsorbents rarely require capture in static conditions. For this reason, breakthrough experiments under CO₂ flow were also performed. The results are shown in Fig. 5, where the CO₂ adsorption capacities of the materials at different temperatures (298, 333, 363 and 423 K, i.e., the same temperatures employed for the static experiments with pure CO₂) are reported as a function of time. The breakthrough curves are compared with the “blank” test, namely the reactor without the adsorbent material. As expected, by increasing the temperatures, the adsorption capacities decrease causing a shift of the breakthrough curves to shorter times.

Fig. 5A reports the breakthrough curves, along with the corresponding adsorption capacity (Fig. 5B) obtained at 298 K. The samples with the best adsorption capacities are Na- and CaLTA, about 3.1 and 3.3 mmol g^{−1} respectively (see Table S4 for all the adsorption capacities). Noteworthy, pristine Clino exhibits better performances compared to CaClino. On the other hand, at 298 K, the sample exchanged with Na⁺ (NaClino) shows a higher CO₂ adsorption capacity. These results are in fair agreement with our previous studies [77].

By comparing the breakthrough measurements with the volumetric isotherms at 100 mbar of pure CO₂, some differences in the computed amount of CO₂ adsorbed are detectable, even if the trend among samples at the different temperatures is substantially the same (see Table S1 in comparison with Table S4). The reason of such variations could be due to the different experimental set-up (one working under a N₂–CO₂ flow, the other one working under equilibrium conditions with pure CO₂).

In Fig. 5C and 5D, the CO₂ breakthrough curves and the computed adsorption capacities at 333 K are reported respectively. It is worth noting that the CO₂ adsorption capacity trend is very similar to the situation observed at 298 K. At 363 K, the trend is again similar (Figs. 5E and 5F), except for the NaClino sample which exhibits lower adsorption capacity compared to pristine Clino.

Furthermore, the CaLTA sample has an adsorption capacity decrease, from 293 to 363 K which is higher comparing to NaLTA. This result agrees with the CO₂ volumetric adsorption data.

Finally, the adsorption capacity of the samples was tested at 423 K, and the results are reported in Fig. 5G and 5F. At this temperature, the most efficient adsorbent is Clino, with an adsorption capacity of 0.7 mmol g^{−1}, which decreases of 66 % compared to 298 K. These results are totally in line with the volumetric data. Again, the Clino sample is less affected by the variation of the temperature during the CO₂ adsorption tests, thanks to the presence in its framework of a consistent number of Fe²⁺ cations, which play a key role in the capture process at high temperature.

The ability to maintain good CO₂ capture performances in the middle-high temperature range is not straightforward, especially in zeolites where the high temperature drastically affects the adsorption capacity. Adsorbents for Carbon Capture and Storage are usually classified according to their best working temperature (low, medium and high capture temperature). Activated carbon, zeolites and MOFs are the most studied materials for low temperature applications ($T < 200$ °C) while

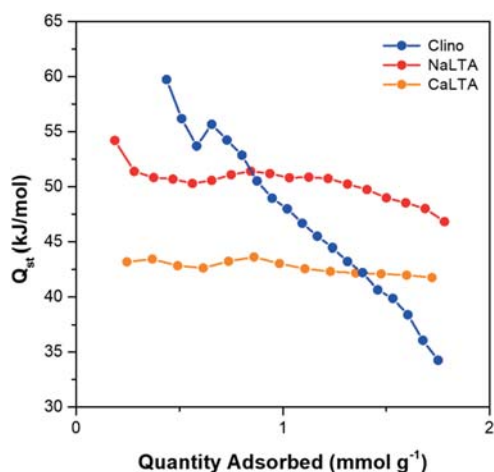


Fig. 4. Isosteric heat of CO₂ adsorption (Q_{st}) as a function of the quantity adsorbed, calculated from the isotherms at 298, 333 and 363 K.

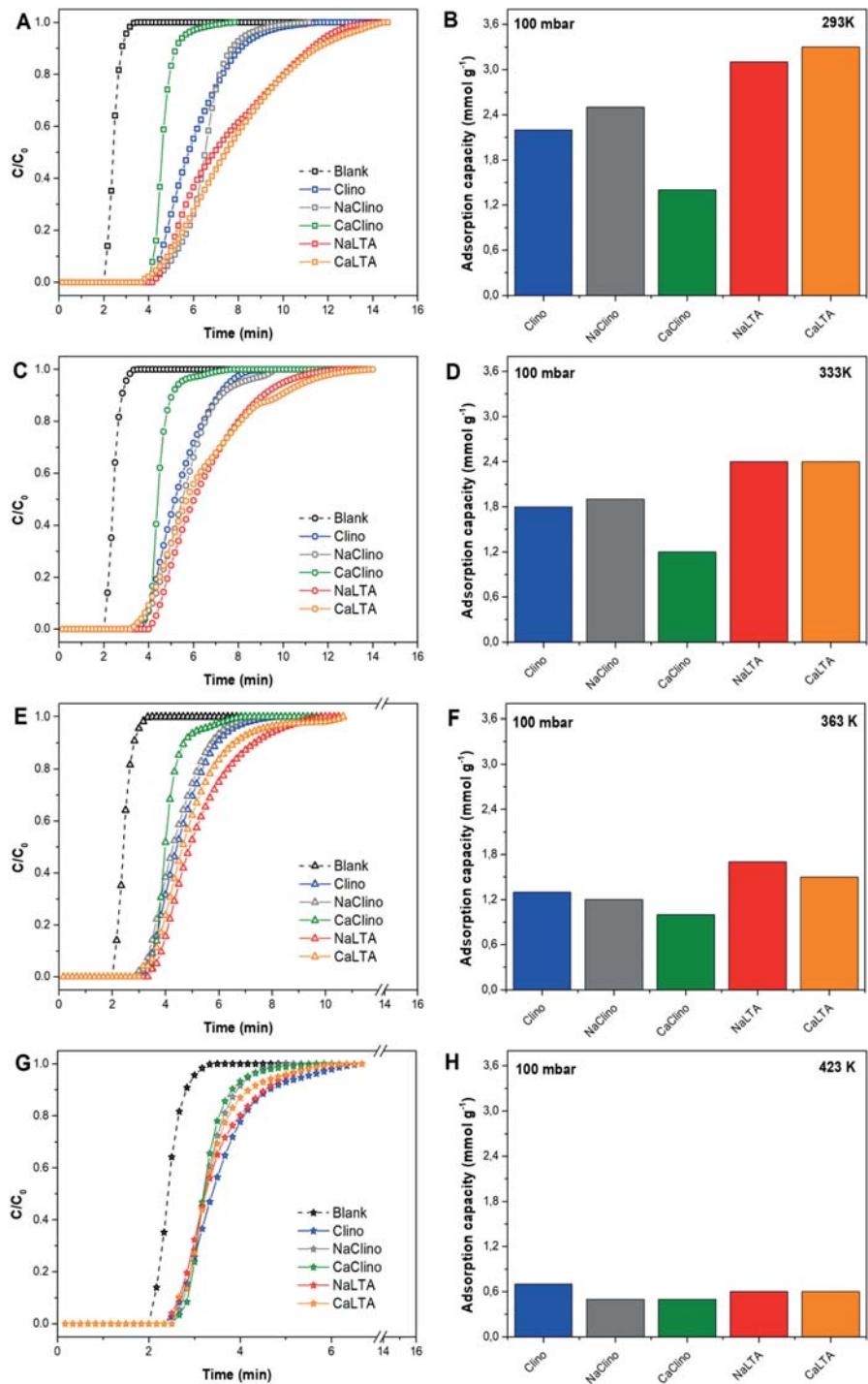


Fig. 5. CO₂ breakthrough adsorption curves over the time at: A) 298, C) 333, E) 363 and G) 423 K. Computed adsorption capacity (mmol_{CO2} g_{adsorbent}⁻¹) at: B) 298, D) 333, F) 363 and H) 423 K.

hydrotalcites and oxides are usually applied for intermediate and high temperature applications respectively ($200 < T < 400\text{ }^{\circ}\text{C}$ and $T > 400\text{ }^{\circ}\text{C}$) [78]. A comparison of those materials with LTA and Clino is reported in Table 3.

Activated carbons are low-cost materials easy to functionalize, displaying a good adsorption capacity at low temperature [85]. On the other hand, the shaping of this adsorbents is not simple and, moreover, they usually have low CO₂ selectivity and show a drop in the CO₂ capture capacity by increasing the adsorption temperature [79,80]. MOFs generally exhibit a higher CO₂ adsorption capacity compared to carbons and zeolites, together with a good selectivity and an easy tunability of the structure [86]. However, few MOFs maintain the same CO₂ capture performances when the temperature increases and most of them are sensitive to water [81]. Additionally, their scale up and shaping can be problematic. For this reason, zeolites seem to be more versatile than other microporous materials, and a lot of literature reports their application as possible carbon capture adsorbents [13]. In particular, 13 × is usually considered a reference zeolite for CO₂ capture. Certainly, its adsorption capacity is much higher than the other zeolitic framework, but the drop in performances by increasing the adsorption temperature is steeper compared to LTA and natural Clino [82].

Similarly to what described for low temperature materials, also hydrotalcites, which are usually employed for capture at intermediate temperature, show uncompetitive adsorption capacity at lower temperature [84]. Finally, for high temperature applications, different types of oxide are usually employed. In this case, a direct comparison with the previously mentioned materials is difficult, because the CO₂ capture can be considered as a high temperature absorption process [87].

Beside the excellent CO₂ uptake performances at medium-high temperature and the fair CO₂ capture capacity at low T, natural Clino has also a low commercial value compared to both LTA and 13X zeolites. Indeed, making an evaluation of the middle selling price of the three zeolites, an average cost for the capture of 1 kg of pure CO₂ can be computed, as reported in Table 4. This remark is particularly relevant if the adsorbents have to be used for large scale CO₂ capture.

Table 3
Comparison of CO₂ uptake capacities in the 298–673 K temperature range and 1 bar for different adsorbents.

Sample	Capture temperature (K)	CO ₂ uptake at 1 bar (mmolCO ₂ /g _{adsorbent})	Ref.
Activated Carbons	298	0.32–1.9	[79]
	348	0.2–1.7	[79]
	393	0.09–0.5	[80]
	423	–	–
CPO-27-Ni	303	0.52	[81]
	313	0.41	
	353	0.20	
	298	4.7	[79]
13X	348	3.2	[79]
	393	1.57	[82]
	423	–	–
	323	0.33	[83]
MCM-41 ^a	348	0.20	
	373	0.15	
	298	2.3	This work
	348	–	
Clinoptilolite	363	1.8	
	423	1.4	
	298	4.1	This work
	348	–	
CaLTA	363	2.9	
	423	1.3	
	323	1–1.4	
	473	0.6–0.9	[84]
Hydrotalcite MG305070	673	0.7–0.95	

^a Results obtained through TGA measurements.

Table 4
Comparison of average costs to capture 1 kg of CO₂ for different zeolites.

	Sample		
	Clino	LTA	13 X
Average price (\$ for Ton) ^a	300 \$	1300 \$	2500 \$
Cost to capture 1 kg of CO ₂ ^b	3.02 \$	8.64 \$	12.08 \$

^a Average prices based on the prices per ton of material provided by large Asian suppliers.

^b Cost calculated assuming pure CO₂ capture at 1000 mbar and 298 K.

4. Conclusions

In this work, the CO₂ capture performances of a synthetic (LTA) and a natural (Clinoptilolite) zeolite are deeply investigated by means of advanced characterization approach. The two zeolites were studied in raw form and after ion exchange with Na⁺ and Ca²⁺, with the aim to possibly enhance the CO₂ adsorption capacity. The success of the exchange procedure was proved by means of EDX analysis, while XRD patterns highlighted the preservation of the crystalline structure. IR spectroscopy was used to investigate the accessibility of the different ions present inside the microporous structure and the strength of their interaction with the adsorbates. The specific surface area of the materials, measured using both N₂ and CO₂, showed that CaLTA was the only accessible material for N₂ molecules, while all the other displayed a great selectivity towards CO₂. Their potential application as solid CO₂ adsorbents was investigated by collecting both pure CO₂ adsorption/desorption isotherms and breakthrough curves under a N₂/CO₂ flow in a wide range of temperature (298–423 K).

Both the isotherm and the breakthrough curves of the materials exhibit a similar trend in CO₂ capture capacity with small discrepancies due to the different experimental conditions.

The cations exchanged process have a different impact on the CO₂ adsorption performances of the two zeolites. Indeed, the Ca²⁺ exchanged LTA gains both in adsorption capacity and reversibility compared to the standard LTA in sodic form. In contrast, the Na- and the Ca- form of Clinoptilolite have a higher CO₂ reversibility, but do not display a significant increment of the CO₂ uptake. By performing IR experiments with specific probe molecules, it was demonstrated that the presence of a consistent number of Fe²⁺ ions in the framework of natural Clino was responsible for the capacity of this material to strongly interact with CO₂.

Concerning the capture capacity, NaLTA and CaLTA exhibit a higher CO₂ uptake at lower temperature (i.e. 298 and 333 K), whereas the CO₂ adsorption performances of natural Clino, thanks to the presence of Fe²⁺ cations, are interesting also at medium-high temperature, being the most performant material at 423 K. In particular, the CO₂ capture capacity of pure Clino decreases of only 65 % passing from 298 to 423 K, compared to the reduction of 90 % observed for the CaLTA sample in the same range of temperature.

An industrially feasible adsorbent suitable for carbon capture should meet different requirements, not only in terms of mere carbon dioxide absolute loading. A good compromise could be a material easy to shape, exhibiting cyclic adsorption capacity, capable to maintain good adsorption performances in a wide range of temperature with possibly low production costs and, above all, with low sensitivity/selectivity to water. The CO₂/H₂O competitiveness and/or the sensitivity to moisture are key issues for different potential CO₂ adsorbents, as zeolites or MOFs, which often require a H₂O pre-capture step. Unfortunately, a CO₂ adsorbent which meet all those requirements does not still exist, despite the wide availability of literature data on carbon capture materials.

Assuming to previously dehydrate the flue gas (possibly using the same materials, since LTA is well-known as an industrial desiccant), the zeolites reported in this work possess some important features for potential CO₂ capture applications: they exhibit good CO₂ adsorption performances and reversibility in a wide range of temperature and are

already available in shaped form. Therefore, natural Clinoptilolite, commercialized in rock fragments (ϕ 0.15 mm), could be a possible interesting candidate for CO₂ capture until 423 K, with an average cost of 3\$ per kg of captured CO₂.

CRedit authorship contribution statement

Margherita Cavallo: Conceptualization, Methodology, Validation, Investigation, Data curation, Writing – original draft, Visualization. **Melodj Dosa:** Methodology, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Natale Gabriele Porcaro:** Conceptualization, Methodology, Validation, Investigation. **Francesca Bonino:** Conceptualization, Resources, Writing – review & editing, Visualization, Supervision. **Marco Piumetti:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Valentina Crocellà:** Conceptualization, Resources, Validation, Investigation, Data curation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgment

The study reported in this work is part of the research project SAT-URNO “Scarti organici e Anidride carbonica Trasformati in carbURanti, fertilizzanti e prodotti chimici; applicazione concreta dell’econOMia circolare” funded by “Piattaforma Tecnologica Bioeconomia-POR FESR 2014–2020 Region Piedmont” and carried out in collaboration with Università di Torino, Turin, Italy.

Support of Zeolado in providing the Clino used through the investigation is gratefully acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2022.102335.

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Cite this: *J. Mater. Chem. A*, 2023, **11**, 5568Cooperative CO₂ adsorption mechanism in a perfluorinated Ce^{IV}-based metal organic framework†Margherita Cavallo,^a Cesare Atzori,^{ib} Matteo Signorile,^{ib}^a Ferdinando Costantino,^{ib}^c Diletta Morelli Venturi,^c Athanasios Koutsianos,^{†d} Kirill A. Lomachenko,^{ib}^b Lucia Calucci,^{ib}^{ef} Francesca Martini,^{ib}^{fg} Andrea Giovanelli,^{ib}^g Marco Geppi,^{ib}^{fg} Valentina Crocellà^{ib}^{*a} and Marco Taddei^{ib}^{*fgh}

Adsorbents able to uptake large amounts of gases within a narrow range of pressure, *i.e.*, phase-change adsorbents, are emerging as highly interesting systems to achieve excellent gas separation performances with little energy input for regeneration. A recently discovered phase-change metal–organic framework (MOF) adsorbent is F4_MIL-140A(Ce), based on Ce^{IV} and tetrafluoroterephthalate. This MOF displays a non-hysteretic step-shaped CO₂ adsorption isotherm, reaching saturation in conditions of temperature and pressure compatible with real life application in post-combustion carbon capture, biogas upgrading and acetylene purification. Such peculiar behaviour is responsible for the exceptional CO₂/N₂ selectivity and reverse CO₂/C₂H₂ selectivity of F4_MIL-140A(Ce). Here, we combine data obtained from a wide pool of characterisation techniques – namely gas sorption analysis, *in situ* infrared spectroscopy, *in situ* powder X-ray diffraction, *in situ* X-ray absorption spectroscopy, multinuclear solid state nuclear magnetic resonance spectroscopy and adsorption microcalorimetry – with periodic density functional theory simulations to provide evidence for the existence of a unique cooperative CO₂ adsorption mechanism in F4_MIL-140A(Ce). Such mechanism involves the concerted rotation of perfluorinated aromatic rings when a threshold partial pressure of CO₂ is reached, opening the gate towards an adsorption site where CO₂ interacts with both open metal sites and the fluorine atoms of the linker.

Received 14th December 2022
Accepted 9th February 2023

DOI: 10.1039/d2ta09746j

rsc.li/materials-a

Introduction

Solid adsorbents for gas separations are the object of intensive research, due to their potential advantages, in terms of energy intensity and recyclability, over state-of-the-art technologies based on either cryogenic distillation or absorption/scrubbing.^{1–5} Metal–organic frameworks (MOFs) are among the candidates investigated to this end, alongside zeolites, activated carbons and amine-functionalised porous silicas.^{3,4,6,7} If

compared to the other classes of adsorbents, MOFs offer superior structural control at the atomic level and virtually unlimited possibilities for functionalisation and tuning of the physico-chemical properties.¹ One of the most intriguing aspects of MOF adsorbents is that they can display unique adsorption phenomena, associated with either highly specific interaction of the adsorbate with the surface, structural flexibility, or combinations thereof.^{8–16}

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So-called “phase-change” MOFs are of particular interest for gas separations because they display steep gas uptake when a threshold partial pressure of a given adsorbate is reached, with potential benefits in terms of achievable working capacity, selectivity and energy efficiency.^{17,18} This behaviour is determined by an adsorption-induced structural rearrangement, which can be either (i) a breathing/swelling effect, due to the flexible nature of the framework, which leads to significant variations in the volume of the unit cell;^{9,19–22} (ii) a cooperative adsorption mechanism, such as the CO₂ insertion occurring in so-called amine-appended MOFs, which involves changes in the coordination environment of the metal and highly specific hydrogen bonding interactions;^{18,23,24} or (iii) the concerted rotation of organic rings within the framework, which results in a ring configuration that maximises the host-guest interaction.^{25–27}

Some of us recently reported the discovery of F4_MIL-140A(Ce), an ultramicroporous MOF based on Ce^{IV} and tetra-fluoroterephthalate (Fig. 1).²⁸ F4_MIL-140A(Ce) is built from the connection of one-dimensional inorganic building units, made up of octacoordinated Ce^{IV} ions, carboxylate groups belonging to the linker and μ_3 -O species, *via* the perfluorinated aromatic rings of the linker. This structure features narrow triangular channel-like pores lined with the fluorine atoms belonging to the linkers (Fig. 1a). Different from its Zr^{IV}-based MIL-140 analogues,²⁹ F4_MIL-140A(Ce) contains one water molecule per Ce atom, located in the proximity of the metal atom and at distances compatible with a number of non-covalent interactions with the organic linker (Fig. 1b).

F4_MIL-140A(Ce) displays a non-hysteretic step-shaped CO₂ adsorption isotherm, with steep uptake increase at pressure <0.2 bar at 298 K, leading to reach saturation within a narrow range of pressure.²⁸ Such behaviour is not observed when the MOF is exposed to other gases, *e.g.*, N₂ or C₂H₂, endowing this material with high CO₂/N₂ selectivity and with reverse CO₂/C₂H₂ selectivity, a highly sought-after feature.³⁰ Furthermore, this MOF can be synthesised from commercially available reagents in mild conditions and in aqueous medium, an attractive method for prospective bulk production.³¹ Considering such a unique combination of features, we believe that understanding the adsorption mechanism in F4_MIL-140A(Ce) becomes an issue of primary concern. Besides the fundamental interest in describing a potentially novel phenomenon, the knowledge deriving from such an endeavour might help to engineer new materials with the same working principle and improved separation performance.

A mechanism was in fact recently proposed based on powder X-ray diffraction (PXRD) data, infrared (IR) spectroscopy data, and density functional theory (DFT) simulations, claiming that CO₂ adsorbs in a site located among three fluorinated rings, where the Lewis acidic C atom interacts with four electron-rich F atoms,³⁰ akin to what observed in SIFSIX-3 materials^{32,33} and in fluorinated bis(pyrazolyl)-based MOFs.³⁴ In the present work, we propose an alternative mechanism, deduced from the combination of data obtained from a wide pool of characterisation techniques, including gas sorption analysis, *in situ* IR spectroscopy, *in situ* PXRD, *in situ* X-ray absorption spectroscopy (XAS) at the Ce K-edge, ¹H, ¹³C and ¹⁹F solid state nuclear magnetic resonance (SSNMR) spectroscopy and adsorption microcalorimetry, with periodic DFT simulations.

Results and discussion

Adsorption properties

Gas adsorption volumetry. CO₂ adsorption/desorption volumetric isotherms were collected at 298, 313, 328 and 343 K in the 0–5 bar pressure range to study the pure CO₂ adsorption capacity of the material (Fig. 2a). All the isotherms exhibit a peculiar step, which moves to progressively higher pressure by increasing the temperature and the pressure range over which saturation occurs becomes broader. The maximum amount of adsorbed CO₂ on F4_MIL-140A(Ce) is around 2.6 mmol g^{−1} at 298 K and 5 bar and shows the usual decrease by increasing the

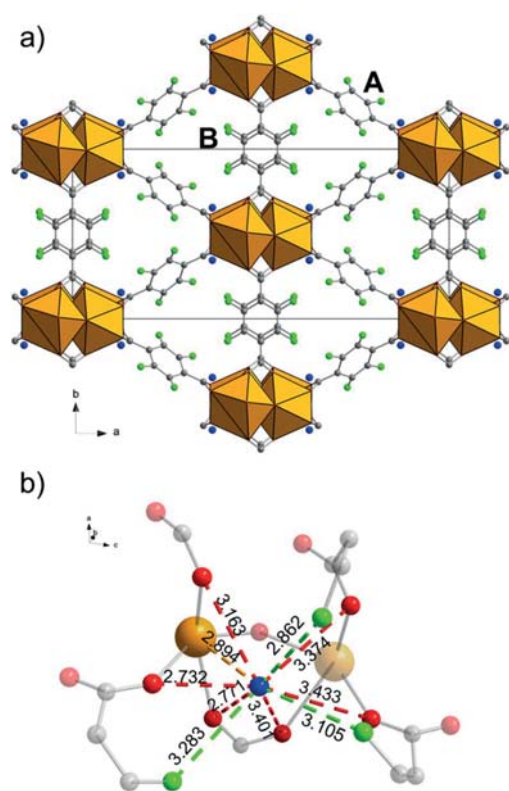


Fig. 1 Crystal structure of as-synthesised F4_MIL-140A(Ce) viewed along the crystallographic *c* axis (a) and local environment around the water molecule (b). In (a) the two crystallographically independent linkers sitting on an inversion centre and on a two-fold axis are identified with A and B, respectively. In (b) a threshold distance of 3.5 Å between the O atom of water and surrounding atoms was chosen to identify possible interactions, represented as dashed lines having the same colour of the interacting atom. Non-interacting atoms in (b) are shaded. Colour code: Ce, orange; F, green; C, grey; O, red; H₂O, blue. H atoms are not shown because the structure was determined from PXRD data.



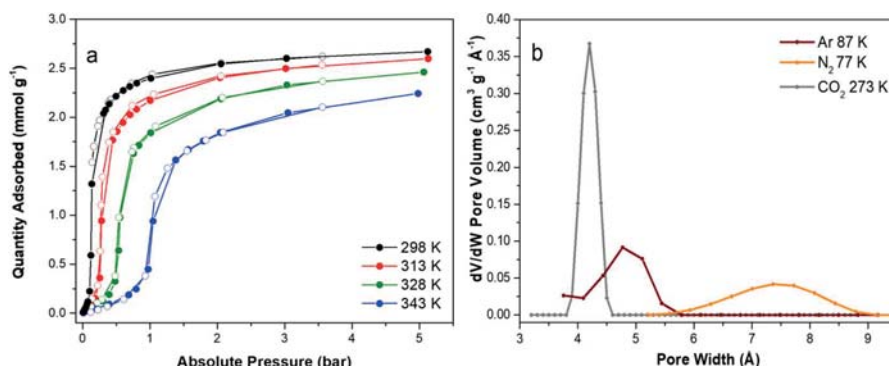


Fig. 2 CO₂ adsorption (filled circles) and desorption (empty circles) isotherms collected on F4_MIL-140A(Ce) at 298 K (black), 313 K (red), 328 K (green) and 343 K (blue) up to 5 bar (a) and pore size distributions of F4_MIL-140A(Ce) computed by NL-DFT of: Ar at 87 K (dark red), N₂ at 77 K (orange) and CO₂ at 273 K (grey) (b).

temperature (2.2 mmol g⁻¹ at 343 K and 5 bar). The isotherms were fitted with a dual site Langmuir-Freundlich model (Fig. S1–S4†) and the pressure at which they display the maximum slope ($P_{\max}$) was determined from the first derivative curve. Plotting $\log P_{\max}$ versus temperature, a linear trend emerges between 298 and 343 K, in principle allowing to predict which pressure the step will take place at within the investigated temperature range (Fig. S5†). The isosteric heat of adsorption (Q_{st}), extracted from the fitted isotherms using the linear version of the Clausius–Clapeyron equation (Fig. S6†), ranges between 35 and 45 kJ mol⁻¹.

The sharp uptake of gas (*i.e.* the isotherm step) moves to higher pressures by increasing the temperature. This peculiar adsorption feature allows easily adapting the phase transition mechanism of this MOF to the partial pressure of common post-combustion streams. Additionally, this characteristic isotherm is known to be particularly suitable for adsorption processes thanks to the large working capacity that can be achieved upon small swings in temperature and/or pressure. Such step-shaped isotherms have previously been observed in other MOFs exhibiting higher CO₂ adsorption capacities at saturation, as in the amine-appended Mg₂(dobpdc)¹⁸ (3.4 mmol g⁻¹ at 298 K and 5 bar) and in ELM-11 (ref. 9) (3.6 mmol g⁻¹ at 273 K and 0.3 bar). However, in the former case, the material displays a much higher isosteric heat of CO₂ adsorption (around -70 kJ mol⁻¹), whereas in the latter the phase transition occurs in a higher pressure range (300 mbar at 273 K). This leads, on the one hand, to stronger interaction energies and, consequently, to higher regeneration energies, on the other hand, to a low adsorption of CO₂ at low pressures. To further investigate the peculiar adsorption mechanism of F4_MIL-140A(Ce), the textural properties were accurately studied by collecting low pressure adsorption/desorption volumetric isotherms using three different adsorptives: N₂ at 77 K, Ar at 87 K and CO₂ at 273 K (Fig. S7† in the ESI†). The isotherms were measured consecutively using the same MOF powder. Therefore, the differences observed with the selected probe molecules can be attributed to the nature of the probe molecule at the analysis temperature. Ar

and N₂ show the typical type I(a) isotherm characteristic of microporous materials, while CO₂ exhibits the less common step-shaped isotherm specific of the so-called “phase change” adsorbents (Fig. S7a† in the 0 < p/p^0 < 0.03 range and Fig. S7b† in the whole p/p^0 range), in agreement with the previous results reported by D’Amato *et al.*²⁸ The semi-logarithmic isotherms reported in the inset of Fig. S7a† show that the pore filling with Ar occurs at higher relative pressure regions compared to N₂. The difference in relative pressures becomes more significant if the MOF possesses open metal sites, highlighting the advantage of using monoatomic inert Ar for the characterization of ultramicroporous MOFs. The BET area values (Table S2 and Fig. S8–S10†) display an incremental trend, suggesting a different interaction of the molecules with the material (Table S2†). The BET area obtained by Ar isotherm (213.8 m² g⁻¹) is lower compared to N₂ (244.8 m² g⁻¹). The spherical Ar molecules display a more ideal packing on the surface compared to diatomic N₂ molecules, whose orientation on the surface can be affected by the possible presence of open metal sites able to interact with N₂ itself. As a consequence, an uncertainty in the evaluation of the cross-sectional area of nitrogen gas is very likely, resulting in an overestimation of the computed BET area with this probe.^{35,36} The highest BET area value is the one derived from the CO₂ isotherm at 273 K (262 m² g⁻¹), suggesting that a structural rearrangement might occur when F4_MIL-140A(Ce) interacts with CO₂, as highlighted by the peculiar step-shaped isotherm collected by using this molecule as adsorptive (Fig. S7†).

The pore size distribution (PSD) was also evaluated by applying the non-local density functional theory (NL-DFT) to the adsorption isotherms. It is well-known that the PSD computed by NL-DFT methods depends on the selected kernel of isotherms. However, despite the high number of MOF structures reported to date, proper DFT kernels to study the unique pore size and shapes of these microporous materials are still missing.³⁶ For this reason, the PSD data for MOFs should be considered as merely indicative. Moreover, the goodness of the PSD obtained by DFT depends on the goodness of the fitting of



the experimental isotherm (see Fig. S11, S12 and S13†). In all the investigated cases, the fit between the calculated and the experimental isotherms was imperfect (the best fit is the one obtained with the N₂ isotherm). Again, this suggests that PSD data should be merely considered as a possible (and not unquestionable) description of the intrinsic porosity of the investigated MOF. The PSDs computed from the three molecular probes are compared in Fig. 2b and Table S1.† N₂, a non-ideal molecule for the analysis of microporous materials, gives the highest value (~7.4 Å), while Ar and CO₂ PSDs show the presence of a family of ultramicropores of around 4.8 and 4.2 Å diameter, respectively, values in better agreement with that estimated on the basis of the crystal structure of as-synthesised F4_MIL-140A(Ce) (between 4.8 and 5.8 Å, measured from the atomic centres).²⁸ The result obtained with N₂ does not surprise, indeed it is known that this probe can significantly overestimate the PSD of MOFs with very small micropores, especially if the pore dimension is close to the kinetic diameter of the molecule (3.64 Å for N₂).³⁶ The micropore size obtained by both Ar and CO₂ is more reliable and the PSD derived from CO₂ at 273 K is very narrow. This could be a further proof of a possible structural rearrangement of the material in the presence of CO₂, which allows the detection of the actual micropores size just with an adsorptive inducing a “phase change” adsorption. Still, it is worth noting that N₂ and Ar show a compatible micropore volume (Fig. S14†) while CO₂ displays a higher value, which might be seen as a further proof of a structural transition caused by this molecule.

In situ IR spectroscopy. As mentioned in the Introduction, a notable feature of as-synthesised F4_MIL-140A(Ce) is that it contains one H₂O molecule per formula unit, located in the proximity of a Ce atom.²⁸ Hydrogen bonding-like interactions are also likely to exist with F atoms and carboxylate groups from the surrounding organic linkers (Fig. 1b). According to the thermogravimetric curve (Fig. S15†), removal of H₂O is completed at a temperature as high as 423 K, suggesting that it is strongly adsorbed. The evacuation process of F4_MIL-140A(Ce) was further investigated using *in situ* IR spectroscopy (Fig. 3). Activation at 393 K for 12 h under vacuum was effective to remove the adsorbed H₂O before the spectroscopic experiments (see black spectrum in Fig. 3). The evacuated F4_MIL-140A(Ce) was then exposed to increasing pressures of H₂O, observing significant changes in the IR spectrum, especially in the 3700–3500 cm⁻¹ and 800–770 cm⁻¹ spectral ranges (Fig. 3b and c). In the former spectral region, two well-defined bands at 3643 and 3556 cm⁻¹ appear upon sending increasing H₂O doses. The presence of those peculiar narrow bands in the O–H stretching region is ascribable to the interaction of H₂O with specific acid sites.³⁷ In the 800–770 cm⁻¹ region, two initial bands at 790 and 779 cm⁻¹ are observed in the evacuated sample (see black spectrum in Fig. 3c). After sending 0.3 mbar of H₂O (corresponding to about 0.3–0.4% relative humidity, assuming a local temperature of around 313–318 K under the IR beam; vapour pressure of H₂O at 313 K is 74 mbar, at 318 K is 96 mbar) the 779 cm⁻¹ band shifts to 776 cm⁻¹, before going back to the original position upon further increasing the H₂O pressure. A new band at 771 cm⁻¹ also appears at high H₂O

pressure. The 790 cm⁻¹ signal decreases until 0.3 mbar of H₂O, then it slowly shifts to 793 cm⁻¹, changing again its intensity. The spectral modifications observed upon H₂O contact in this region are probably due to changes occurring on the fluorinated rings. A more specific assignment of the bands present in those two spectral regions is provided by DFT calculations: in the high frequency region, the signals at 3643 and 3556 cm⁻¹ can be disambiguated as the O–H stretching mode of water forming distinct H-bonds with F atoms on aromatic rings and O atoms from carboxylates, respectively. The assignment of bands in the low frequency region is less trivial, due to the coupling of different vibrations generating complex vibrational modes. In a simplified view, the observed signals can be attributed to the out-of-plane bending modes of carboxylate groups with respect to the aromatic rings. The coexistence of multiple features is explained by the presence of two crystallographically independent linkers (Fig. 1), as well as by the perturbation induced by adsorbates on the linkers themselves. It is worth noting that the main changes in the 800–770 cm⁻¹ spectral region were observed with a H₂O dose of 0.3 mbar (green curve in Fig. 3). This suggests that the exposure of the sample to a specific H₂O pressure is responsible for a sudden change in the structure, hinting at an adsorption process similar to the one displayed by CO₂ and possibly involving the same adsorption sites. This is supported by the very similar saturation loading of about 2.5 mmol g⁻¹ for both water and CO₂, corresponding to one adsorbate molecule per formula unit (see Fig. 2a and S15†).

In situ IR analysis using CO and N₂ as molecular probes at liquid nitrogen temperature was performed to further study the presence of Lewis acidic adsorption sites in the evacuated MOF (Fig. S16†). Both the CO and N₂ IR measurements highlight that, after H₂O removal, F4_MIL-140A(Ce) features accessible Ce^{IV} sites available for interaction with Lewis bases, even as weak as N₂. Detailed discussion of these results is available in Section S4 of the ESI.†

Next, we investigated the vibrational behaviour of evacuated F4_MIL-140A(Ce) when exposed to an increasing CO₂ pressure in the range between 110 and 550 mbar, at beam temperature (*i.e.*, around 313 K). The CO₂ pressure range was accurately selected by considering the position of the step of the CO₂ isotherm collected at 313 K (Fig. 4a). The incremental CO₂ doses are responsible for significant changes in the CO₂ asymmetric stretching region between 2400 and 2250 cm⁻¹ (Fig. 4b) and in the 800–770 cm⁻¹ spectral range (Fig. 4c). Upon sending CO₂ doses below the isotherm step (*i.e.*, until around 110 mbar), a new, quite broad band at 2344 cm⁻¹ appears, slightly shifted to lower frequencies compared to the antisymmetric CO₂ stretching vibrational mode (at 2349 cm⁻¹). At the same time, no significant changes are detected in the low frequency region, showing only a slight decrease in intensity of the 790 and 779 cm⁻¹ bands. These spectral modifications suggest that, below the isotherm step, CO₂ weakly interacts with the sorbent, likely because access to the open metal sites is prevented by the structural arrangement within channels. By increasing the CO₂ pressure and approaching the isotherm step, a new band at 2361 cm⁻¹, probably due to the interaction of CO₂ with Ce^{IV}, appears, while the 2344 cm⁻¹ band increases giving rise to an

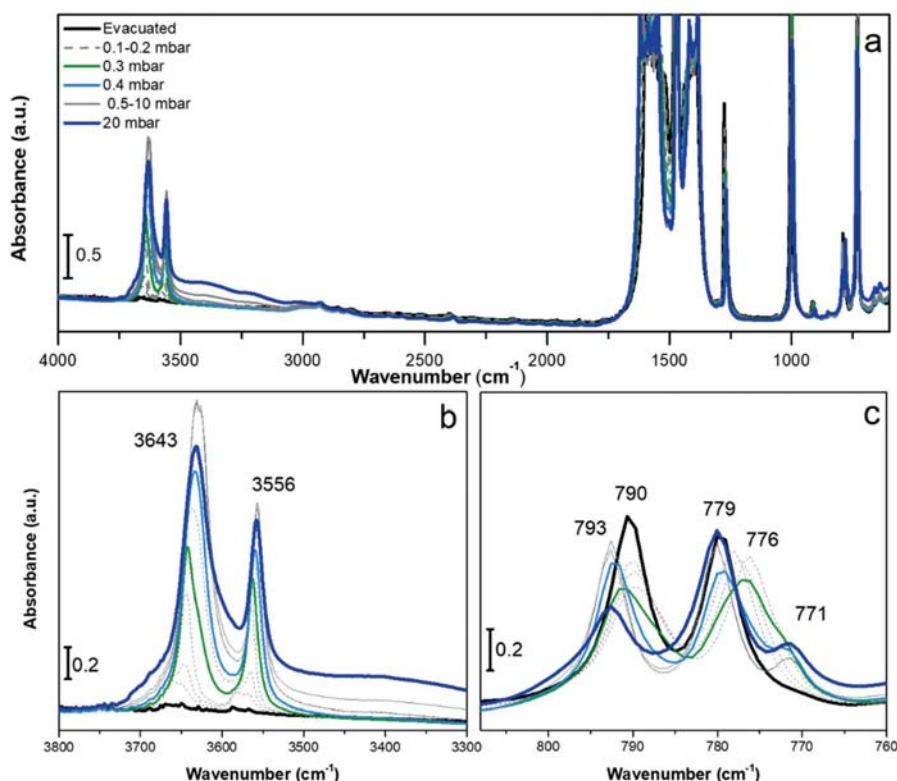


Fig. 3 IR spectra of F4_MIL-140A(Ce) collected dosing 0.1–20 mbar of H₂O on the evacuated sample, reported in the full spectral range (a), and in the 3800–3300 cm⁻¹ (b) and 810–760 cm⁻¹ (c) regions.

intense band with apparent maxima at 2344 and 2330 cm⁻¹. In general, the assignment of the above-mentioned bands is not straightforward because the rotovibrational profile of gaseous CO₂, which falls in the same spectral region and prevails at high CO₂ coverages, superimposes on those components. Concurrently, the bands at 790 and 779 cm⁻¹ are shifted to 788 and 782 cm⁻¹, respectively, suggesting that changes are occurring on the fluorinated aromatic rings. The CO₂ doses corresponding to the final part of the adsorption step and the beginning of the isotherm plateau cause no further changes in the low frequency spectral range, while both the 2361 and the 2344 and 2330 cm⁻¹ bands go out of scale. The predominance of the band at 2361 cm⁻¹, possibly related to the direct interaction of CO₂ with Ce^{IV} open metal sites, at CO₂ pressures that correspond to the isotherm step could be a further proof of the occurrence of a phase-change adsorption process that enables the establishment of a strong adsorbate/surface interaction.

DFT optimisation of molecular adducts. IR experiments provided good evidence of the presence of open metal sites able to interact with various adsorbates. The energetics of interaction of F4_MIL-140A(Ce) with H₂O, CO, N₂ and CO₂ were then investigated by means of periodic DFT calculations. Initially, the experimental structure of the MOF from ref. 28 was

optimized in the absence of any adsorbed molecule, *i.e.* in its evacuated form. The adsorption of H₂O, CO, N₂ and CO₂ was then simulated by manually placing the adsorbates at opportune positions within the MOF (*i.e.*, in the vicinity of the inorganic building unit) and by reoptimising the obtained structure. To fully exploit the framework symmetry, only full coverage (*i.e.*, 1 : 1 adsorbate/Ce ratio) was studied. For H₂O, CO and N₂, the molecule was positioned in direct interaction with the Ce open metal site through the O atom, the C atom and one of the N atoms, respectively. In the case of CO₂, two possible adsorption sites were considered: (i) as for the other adsorbates, with an O atom in direct interaction with Ce (referred as “Ce” site); and (ii) positioned in the pore and interacting with the surrounding perfluorobenzene rings, as recently proposed by Zhao and coworkers³⁰ (labelled here as “channel” site). The graphical representation of these adducts is presented Section 5 of the ESI†, whereas the main structural parameters are listed in Table S3.† The adsorption energetics for these adducts were also computed (details in Section 5 of the ESI†), as reported in Table 1.

The energetic description of the adsorption phenomena suggests a strong preference of F4_MIL-140A(Ce) for H₂O over the other investigated adsorbates. Interestingly, in the case of



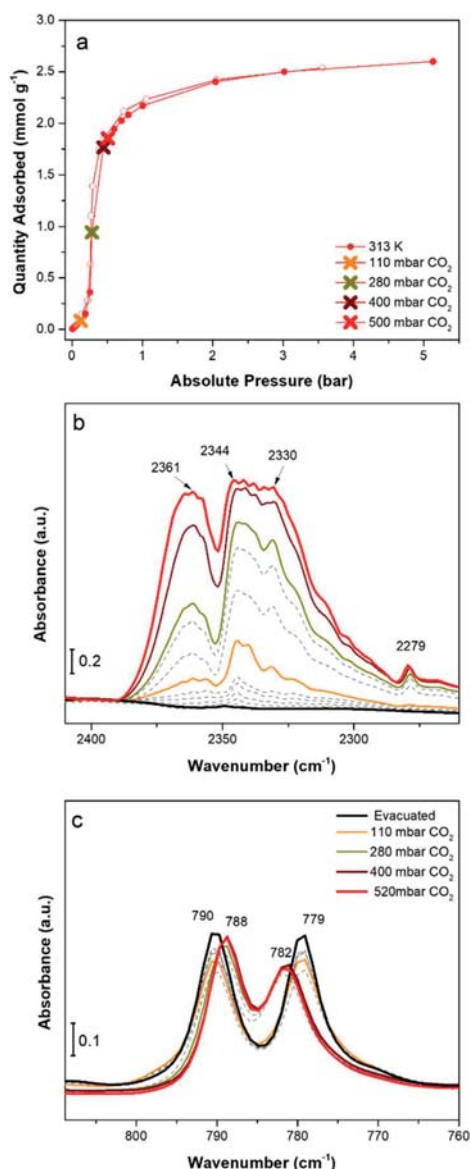


Fig. 4 CO₂ adsorption (filled circles) and desorption (empty circles) isotherms collected on F4_MIL-140A(Ce) at 313 K (40 °C) up to 5 bar (a). IR spectra of CO₂ adsorption on evacuated F4_MIL-140A(Ce) reported in the 2410–2260 cm^{−1} (b) and 810–760 cm^{−1} (c) spectral ranges. The same incremental pressure doses of CO₂ reported with coloured crosses in the volumetric isotherm of panel (a) were employed during the IR experiment. Dashed lines represent intermediate pressures.

CO₂, distinct interaction energies are computed depending on the adsorption site. In particular, the “channel” site, analogous to what previously proposed by Zhao and coworkers as the

Table 1 Adsorption electronic energy (ΔE) enthalpy (ΔH) and Gibbs free energy (ΔG) for F4_MIL-140A(Ce) in interaction with H₂O, CO₂ (for the latter, at both the “Ce” and the “channel” sites), CO and N₂. All values are corrected for the basis set superposition error and given per adsorbed molecule. ΔH and ΔG values are computed at a temperature of 298.15 K and a pressure of 1013 mbar

Model	ΔE (kJ mol ^{−1})	ΔH (kJ mol ^{−1})	ΔG (kJ mol ^{−1})
+H ₂ O	−86.0	−77.8	−35.8
+CO ₂ (Ce)	−55.2	−46.1	−7.5
+CO ₂ (channel)	−35.2	−26.1	10.5
+CO	−40.5	−36.1	1.0
+N ₂	−32.2	−28.0	6.8

preferred one for CO₂ adsorption, shows a lower interaction energy compared to that of CO₂ in direct interaction with the open metal site. Furthermore, the ΔG values estimated for the adsorption occurring at the two sites point out that the interaction is thermodynamically favoured only for the “Ce” site, whereas the “channel” site is not providing a stable adduct at ambient conditions. In fact, the computed ΔG value for CO₂ adsorption at the “channel” site is the highest observed in Table 1, suggesting that the involvement of the Ce^{IV} site is key for a favourable interaction with the adsorbates. A close inspection of the optimised crystal structures reveals that both H₂O and CO₂ are stabilised by interactions with both the metal centre (a Lewis acid), through their negatively polarised oxygen atoms, and the fluorine atoms belonging to the organic linker (Lewis bases), through the H atoms and C atom, respectively (Fig. S18–S24†). Thus, the ability of H₂O and CO₂ to behave as both Lewis acids and bases appears to be crucial to maximise their affinity for the adsorbent surface. We also simulated the interaction of CO₂ with a fully hydrogenated MIL-140A(Ce) (Fig. S25†), observing a significant reduction in binding energy to the “Ce” site down to −39.4 kJ mol^{−1}. This value is comparable to the strength of the interaction computed in the case of CO with F4_MIL-140A(Ce). Notably, the Gibbs free energy becomes positive in MIL-140A(Ce) (5.8 kJ mol^{−1}), suggesting that the interactions with the linker also play a key role in stabilising the MOF-CO₂ adduct.

Structural characterisation

Powder X-ray crystallography: long range structure. To investigate the structural response of F4_MIL-140A(Ce) upon evacuation and CO₂ adsorption, we carried out an *in situ* synchrotron PXRD study. The as-synthesised MOF was first kept under dynamic vacuum, progressively heating up to 403 K. A phase transition occurs already below 373 K, corresponding with the removal of the adsorbed H₂O molecules, and the new phase is stable when cooled down to 298 K (Fig. S26†). The structure retains the monoclinic C2/c space group during the phase transition. The main change in the unit cell is the increase of the β angle from 96.35(5)° in the as-synthesised MOF to 103.99(2)° in the evacuated one, which leads to a 2.7% decrease in volume from 2402(2) Å³ to 2336.0(5) Å³, respectively



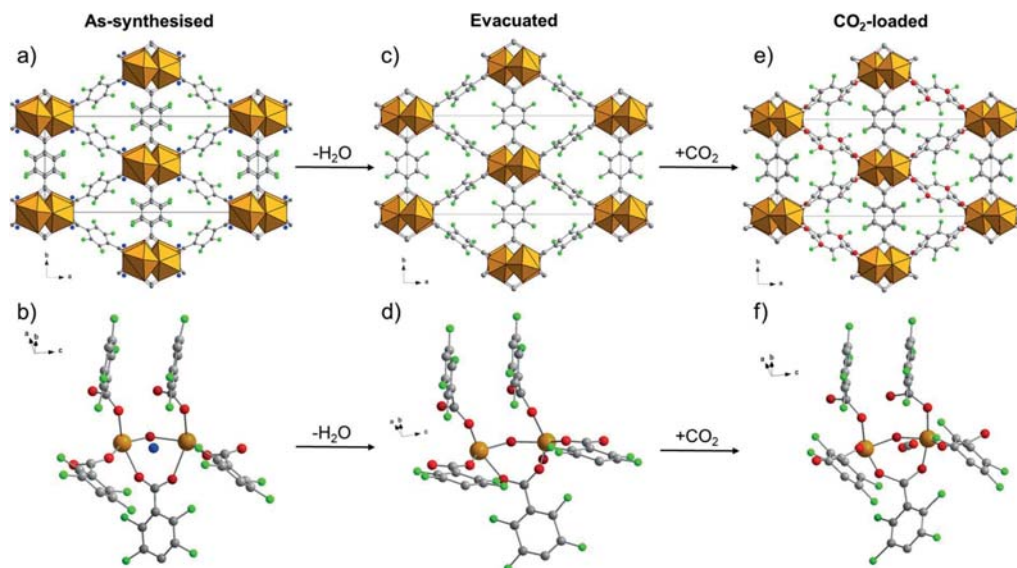


Fig. 5 Comparison of the crystal structure viewed along the *c* axis and the local environment around the adsorption site of the as-synthesised (a and b, respectively), evacuated (c and d, respectively) and CO_2 -loaded (e and f, respectively) forms of F4_MIL-140A(Ce). Colour code: Ce, orange; F, green; C, grey; O, red; H_2O , blue. H atoms not shown because their positions cannot be determined from PXRD data.

(Table S4†). The trend is in agreement with what suggested by DFT optimisation (Table S3†). Rietveld refinement of the PXRD pattern for the evacuated MOF was carried out starting from the DFT-optimised model, finding that H_2O removal leads to rotation of the aromatic rings belonging to linker A (Table S5, Fig. S28–S29 and S44†). This structural rearrangement occurs in response to the loss of several interactions between the framework and the water molecules: H_2O interacts with one Ce atom *via* its electron rich O atom and with at least three coordinated carboxylic O atoms and three F atoms (belonging to both linkers A and B) through hydrogen bonding (Fig. 1 and S44†).

The evacuated F4_MIL-140A(Ce) was then held at a constant temperature of 328 K and exposed to increasing CO_2 pressures in the 0.055–1.485 bar range. As displayed in Fig. S30,† a phase transition occurs between 0.367 and 0.745 bar, corresponding to the pressure range where the CO_2 adsorption isotherm collected at the same temperature displays the step (Fig. S31†). Upon reduction of the pressure from 1.485 down to 0.322 bar, the reverse transition takes place, regenerating the evacuated form of the MOF (Fig. S32†). An analogous, reversible phase transition is observed between 0.222 and 0.527 bar at 313 K, and between 0.833 and 1.490 bar at 343 K, in both cases in excellent agreement with the step position in the corresponding CO_2 adsorption isotherms (Fig. S33–S36†). The PXRD pattern of the CO_2 -loaded MOF is consistent at the three temperatures, suggesting that the equilibrium structure is the same in the investigated temperature range (Fig. S37†). We also performed an isobaric experiment exposing the MOF to a constant pressure of 0.498 bar and decreasing the temperature from 343 to 313 K

in 5 K steps (Fig. S38†). The MOF switches from the evacuated to the CO_2 -loaded form between 328 and 323 K, again in excellent agreement with what expected from the adsorption isotherms measured at different temperatures (Fig. S39†). Again, the unit cell parameters are only slightly affected by the phase transition, with the β angle decreasing from $103.99(2)^\circ$ in the evacuated MOF to $97.68(1)^\circ$ in the CO_2 -loaded one (Table S4†). This trend is also in agreement with what suggested by DFT optimisation (Table S3†). For the sake of Rietveld refinement of the CO_2 -loaded MOF, a structural model with CO_2 adsorbed at the “Ce” site was adopted as the most probable guess, based on the DFT results previously discussed. Rietveld refinement was carried out on the PXRD pattern for the CO_2 -loaded MOF at 313 K, finding that the insertion of CO_2 triggers rotation of linker A to a position similar to that observed for the as-synthesised MOF (Table S5,† Fig. S41). The CO_2 molecule displays coordination-like interaction with two Ce atoms, *via* one of its electron-rich O atoms, besides additional interactions with three F atoms (belonging to both linkers A and B) and with two coordinated carboxylic O atoms, *via* the electron-poor C atom (Fig. S42†). Thus, CO_2 appears to be adsorbed in a pocket where it is stabilised by a wealth of non-covalent interactions, akin to what seen for H_2O in the as-synthesised MOF. The step observed in the CO_2 adsorption isotherm most likely arises from the concerted rotation of perfluorinated aromatic rings upon the insertion of CO_2 in such an adsorption site, once the activation barrier for ring rotation is overcome and the site is made accessible. Further support to this interpretation is provided herein by means of other characterisation techniques.



Comparing the three forms of F4_MIL-140A(Ce), it is evident that the as-synthesised and the CO₂-loaded ones have common features, ascribable to the presence of the adsorbate, which are not shared by the evacuated form. By examining the torsional angles between the carboxylate groups and the aromatic rings for each linker in the different forms of the MOF (Table S5[†]), it can be seen that O2–C1–C2–C3 (linker A) and O5–C10–C9–C8 (linker B) torsional angles significantly change when adsorbates are present, by bringing the aromatic rings more out-of-plane respect to the carboxylates, as a result of interactions with the adsorbate. The third torsional angle, O4–C5–C6–C7 belonging to linker B, is instead only slightly affected, because of the lack of interactions with the adsorbates on that side of the linker (Fig. S43[†]).

XAS (Ce K-edge): local structure of the metal ion. To complement the long-range structural analysis carried out by PXRD, Ce K-edge XAS spectra were collected on the as-synthesised, evacuated and CO₂-loaded F4_MIL-140A(Ce) samples, respectively (Fig. S45[†]). This allowed us probing the local structure of Ce centres and gathering sensible information by fitting the extended X-ray absorption fine structure (EXAFS) signal as already done for several MOFs.^{38–42} The experiments were carried out at 328 K in dynamic conditions, *i.e.*, under a He flow for the evacuation step and under a controlled mixing of He and CO₂ to follow the adsorption/desorption of CO₂ within the porous system. The changes displayed by the EXAFS signal (Fig. S46a[†]) collected on F4_MIL-140A(Ce) during the adsorption process agree with what expected on the basis of the CO₂ adsorption isotherm measured at 328 K (Fig. S9[†]). Moreover, the Fourier transform of the EXAFS signal (Fig. S46b[†]) shows evident changes in the 2.5–4 Å range, *i.e.*, the second shell of ligands from Ce centres. The signals observed in this region can be assigned, by looking at the crystallographic structure, to Ce–Ce, Ce–H₂O and Ce–CO₂ distances which are indeed being

modified by adsorption/desorption processes. The scattering length of these three paths was parametrised in order to achieve a satisfactory data/parameter ratio allowing us to refine one Ce–O_w and two Ce–C_{CO₂} distances in addition to the Ce–Ce ones. By fitting the EXAFS signal using paths whose starting position is calculated from the crystallographic data coming from the Rietveld refinement, results in Fig. 6 and Table S6[†] are obtained.

Ce–Ce paths, whose refinement was compulsory because their distances fall very close to the Ce-adsorbates ones, gave values in excellent agreement with the ones observed by PXRD. The Ce-adsorbate distance for the as-synthesised material (Ce–O_w) was refined at 3.368(3) Å, whereas the Ce–C_{CO₂} distances for the CO₂-loaded one were fitted respectively to 4.06(3) Å and 4.44(4) Å. Such values are in agreement with those refined from PXRD data through Rietveld method (2.89 and 3.62 for Ce–O_w; 4.04 and 4.44 for Ce–C_{CO₂}) and from DFT optimisation (2.63 and 3.13 for Ce–O_w; 3.93 and 4.20 for Ce–C_{CO₂}), thus strengthening their reliability and consistency.

SSNMR: local structure of the adsorbate and the organic linker. The local structure of as-synthesised, evacuated, and CO₂-loaded F4_MIL-140A(Ce) was further characterized by multinuclear SSNMR spectroscopy exploiting the ¹⁹F and ¹³C nuclei of the linkers. Moreover, for the as-synthesised and the CO₂-loaded samples, ¹H and ¹³C nuclei of water and CO₂ were respectively investigated to unravel the state of the adsorbates in the MOF.

The ¹H direct excitation (DE) static spectrum of as-synthesised F4_MIL-140A(Ce) indicates the presence of both weakly physisorbed and structural water, which is completely removed after heating under vacuum, as shown by the absence of any signal in the spectrum of evacuated F4_MIL-140A(Ce) (Fig. S47[†]). The ¹³C DE spectrum of CO₂-loaded F4_MIL-140A(Ce) (Fig. 7a), recorded under magic angle spinning

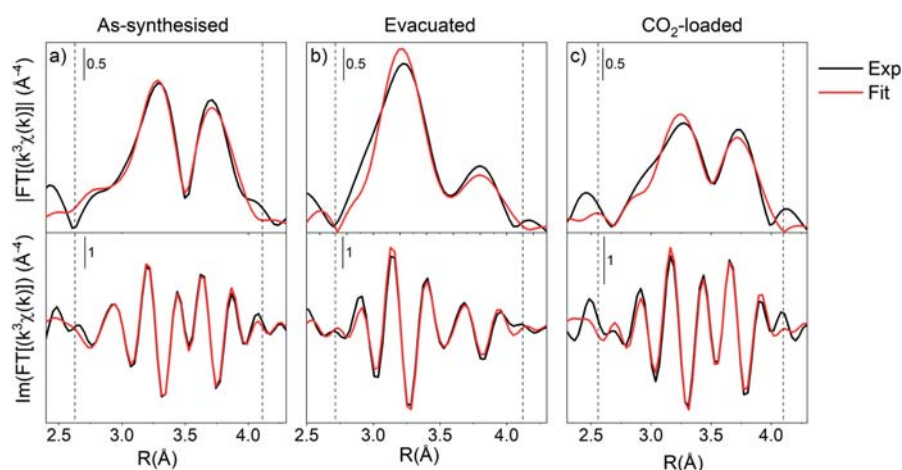


Fig. 6 Comparison between experimental (black lines) and fitted values (red lines) of magnitude (top) and imaginary part (bottom) of phase-uncorrected Fourier transform of k^3 -weighted Ce K-edge EXAFS spectra for the as-synthesised (a), evacuated (b) and CO₂-loaded (c) states. Dashed lines delimit the fitting range.



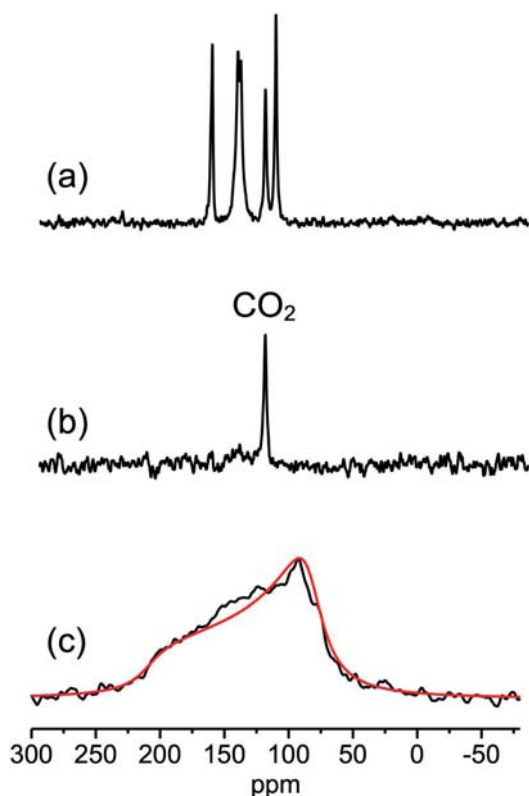


Fig. 7 ^{13}C DE spectra of CO_2 -loaded F4_MIL-140A(Ce) recorded (a) under MAS with a recycle delay of 150 s, (b) under MAS with a recycle delay of 2 s, and (c) in static conditions with a recycle delay of 2 s.

(MAS) at a rate of 15 kHz and with a recycle delay between subsequent scans (150 s) sufficient to quantitatively observe the signals of MOF and CO_2 carbons, indicates that almost one CO_2 molecule (signal at 124.7 ppm) per Ce atom was adsorbed in the MOF when loaded at a CO_2 pressure of 1 bar. When the ^{13}C DE-MAS spectrum is acquired with a short recycle delay of 2 s, the sole signal of CO_2 is selectively observed (Fig. 7b), since the ^{13}C longitudinal relaxation time of CO_2 carbons is much shorter than those of the linker carbons, in agreement with ref. 43. The ^{13}C DE static spectrum recorded with the short recycle delay shows a powder pattern with a line shape arising from the anisotropic ^{13}C chemical shift (CS) interaction averaged by CO_2 dynamics (Fig. 7c), as found in other MOFs.⁴⁴ The observed residual chemical shift anisotropy (CSA) indicates that CO_2 reorientation in F4_MIL-140A(Ce) is not isotropic, the CO_2 mobility being restricted by the interactions with the MOF linkers and Ce atoms and/or by steric hindrance in the pores. Generally, the CS interaction can be described with a second rank tensor with three principal components δ_{11} , δ_{22} , and δ_{33} , with $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ ("Mehring notation"). Three parameters are sufficient to describe the tensor: following the "Maryland

notation", they are the isotropic chemical shift [$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$], the span ($\Omega = \delta_{11} - \delta_{33}$), and the skew [$\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$].⁴⁵ The span measures the breadth of the observed powder pattern and is used to indicate the extent of the CSA, while the skew, ranging from -1 to 1 , gives an indication of the symmetry of the CS tensor, the two limit values of κ corresponding to an axial symmetry. For CO_2 in the solid state, an axial CS tensor is reported in the literature, with $\Omega = 315\text{--}335$ ppm and $\kappa = 1$.^{46,47} The signal observed for CO_2 adsorbed on F4_MIL-140A(Ce) is instead characterised by $\Omega \approx 127$ ppm and $\kappa = -0.98$. The span reduction with respect to fully immobilised CO_2 indicates that a motion with a rate higher than the spectral broadness in frequency units occurs for CO_2 in F4_MIL-140A(Ce) at room temperature. Wobbling on an individual adsorption site and hopping among symmetry equivalent adsorption sites have been found for CO_2 in other MOFs by ^{13}C SSNMR spectroscopy.^{48–53} In our case, the negative value of κ suggests that a wobbling or hopping motion occurs with an angle (β) between the C_∞ symmetry axis of CO_2 and the motion axis larger than the magic angle (54.74°),⁵³ while the axial line shape indicates a 3-fold or higher symmetry for the motion, which should occur in the fast regime. A satisfactory simulation of the spectral line shape (Fig. 7c) could indeed be obtained with a wobbling in a cone motion among 3 (or more) equivalent sites in the fast regime with $\beta = 75^\circ$. It must be pointed out that this motion could be associated either to a reorientation of CO_2 about a local axis or to the hopping of CO_2 molecules among equivalent adsorption sites, also in combination with translation. The occurrence of both wobbling and hopping motions cannot be excluded. Further variable temperature ^{13}C SSNMR static experiments on F4_MIL-140A(Ce) loaded with ^{13}C isotopically enriched CO_2 and line shape analyses are necessary to characterise CO_2 dynamics in more detail.

^{19}F DE and ^{19}F - ^{13}C cross polarization (CP) experiments were also recorded under MAS on all samples to highlight possible effects of H_2O or CO_2 adsorption on linkers. The spectra, showing signals from the linker fluorine and carbon atoms, respectively, are reported in Fig. S48† and 8.

^{19}F DE-MAS spectra show broad spinning sideband patterns (Fig. S48†) due to the large chemical shift anisotropy typical of ^{19}F nuclei.⁵⁴ The ^{19}F isotropic signals (Fig. 8a) lie in the spectral region between -150 and -135 ppm. A spectral deconvolution of the whole spinning sideband profiles showed that inequivalent fluorine atoms are present in all samples: two in the as-synthesised MOF, with isotropic chemical shifts of -143.1 and -144.8 ppm and intensities in a 3 : 1 ratio; three in the evacuated MOF, with chemical shifts of -141.0 , -142.0 , and -143.0 ppm and intensities in a 1 : 2 : 1 proportion; two in the CO_2 -loaded MOF with isotropic chemical shifts of -138.9 and -142.1 ppm and 1 : 3 relative intensities. In the ^{19}F - ^{13}C CP-MAS spectra (Fig. 8b), the signals of fluorinated (CF), quaternary (Cq), and carboxylic (COO^-) carbons of the linkers can be recognised in three distinct spectral regions. For each kind of carbon, several peaks are observed, as better appreciated after spectral deconvolution (Fig. S49†). The observed ^{19}F and ^{13}C multiple signals are ascribable to the two crystallographically inequivalent linkers in the structure of F4_MIL140 (Ce), namely,



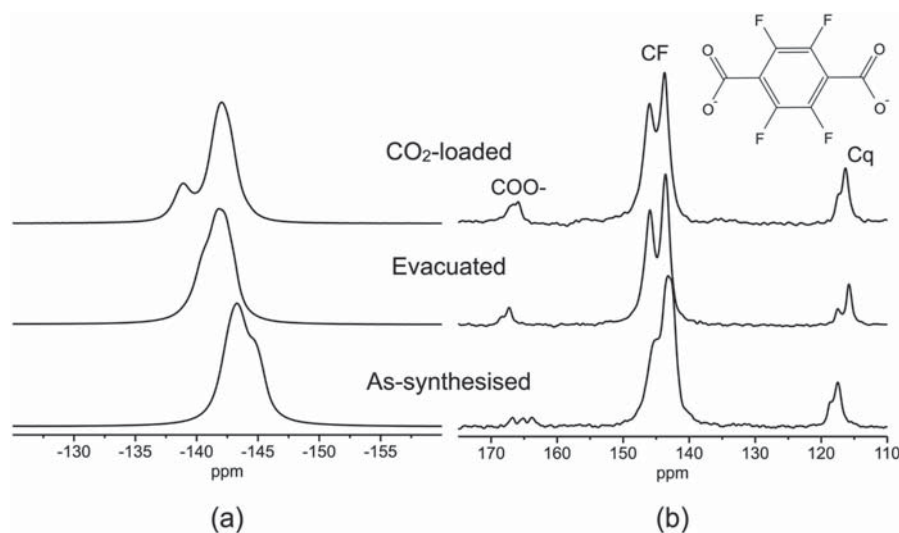


Fig. 8 (a) ^{19}F DE-MAS spectra and (b) ^{19}F - ^{13}C CP-MAS spectra (ct = 1 ms) recorded on (from bottom to top) as-synthesised, evacuated, and CO_2 -loaded F4_MIL-140A(Ce).

linker A and linker B. Analogous results were reported for MIL-140A(Zr).⁵⁵ To distinguish signals arising from linkers A and B, the correlations occurring in 2D ^{19}F - ^{13}C HETCOR spectra (Fig. S50–S52†) between signals of ^{13}C and ^{19}F nuclei in spatial proximity were also used. Therefore, signal assignment was possible combining the analysis of 1D ^{19}F and ^{19}F - ^{13}C CP-MAS spectra (recorded at different contact time values) with that of 2D ^{19}F - ^{13}C HETCOR spectra. The results, shown in Table 2 for as-synthesised, evacuated, and CO_2 -loaded F4_MIL-140A(Ce), clearly indicate the presence of two different linkers with symmetry compatible with that found by the PXRD structural analysis (see Section 8 in the ESI† for a detailed description of signal assignment).

Interestingly, shifts of ^{13}C and ^{19}F signals are observed among the as-synthesised, evacuated, and CO_2 -loaded MOF

(Fig. 8 and Table 2), ascribable to the change of local chemical environment caused by adsorption of water or CO_2 . For instance, the shielding of ^{19}F nuclei could be related to the interaction between the linker fluorine atoms and the adsorbate molecules,^{56,57} although the rotation of the phenyl rings out of the plane of carboxylates could also play a role. For as-synthesised F4_MIL-140A(Ce), ^{13}C signals from COO^- and Cq carbons spatially close to water ^1H nuclei are highlighted in the ^1H - ^{13}C CP-MAS spectrum shown in Fig. S53,† since only for these carbons ^1H - ^{13}C magnetisation transfer can effectively take place through dipolar coupling.

On the other hand, the signal of CO_2 carbons was not observed in ^{19}F - ^{13}C CP MAS spectra of CO_2 -loaded F4_MIL-140A(Ce) (Fig. 8b), even at contact time values as long as 10 ms. The distances between linker fluorines and CO_2 in the

Table 2 Assignment of signals in 1D ^{19}F DE-MAS and ^{19}F - ^{13}C CP-MAS spectra (Fig. 8) and in 2D ^{19}F - ^{13}C HETCOR spectra (Fig. S50–S52) of as-synthesised, evacuated, and CO_2 -loaded F4_MIL-140A(Ce)

Linker	Position	Atom	As-synthesised		Evacuated		CO_2 -loaded	
			$\delta(^{13}\text{C})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)	$\delta(^{19}\text{F})$ (ppm)
A	CF	C4	145.3	−143.1	146.0	−142.0	143.6	−142.1
		C3	145.3	−143.1	146.0	−142.0	145.7	−142.1
	Cq	C2	117.6		115.8		116.3	
		C1	163.7		168.4		165.8	
B	CF	C8	143.5	−143.1	143.6	−141.0	145.7	−142.1
		C7	142.6	−144.8	143.6	−143.0	143.6	−138.9
	Cq	C9	117.6		117.4		117.2	
		C6	118.7		115.8		116.3	
	COO^-	C10	166.9		167.3		167.2	
		C5	165.2		167.3		166.5	



Rietveld-refined structure of CO₂-loaded F4_MIL-140A(Ce) (Fig. S42 and S43†) would allow sufficiently strong dipolar interactions to occur for an efficient magnetization transfer between ¹⁹F and ¹³C nuclei, as observed by other authors.⁵⁸ The scarce CP efficiency found in our case should therefore be ascribed to a reduction of the dipolar interactions and/or of the residence time of CO₂ in the adsorption site due to reorientational and translational motions.^{59–61}

Energetics of the cooperative CO₂ adsorption mechanism.

The foregoing discussion on the adsorption properties and structural response of F4_MIL-140A(Ce) to adsorption and desorption of H₂O and CO₂ suggests that a concerted mechanism takes place when CO₂ is involved, due to the ease of rotation of the perfluorobenzene rings. The peculiar CO₂ adsorption mechanism was further investigated by performing adsorption microcalorimetry at 303 K to directly measure the CO₂ molar adsorption heat at different coverages (see the ESI† for further details). Fig. 9 reports the volumetric CO₂ isotherms (a) and the differential molar adsorption heats (b) of F4_MIL-140A(Ce). The volumetric isotherm collected in the 0–0.6 bar pressure range with the microcalorimetric apparatus (dark grey curve in Fig. 9a) is perfectly in agreement with the isotherm obtained by the standard automatic volumetric instrument (light blue curve in Fig. 9a and S54† shows a comparison with the isotherms collected at 298 and 313 K). The differential molar adsorption heat curve ($-q_{\text{diff}}$, Fig. 9b) unusually starts from low values, close to the molar heat of liquefaction of CO₂ (17 kJ mol^{−1}). The differential heat then increases until 25 kJ mol^{−1} and rapidly decreases to 22 kJ mol^{−1}. After this intermediate step, $-q_{\text{diff}}$ reaches a plateau at ~34 kJ mol^{−1} corresponding to a coverage above 0.2 mmol g^{−1}, *i.e.*, exactly where the step in the isotherm is taking place. These unusual values of differential heat clearly suggest that some endothermic modification of the adsorbent is occurring concurrently with the exothermic adsorption of CO₂. Indeed, microcalorimetry provides the “average” heat of adsorption which could

derive from different contributions generated by the interaction between the porous adsorbent and the adsorptive. If the endothermic event is particularly heat-demanding, the resulting net differential heat displays this peculiar trend.⁶² After reaching the value of 34 kJ mol^{−1}, $-q_{\text{diff}}$ remains constant until a coverage of 2 mmol g^{−1} (a value corresponding to the decrease in the slope of the adsorption isotherm immediately after the step). The relatively high value of $-q_{\text{diff}}$ over a wide range of coverages suggests that CO₂ strongly interacts with a homogeneous set of adsorption sites distributed on the internal surface of F4_MIL-140A(Ce).³⁸ When all the available adsorption sites are covered by CO₂, the differential heat curve steeply decreases, again approaching the heat of liquefaction of CO₂. At the step, the differential heat curve is in agreement with the isosteric heat of adsorption plot, indirectly extracted from the CO₂ isotherms by applying the Clausius–Clapeyron equation (Fig. S6†). However, the Clausius–Clapeyron model fails in identifying a region of low heat of adsorption before the step takes place.

DFT also provides further insights in the description of the adsorption phenomena: the initial q_{diff} is closely approached by the ΔH value computed for CO₂ adsorbed at the “channel” site (see Table 1). At plateau, the q_{diff} value is instead comparable to that computed for CO₂ at the “Ce” site, though slightly lower. The peculiar energy profile revealed by adsorption microcalorimetry could be explained by a scarce initial affinity of CO₂ for the surface of the adsorbent. As a matter of fact, even though the “channel” site is not the most favourable adsorption site for CO₂, the adsorptive must necessarily pass through the porous system to reach the most favourable “Ce” site. Furthermore, the displacement of CO₂ implies the rearrangement of the material, *i.e.*, the concerted rotation of the perfluorobenzene rings, to enable access to the most energetic adsorption site. The occurrence of this endothermic phenomenon is clearly proved by the differential heat trend observed at the onset of the isotherm step.

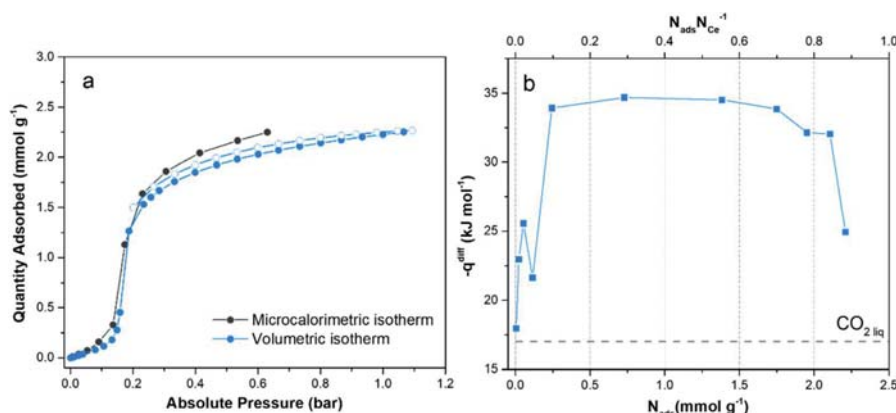


Fig. 9 Comparison of volumetric isotherms obtained by performing CO₂ adsorption at 303 K with the automatic volumetric instrument (blue) and with the volumetric line coupled with the microcalorimeter (black) (a). Differential molar adsorption heats curve related to the adsorption of CO₂ at 303 K (b). The dotted horizontal line represents the standard molar heat of liquefaction of CO₂ at 303 K: 17 kJ mol^{−1}.



To give a quantitative description of the phenomenon, a relaxed potential energy surface scan was performed by DFT. In brief, CO₂ initially modelled in the “channel” site, was stepwise approached to the “Ce” site. At each step, the whole structure was reoptimized, keeping the distance between the centre of mass of CO₂ (*i.e.*, its C atom) and Ce constant. The

trends of the energetic (ΔH and ΔG) and selected structural (β cell angle, O2–C1–C2–C3 torsional angle in linker A, O5–C10–C9–C8 and O4–C5–C6–C7 torsional angles in linker B) descriptors are reported as a function of the Ce–CO₂ distance in Fig. 10.

The energy trend clearly shows the existence of an activation barrier (ΔG barrier of ~ 10 kJ mol^{−1}) that the CO₂ molecule must overcome to reach the most favourable “Ce” site. As the barrier is overtaken, a drastic modification in the structural features of the MOF takes place, accompanied by a progressive stabilisation of the MOF–CO₂ adduct. This rearrangement implies the distortion of the unit cell through a decrease of the β cell angle, as well as the rotation of the perfluorobenzene rings, as testified by the concomitant variation of their torsional angles compared to the carboxylates. The trend from DFT simulation is in full agreement with that observed by PXRD. The key role played by the Ce^{IV} open metal site in F4_MIL-140A(Ce) also explains the lack of step observed in the CO₂ isotherm of its Zr-based analogue, recently reported by Zhao and co-workers.³⁰ Indeed, Zr^{IV} is seven-coordinate in the MIL-140 topology, with no H₂O coordinated in its as-synthesised form and, therefore, no available open metal sites for adsorbates to interact upon evacuation.

Conclusions

Through a combination of experimental and computational methods, we have produced a coherent set of evidence supporting the existence of a cooperative mechanism of CO₂ adsorption in F4_MIL-140A(Ce), which involves the concerted rotation of perfluorinated aromatic rings. This phenomenon opens the gate for CO₂ to reach a highly favourable adsorption site, where it is stabilised by interactions with both coordinatively unsaturated Ce^{IV} sites and the organic linkers. The step-shaped isotherm of F4_MIL-140A(Ce) resulting from this phase-change behaviour allows to reach saturation in a narrow range of partial pressure compatible with real-life post-combustion capture requirements. While several MOFs are known to display either adsorption at coordinatively unsaturated metal sites or concerted ring rotation, to the best of our knowledge the combination of these two features is observed in F4_MIL-140A(Ce) for the first time. Furthermore, the phase transition has a low activation barrier and does not involve major restructuring of the framework, resulting in a complete reversibility in desorption and leading to a non-hysteretic behaviour. Based on the knowledge acquired with this work, we expect that the CO₂ adsorption behaviour of F4_MIL-140A(Ce) can be finely tuned by both varying the fluorination degree of the organic linker and preparing mixed Ce/Zr analogues, paving the way towards the development of a class of adsorbents based on the same working principle. In view of the practical application of F4_MIL-140A(Ce) in post-combustion CO₂ capture, its high affinity for water could be detrimental to the capture performance, as water might preferentially adsorb over CO₂. We are currently investigating this aspect using dynamic breakthrough analysis, testing both dry and humid gas mixtures.

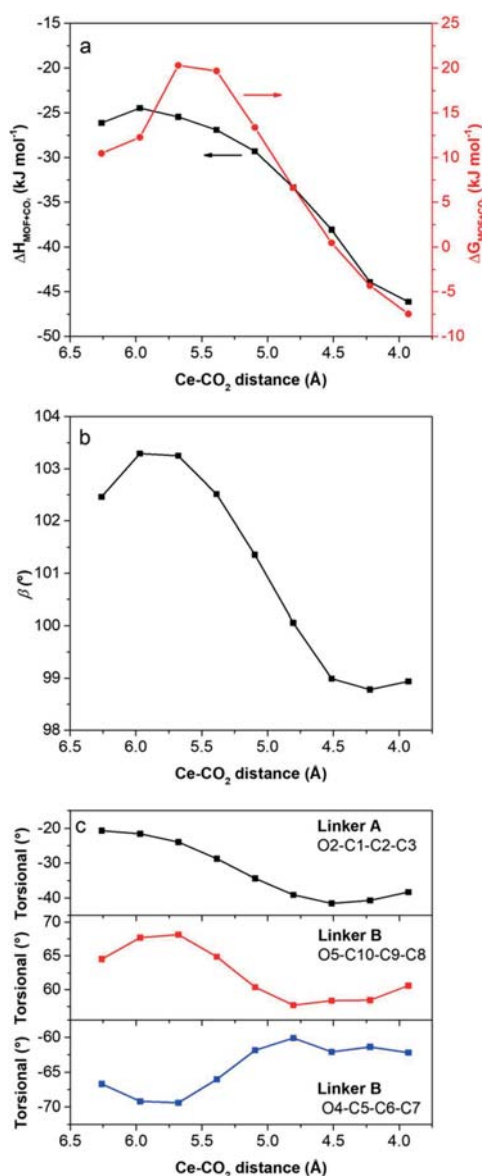


Fig. 10 Trends of: (a) ΔH and ΔG for CO₂ adsorption; (b) β angle of the monoclinic unit cell; and (c) perfluorobenzene ring-carboxylate torsional angles as a function of the Ce–CO₂ distance. ΔH and ΔG values are computed at a temperature of 298.15 K and a pressure of 1013 mbar.



Experimental procedures

Gas adsorption volumetry

N₂, Ar and CO₂ isothermal physisorption measurements were performed on a Micromeritics ASAP 2020 analyser at 77 K, 87 K and 273 K, respectively. For CO₂ adsorption the temperature was kept constant thanks to a home-made patented glass coating cell⁶³ in which a coolant or heating fluid, connected to a thermostatic bath (JULABO F25), is recirculating. Prior to the measurement, the sample was heated overnight at 393 K under vacuum. Specific surface areas were determined by using the Brunauer–Emmett–Teller (BET) method, following the Rouquerol consistency criteria.⁶⁴ Cumulative pore volume and pore size distribution were derived from adsorption isotherms by applying the NL-DFT method (see ESI,† Section 3, for further information).

High pressure CO₂ adsorption–desorption isotherms up to 5 bar were measured with a Quantachrome iSorb High Pressure Gas Analyser at 298, 313, 328 and 343 K. About 200 mg of sample was used for the adsorption studies. The sample was degassed at 393 K under dynamic vacuum for 12 h prior to analysis and at 393 K for 1 h in between subsequent measurements.

In situ IR spectroscopy

IR spectroscopy was performed on a Bruker Vertex 70 instrument equipped with a MCT (mercury cadmium tellurium) cryodetector. All the spectra were recorded in the 4500–600 cm^{−1} spectral range with a resolution of 2 cm^{−1} and an average of 32 scans. Before the analysis, F4_MIL-140A(Ce), as self-supported pellet, was held in vacuum at 393 K for 12 h. Both CO and N₂ interactions with the sample were studied by dosing a proper amount of gas (~60 mbar) into the cell and cooling down to 77 K with liquid nitrogen. The spectra reported for both the experiments were collected in outgassing through subsequent expansions until complete desorption. H₂O adsorption was carried out by sending incremental doses of H₂O (from 0.1 to 20 mbar) on the evacuated F4_MIL-140A(Ce). The CO₂ interaction with F4_MIL-140A(Ce) was studied by sending increasing CO₂ doses on the sample after applying the same evacuation procedure previously described. The increasing doses of CO₂ were chosen to be compatible with the equilibrium pressures involved in the adsorption/desorption isotherm at 313 K (40 °C) which is approximately the IR beam temperature.

Periodic DFT simulations

Vibrational and energetic features of F4_MIL-140A(Ce), also in the presence of relevant adsorbates, were simulated at the DFT level of theory with the CRYSTAL17 code.^{65,66} In detail, the B3LYP hybrid GGA functional^{67,68} was exploited in conjunction with a double- ζ quality basis set (C and O from ref. 39; F from ref. 69; and Ce from ref. 70). A larger Ahlrichs TZV2p basis³⁹ described atoms belonging to adsorbed molecules (H₂O, CO₂, CO and N₂). Dispersive interactions were empirically included in the Hamiltonian according to the Becke–Johnson damped version of the Grimme's D3 scheme.^{71,72} Such computational

setup provided a satisfactory structural and electronic description of Ce^{IV}-MOFs.⁷³

In situ PXRD

The *in situ* PXRD study here described took place at Beamline P02.1 (PETRA III, DESY, Hamburg).⁷⁴ PXRD patterns were collected using 60.0 keV (0.207124 Å) radiation. The sample was held in a 0.5 mm internal diameter glass capillary, which was mounted on a custom-built spinner device that allows for rotating a gas-filled capillary mounted on a commercial Huber goniometer head by 360° forth and back. The temperature of the sample was controlled between 298 and 413 K with an Oxford Hot-Air Blower. The beamline was equipped with a PerkinElmer XRD1621 CN3 – EHS detector (200 × 200 μm² pixel size, 2048 × 2048 pixel area). The detector was positioned at 1000 mm from the sample stage. Each PXRD pattern was collected in the 0.0071–16.3041 °2 θ range, with a 0.0067 °2 θ step size and a total acquisition time of 30 s. The resulting 2D images were azimuthally integrated to 1D diffraction patterns using the software Fit2D.⁷⁵

In situ XAS

Ce K-edge XAS data were collected at the BM23 (ref. 76) beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The storage ring was operating in the 32-bunch mode with a target current of 150 mA. The measurements were conducted in transmission mode using a Si(311) double-crystal monochromator. The intensity of the X-ray beam was measured by means of three ion chambers (30 cm, 1 kV) placed before the sample (I₀, filling 0.28 bar Kr + 1.72 bar He), after the sample (I₁, filling 1.35 bar Kr + 0.65 bar He) and after the CeO₂ reference sample (I₂, filling 1.35 bar Kr + 0.65 bar He). This experimental setup allowed us to reference the energy to the edge of the reference sample and thus calibrate the energy for each spectrum.

SSNMR spectroscopy

SSNMR spectroscopy measurements were carried out on a Bruker Avance Neo spectrometer working at Larmor frequencies of 500.13, 470.59, and 125.77 MHz for ¹H, ¹⁹F, and ¹³C nuclei, respectively, equipped with a double-resonance cross polarization – magic angle spinning (CP-MAS) probe head accommodating rotors with an external diameter of 4 mm. MAS experiments were performed at a spinning frequency of 15 kHz. All spectra were acquired at room temperature using air as spinning gas. The chemical shift for all nuclei was referenced to the ¹³C signal of adamantane at 38.46 ppm. Further details on experimental settings for the acquisition of specific spectra are given in Section 8 of ESI.†

Evacuated and CO₂-loaded F4_MIL140A(Ce) samples for SSNMR measurements were prepared using a home-made cell provided with a mechanical lever operated from outside enabling the capping of the rotor without disturbing the cell atmosphere. For preparing the evacuated sample, the unsealed rotor containing the as-synthesised packed sample was heated overnight under vacuum (0.1 mbar) at the temperature of 423 K



within the cell and then sealed under N₂ atmosphere. For CO₂ loading, the home-built cell containing the evacuated sample packed into the rotor was loaded with CO₂ at 1 bar pressure and the rotor was sealed under the gas atmosphere.

Adsorption microcalorimetry

The molar differential heat of CO₂ adsorption was evaluated on F4_MIL-140A(Ce) by means of a heat flow microcalorimeter (Calvet C80 by Setaram) connected to a high-vacuum ($\approx 10^{-4}$ mbar) glass line equipped with a Varian Ceramicell 0–100 mbar gauge and a Leybold Ceramicell 0–1000 mbar gauge. The sample was held in vacuum at 393 K for 12 h before being placed into the calorimeter under isothermal conditions. The measurement was performed at 303 K by following a well-established step-by-step procedure described elsewhere.⁷⁷

Author contributions

M. C., V. C. and M. T. carried out the gas sorption experiments and data analysis. M. C., C. A. and V. C. carried out the IR and adsorption microcalorimetry experiments and data analysis. C. A., D. M. V., K. A. L. and M. T. carried out the EXAFS experiments. C. A. carried out EXAFS data analysis. M. S. performed the DFT calculations and data analysis. F. C., A. K. and M. T. carried out the PXRD experiments. M. T. carried out PXRD data analysis. L. C., F. M., A. G. and M. G. carried out the SSNMR experiments and data analysis. M. C., C. A., M. S., L. C., F. M., V. C. and M. T. drafted the manuscript. V. C. and M. T. coordinated the work. M. T. conceived the study.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The *in situ* PXRD experiments were carried out at P02.1/PETRAIII at DESY, a member of the Helmholtz Association (HGF) (Proposal I-20190224 EC). The research leading to this result has been supported by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON2020. The *in situ* XAS experiments were performed on beamline BM23 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. D. M. V. and M. T. acknowledge the ESRF for covering the travel expenses for this beamtime. The authors acknowledge the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no 663830 (M.T.). The authors acknowledge the University of Pisa for funding through the Progetti di Ricerca di Ateneo scheme (PRA2020_39) (M.T.). The authors thank the Italian MUR through the Project PRIN 2020 doMino (ref. 2020P9KBKZ) (M. S., F. C., L. C., V. C., M. T.). The authors acknowledge the CINECA award under the ISCRA initiative, for the availability of high performance computing resources and support, through the IsC92 project "ULTRADS" (M.S., M. C., C. A., V. C., M. T.).

The authors acknowledge Dr Alexander Schökel and Dr Sergej Wenz (Beamline P02.1 at PETRAIII, DESY) for technical assistance during the beamtime. The authors thank Prof. Silvia Bordiga (University of Torino) for facilitating this work in the early stages. The authors thank Dr Susanna Monti (ICCOM-CNR) and Dr Giovanni Barcaro (IPCF-CNR) for helpful discussion. Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP) is acknowledged for the use of the Bruker Avance Neo 500 Solid State NMR Spectrometer.

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CO₂ Electrochemical Reduction with Zn-Al Layered Double Hydroxide-Loaded Gas-Diffusion Electrode[†]



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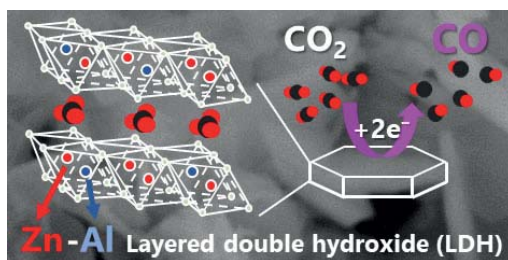
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ABSTRACT

Carbon dioxide electrochemical reduction (CO₂ER) has attracted considerable attention as a technology to recycle CO₂ into raw materials for chemicals using renewable energies. We recently found that Zn-Al layered double hydroxides (Zn-Al LDH) have the CO-forming CO₂ER activity. However, the activity was only evaluated by using the liquid-phase CO₂ER. In this study, Ni-Al and Ni-Fe LDHs as well as Zn-Al LDH were synthesized using a facile coprecipitation process and the gas-phase CO₂ER with the LDH-loaded gas-diffusion electrode (GDE) was examined. The products were characterized by XRD, STEM-EDX, BF-TEM and ATR-IR spectroscopy. In the ATR-IR results, the interaction of CO₂ with Zn-Al LDH showed a different carbonates evolution with respect to other LDHs, suggesting a different electrocatalytic activity. The LDH-loaded GDE was prepared by simple drop-casting of a catalyst ink onto carbon paper. For gas-phase CO₂ER, only Zn-Al LDH exhibited the CO₂ER activity for carbon monoxide (CO) formation. By using different potassium salt electrolytes affording neutral to strongly basic conditions, such as KCl, KHCO₃ and KOH, the gas-phase CO₂ER with Zn-Al LDH-loaded GDE showed 1.3 to 2.1 times higher partial current density for CO formation than the liquid-phase CO₂ER.



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Keywords : CO₂ Electrochemical Reduction, CO Formation, Layered Double Hydroxide, Gas-diffusion Electrode

1. Introduction

In recent years, research on carbon dioxide (CO₂) recycling technologies to recycle CO₂ into useful fuel, chemical and polymer precursors or products has attracted considerable attention from a carbon-neutral perspective.^{1,2} By using catalysts with highly efficient activity for CO₂ reduction reactions (CO₂RR), CO₂ recycling can be achieved at ambient temperature and pressure.³ The types of CO₂RR catalysts are classified into photocatalysts, enzyme catalysts, and electrocatalysts. The latter are expected to be promising sustainable CO₂RR catalysts with higher productivity and higher energy conversion efficiency than other catalysts. The CO₂

electrochemical reduction (CO₂ER) using electrocatalysts can use excess electricity generated by renewable energy, such as solar power and wind power, as an energy source.⁴ For CO₂ recycling technology, the selectivity of products is an important function. Among various CO₂ER products (carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), formic acid (HCOOH), and C₂ products), CO is an important raw chemical to produce methanol and liquid hydrocarbons.⁵ Au, Ag, and Zn-based electrocatalysts are known to perform highly selective CO-forming CO₂ER, but Au and Ag are precious metals. From practical perspectives, electrocatalysts with earth-abundant elements are desired.⁶ Zn is the only earth-abundant monometallic electrocatalyst with high CO selectivity, but bulk Zn catalysts tend to show large overpotentials and slow reaction rates due to small numbers of active sites.⁷ Monovalent Zn⁺ (3d¹⁰4s¹) has been found to be an active site in many cases due to its coordinatively unsaturated characteristics.⁸ For example, it has been reported that Zn catalysts derived from the electrochemical reconstruction of nanostructured ZnO had high CO₂ER activity (91.6% of CO selectivity at −0.62 V vs. reversible hydrogen electrode (RHE))⁹ and that those with more oxidized Zn species (Zn²⁺) were indicated to be more active (95.3% of CO selectivity at −1.0 V vs. RHE).¹⁰ Also, the low-crystallinity mesoporous ZnGa₂O₄ electrocatalyst, with an abundance of Zn²⁺/Zn⁺ redox

[†]A part of this paper has been presented in the 2022 ECSJ Fall Meeting (Presentation #2K03).

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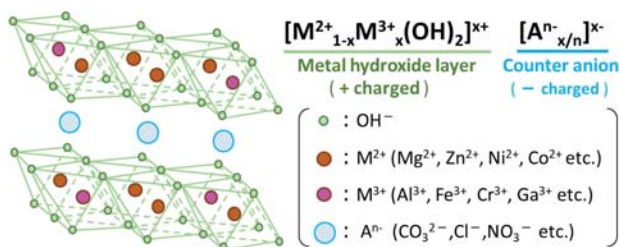


Figure 1. Structure of LDH ($[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{n-}_{x/n}]^{x-}$).

couples, was reported to show higher activity (96 % of CO selectivity at -0.80 V vs. RHE) than the high-crystallinity one (CO selectivity <37 % at -0.70 to -1.0 V vs. RHE).¹¹ Thus, precise nanostructure design is required to obtain highly active Zn-based electrocatalysts.

Based on the above findings, zinc oxide (ZnO) and zinc hydroxide (Zn(OH)₂) are expected to be promising CO-forming CO₂ER catalysts, but these are not electrochemically stable since the reduction to metal species occurs predominantly at more negative potentials than -0.42 V vs. RHE under pH conditions above 8.¹² Furthermore, the CO-forming CO₂ER involves the formation of hydroxide ions (OH⁻), as shown in Eq. 1, and tends to be boosted under alkaline conditions.^{9,13–15} Thus, the catalysts are required to have high electrochemical stability and alkaline tolerance.



(1)

We focused on layered double hydroxide (LDH), which consists of positively charged metal hydroxide layers and charge-compensating anions (A^{n-}) inserted between the layers. They have the general composition $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A^{n-}_{x/n}]^{x-}$ as shown in Fig. 1, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively. Due to the structure, LDHs have characteristics in favour of a CO₂ER catalyst, such as facileness of synthesis,^{16–18} diversity of metal composition,¹⁶ large specific surface area,¹⁶ high hydroxide ion conductivity,^{17,18} and high alkaline tolerance.^{19,20} These properties are also preferable as electrocatalysts for different reactions, so transition metal containing LDHs have been studied as electrocatalysts for oxygen evolution^{19–21} and oxygen reduction reactions.^{19,20,22} Although various material-based CO₂ER catalysts have been reported, there have been few reports on LDH-based CO₂ER catalysts. To our knowledge, the first study using single-phase LDH as a CO₂ER catalyst was reported in 2022. Cu-Al LDH was shown to be a CO₂ER catalyst forming mainly CO and HCOOH.²³ And then, Cu-Mg-Al LDH was reported to be a CO₂ER catalyst forming mainly acetic acid.²⁴ In addition, other LDH-based catalysts, which contain metal species or metal complexes as active species, have been investigated for their CO₂ER activity.^{25–27} However, among the LDH-based CO₂ER catalysts described above, CO selectivity was not high, at most 42 %.²³ On the other hand, it has been reported that M-Al LDHs (M = Ni, Co)²⁸ and Zn-M LDHs (M = Al, Ti, Ga)^{28,29} exhibited catalytic activity for CO₂ “photo-reduction” with Zn-Al LDH showing the highest CO selectivity (90 %).²⁹

The above background motivated a detailed exploration of the CO₂ER activity of LDHs. We found that Zn-Al LDH is a CO-forming CO₂ER catalyst and electrochemically more stable than ZnO, showing a CO selectivity of 77 % with a partial current density for CO formation of 12 mA cm^{-2} under the applied potential of -1.4 V vs. RHE in a potassium bicarbonate (KHCO₃) electrolyte solution.³⁰ However, the reaction treated in that previous study was the liquid-phase CO₂ER as shown in Fig. 2a, and there was a

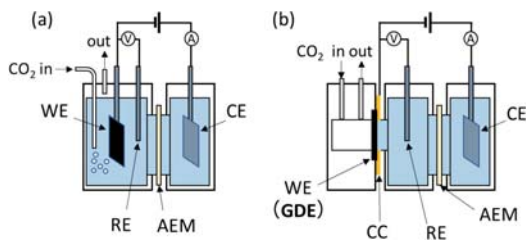


Figure 2. Schematic of a typical CO₂ electrolysis reactor for (a) liquid-phase CO₂ER and (b) gas-phase CO₂ER (GDE: gas diffusion electrode, WE: working electrode, CE: counter electrode, RE: reference electrode, AEM: anion exchange membrane, CC: current collector).

limitation of reaction efficiency because of its common issues, such as low solubility of CO₂ (33.4 mM ($M = \text{mol L}^{-1}$)), the slow diffusion rate of ions (1/1000 of that in the air) and electrolyte species limitations.³¹ The gas-phase CO₂ER with a gas-diffusion electrode (GDE), as shown in Fig. 2b, is a promising reaction that can overcome such limitations.^{31–33} In a GDE, CO₂ is transported in the gas phase and reacts at a thin solid-liquid-gas phase interface. In this process, liquid-phase CO₂ concentration and diffusion do not limit the reaction efficiency, resulting in lower overpotentials and higher current densities for CO₂ER. Furthermore, a strong alkaline electrolyte can be used in the gas-phase CO₂ER since it is not required to dissolve CO₂ into an electrolyte solution.

In the present study, to investigate the potential CO₂ER activity of LDHs, Ni-Al and Ni-Fe LDHs as well as Zn-Al LDH were synthesized using a facile coprecipitation process, and gas-phase CO₂ER with the LDH-loaded GDE was performed. For Zn-Al LDH, gas-phase CO₂ER was conducted using different electrolyte solutions with neutral to strongly basic conditions, where the pH of 1.0 M aqueous electrolyte solutions is 6.5, 8.2 and 14 for potassium chloride (KCl), potassium bicarbonate (KHCO₃), and potassium hydroxide (KOH), respectively.

2. Results and Discussion

2.1 Characterization of M²⁺-M³⁺ LDH (M²⁺ = Zn or Ni, M³⁺ = Al or Fe)

M²⁺-M³⁺ LDH with CO₃²⁻ anions was prepared using a facile and traditional coprecipitation process as shown in Fig. S1.³⁴ Figure 3 shows the X-ray diffraction (XRD) patterns and field emission scanning transmission electron microscopy (FE-SEM) image of the synthesized products. As shown in Fig. 3a, the (003) and (006) plane peaks, characteristic of the layered structure, were observed and no impurity peaks were detected in any of the

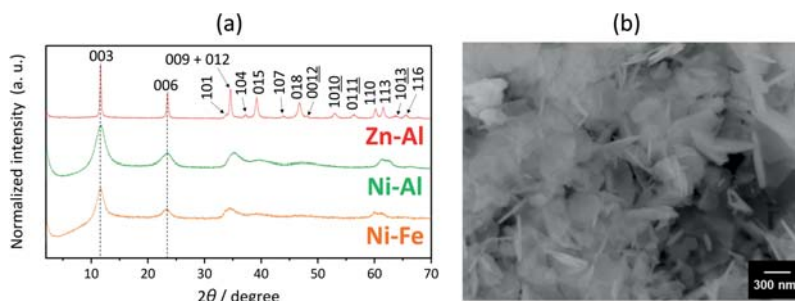


Figure 3. (a) XRD patterns of M^{2+} - M^{3+} LDHs (M^{2+} - M^{3+} = Zn-Al (red line), Ni-Al (green line), or Ni-Fe (orange line)) and (b) FE-SEM image of Zn-Al LDH.

products. Peaks in the Zn-Al system were assigned to the previously reported XRD pattern of Zn-Al LDH with carbonate (CO_3^{2-}) anions as interlayer anions.³⁴ Similarly, for the Ni-Al and Ni-Fe systems, the formation of LDHs with the interlayer carbonate anions was confirmed.^{35,36} However, their peaks were broader than those of Zn-Al LDH, suggesting that the primary grain size was smaller. From the FE-SEM and the bright field transmission electron microscopy (BF-TEM) images, as shown in Figs. 3b and S3a, the plate-like crystals, characteristic of LDH, with a size of one hundred to several hundred nm were observed in Zn-Al LDH. On the other hand, as shown in Figs. S3b and S3c, the BF-TEM images of the Ni-Al and Ni-Fe products showed sub-micron to micron lumped crystals, which were aggregates of fine crystals. The scanning transmission electron microscopy coupled with energy-dispersive X-ray spectrometry (STEM-EDX) mapping showed that elements used as M^{2+} and M^{3+} were homogeneously distributed on the particles in the sub-micron-order as shown in Fig. S3 and the EDX elemental analysis showed the average chemical composition with molar ratios of Zn/Al = 1.96 ± 0.25 , Ni/Al = 1.80 ± 0.24 and Ni/Fe = 2.00 ± 0.16 for each product, which is almost the same as the starting composition ratio. These results indicate that all synthesized products are LDH with the formula $[\text{M}^{2+}_2\text{M}^{3+}_1(\text{OH})_6]^+ [\text{CO}_3^{2-}_{0.5}]^-$.

Figure S5 shows the attenuated total reflectance infrared (ATR-IR) spectra of the dry LDHs. The three LDH samples exhibited a common broad band in the high frequency region ($3500\text{--}2950\text{ cm}^{-1}$) ascribable to the hydroxyl-stretching vibrations of both structural M-OH species ($3500\text{--}3400\text{ cm}^{-1}$) and molecular water present in the interlayer ($3300\text{--}2950\text{ cm}^{-1}$).³⁷ The latter is commonly differentiated between hydrogen-bonded water at around 3300 cm^{-1} and water OH stretching vibrations perturbed by interlayer carbonate anions ($2950\text{--}3050\text{ cm}^{-1}$).³⁷ In the low frequency region, a broad band ($1000\text{--}650\text{ cm}^{-1}$) derived from the superimposition of the ν_2 out of plane stretching mode of interlayer carbonate anions ($\sim 860\text{ cm}^{-1}$) and the lattice HO-M-OH and M-OH (M = Zn, Al, Ni, Fe) vibrational modes ($450\text{--}800\text{ cm}^{-1}$) was present in all the samples.^{38,39} In the intermediate region, a band at 1640 cm^{-1} , which is typical of the bending vibrations of the interlayer water molecules, and an intense peak at around 1350 cm^{-1} with a weak shoulder at $\sim 1410\text{ cm}^{-1}$ due to the ν_3 stretching mode of interlayer carbonate anions were observed.³⁷ It is worth noting that the ν_3 stretching mode of free carbonate anions is reported to be at 1415 cm^{-1} .⁴⁰ However, a change in the symmetry of the molecule could lead to the splitting of the ν_3 in two distinct components at ~ 1365 and $\sim 1415\text{ cm}^{-1}$.⁴¹ Additionally, since pre-treatments of the LDHs at high temperature were not performed to preserve the LDH structure, the additional bands in the $1800\text{--}1200\text{ cm}^{-1}$, partially superimposed to the structural water and carbonates (CO_3^{2-}) signals, are probably related to the formation of surface (non-structural) carbonate species upon the exposure to the CO_2 present in the

atmosphere. In this regard, the Ni-Al and Ni-Fe LDHs interestingly exhibited some additional peaks at 1725 cm^{-1} and 1270 cm^{-1} , which are probably due to the presence of a different family of surface “bridged” carbonate-like species.⁴⁰

In more detail, the difference among the three LDHs upon interaction of CO_2 was investigated by adding CO_2 saturated water on the dry samples (See Figs. S6 and 4 for the $3700\text{--}650\text{ cm}^{-1}$ and the $1800\text{--}1200\text{ cm}^{-1}$ region, respectively). As shown in Fig. S6, the contact with water caused an increase in the high frequency region bands associated to the OH stretching vibrations together with the increment of the 1640 cm^{-1} signal ascribed to the HOH bending vibrations, while the interaction of CO_2 with basic sites was responsible for the appearance of surface (non-structural) carbonates-like species shown in the $1800\text{--}1200\text{ cm}^{-1}$ region. As already mentioned, free carbonate anions generally show a ν_3 asymmetric CO_3^{2-} stretching at around 1415 cm^{-1} , which split in two different signals (the symmetric $\nu_{3\text{sym}}$ and the asymmetric $\nu_{3\text{asym}}$ vibrations) when the symmetry is lowered.⁴⁰ In addition, when CO_2 interacts with the LDH basic sites, both the symmetric and asymmetric vibrations are detected, and the different carbonate-like species, such as unidentate, bidentate, bridged, and polydentate structures or bicarbonates, formed depending on the type and the strength of the surface sites.⁴² To distinguish between carbonates, the most employed criteria is usually based on the $\Delta\nu_3$ splitting even though the frequency of the different species is strongly affected by the structure. The strongest basic sites (unidentate carbonates) are usually associated with the lowest $\Delta\nu_3$ splitting ($\Delta\nu_3 = 100\text{ cm}^{-1}$), followed by basic sites of medium strength (bidentate carbonates) ($\Delta\nu_3 = 300\text{ cm}^{-1}$) and by weak basic sites (bridged species) ($\Delta\nu_3 = 400\text{ cm}^{-1}$).⁴³ However, the appearance of those species on the different LDHs fell in the region deriving from the HOH bending vibration of water ($\sim 1640\text{ cm}^{-1}$) and the interlayer carbonates anions (~ 1350 and 1410 cm^{-1}), whose intense bands strongly affect the identification of surface carbonate species (See Figs. S6 and 4a, 4b and 4c). For this reason, the identification of the main spectral change occurring in the carbonate region upon CO_2 contact is possible just by subtracting the spectra of the corresponding wet N_2 -saturated samples (See Figs. 4d, 4e, and 4f). For all LDHs, the CO_2 contact was responsible for the increase of the intense band at around 1610 cm^{-1} , which shifted to different wavenumbers depending on the kind of LDHs (1606 cm^{-1} for Ni-Fe, 1613 cm^{-1} for Ni-Al and 1623 cm^{-1} for Zn-Al), and the simultaneous decrease of the signal at 1360 cm^{-1} . However, the Ni-Al and Ni-Fe LDHs behave differently compared to Zn-Al one in the remaining spectral regions. In particular, upon CO_2 contact, the Ni-Al and Ni-Fe LDHs exhibit two broad and intense bands at $\sim 1500\text{ cm}^{-1}$ and at $\sim 1295\text{ cm}^{-1}$, which are nearly absent in the Zn-Al one. Additionally, the decrease of the band at 1360 cm^{-1} occurs simultaneously to the component at around 1420 cm^{-1} , which is located at different frequencies in

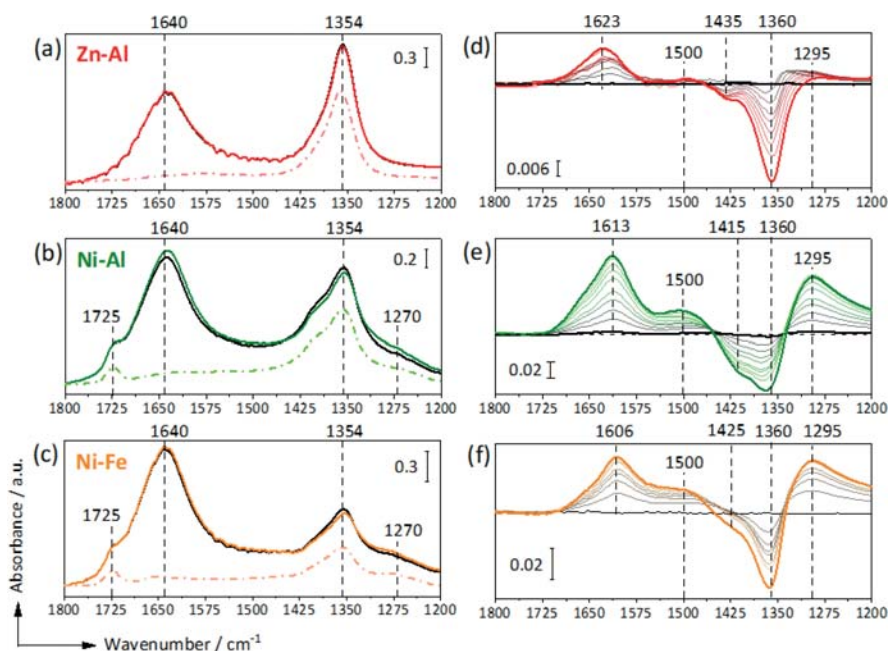


Figure 4. In-situ ATR-IR spectra in the carbonate-like region (1800–1200 cm^{-1}) of: Zn-Al LDH (a), Ni-Al LDH (b) and Ni-Fe LDH (c). The corresponding differential spectra (obtained by subtracting the spectra of the wet N_2 -saturated sample to that of the wet CO_2 -saturated sample) are shown on the right side (d–f). Dotted colored, black, and continuous colored curves represent the dry, wet N_2 -saturated, and wet CO_2 -saturated samples, respectively. The curves of intermediate CO_2 coverage are shown in grey. In adsorption differential spectral patterns (d–f), the bands relative to species that form or increase upon CO_2 contact are pointing up, bands relative to species that decrease are pointing down.

the three LDHs: 1415 cm^{-1} in Ni-Al, 1425 cm^{-1} in Ni-Fe and 1435 cm^{-1} in Zn-Al. Finally, the bands at 1725 cm^{-1} and 1270 cm^{-1} which are originally present in the Ni-Al and Ni-Fe LDHs and assigned to surface “bridged” carbonates were not changed by CO_2 contact, suggesting the stability of these carbonate species in the as-synthesized LDHs (See Figs. 4b and 4c and corresponding differential spectra 4e and 4f). A correct assignment of the carbonate species formed upon CO_2 adsorption is not straightforward for at least two reasons: the superposition of the signals generated by structural carbonate and water molecule and the possible loss of a fraction of deposited sample during the experiment. However, based on the $\Delta\nu_3$ splitting ($\Delta\nu_3 > 100$), the formation of bidentate species likely occurs. Additionally, the presence of bicarbonates is highly unlikely due to the absence of the characteristic sharp band at $\sim 1220 \text{ cm}^{-1}$ associated to the COH bending mode.^{40,44} The differences in the spectra of Ni-Al, Ni-Fe and Zn-Al show the formation of different families of bidentate carbonates with different strength and stability, which also suggests the presence of different basic sites in the three LDHs. These differences could affect the reaction processes such as intermediate formation steps and CO desorption step, and by extension, could lead to different catalytic behaviors in the three LDHs.

2.2 Gas-phase CO_2 ER with LDH-loaded GDE in 1.0 M aqueous KHCO_3 solution

Gas-phase CO_2 ER with the LDH-loaded GDE was carried out by using a custom-made three-electrode setup composed of a three-compartment cell as shown in Fig. S2. The LDH-loaded GDE was prepared by simple drop-casting of the catalyst ink on a carbon sheet with gas-diffusion layer (GDL) as shown in Fig. S7, which

exhibited the cross-sectional SEM image and EDX mapping of Zn for the Zn-Al LDH-loaded GDE. A 1.0 M aqueous KHCO_3 solution was used as the typical electrolyte. The applied potential dependence of Faradaic efficiency (FE) and current density (j) for the cathodes with or without LDHs are shown in Figs. 5 and S8, respectively. Electrode potentials in the study were converted to the reversible hydrogen electrode (RHE) or the standard hydrogen electrode (SHE) according to the following equations: $E_{\text{RHE}} = E_{\text{SHE}} + 0.059 \times \text{pH}$, $E_{\text{SHE}} = E_{\text{Ag}/\text{AgCl}} + 0.222 \text{ V} = E_{\text{Hg}/\text{HgO}} + 1.760 \text{ V}$.

As shown in Fig. S8, for all cathodes, the current density increased with more negative applied potentials, and catalytic currents were observed. Focusing on FE of the cathode with Zn-Al LDH, as shown in Fig. 5a, CO formation was dominated at more negative applied potentials than -1.0 V vs. RHE, with 59 % of the FE at -1.0 V vs. RHE and the highest FE of 67 % was shown at -1.4 and -1.8 V vs. RHE. At the same applied potential, H_2 formation was observed as a major side-reaction with more than 20 % of the FE , and electron consumption by other reactions gave less than 10 % of the FE . On the other hand, in FE of the cathode with Ni-Al LDH, Ni-Fe LDH, or without LDH, H_2 formation was dominated as shown in Figs. 5b, 5c and 5d, respectively. Therefore, it was suggested that only Zn-Al LDH acts as a CO_2 ER catalyst. Methane (CH_4) was detected as a minor product, but its FE was less than 0.1 % for all cathodes. Then, trace amount of formic acid (HCOOH) was detected as the only liquid product, but its concentration is under the limit of quantification. Thus, the FE for CO and H_2 are discussed in this study.

Regarding the stability of Zn-Al LDH during CO_2 ER, a constant current density at all applied potentials was observed for 10 min of

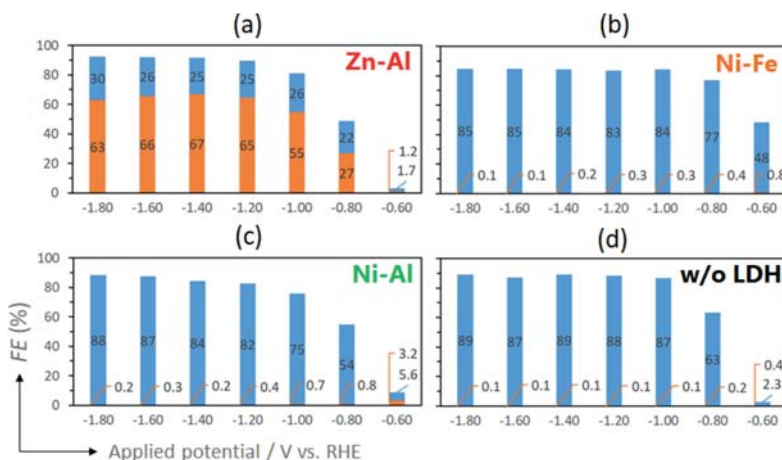


Figure 5. Applied potential dependence of Faradaic efficiency (FE) for CO_2ER in 1.0 M aqueous KHCO_3 solution using each cathode with (a) Zn-Al LDH, (b) Ni-Fe LDH and (c) Ni-Al LDH, and (d) without LDH. (orange bar: CO, blue bar: H_2)

total reaction time in the chronoamperogram as shown in Fig. S9, and the SEM-EDX elemental analysis for the surface of Zn-Al LDH-loaded GDE showed almost no change in the average chemical compositions with the molar ratio of Zn/Al before and after electrolysis, which were 1.92 ± 0.16 and 2.02 ± 0.17 , respectively. In addition, the turnover number (TON) of these reactions, assuming one Zn atom as the active site, were 0.90, 2.0, 3.1, 4.2 and 5.2 at -1.0 , -1.2 , -1.4 , -1.6 and -1.8 V vs. RHE, respectively. Thus, the TON above 1 was gained, indicating that Zn-Al LDH exhibits CO-selective electrocatalytic activity in gas-phase CO_2ER .

Interestingly, the Ni-Al and Ni-Fe LDHs which show the lowest CO evolution also exhibit a different carbonates evolution upon CO_2 adsorption. The accordance of the CO_2ER activity with the in-situ ATR-IR spectroscopy supports the hypothesis that the different carbonates formed in Zn-Al LDH are responsible for a higher CO_2ER activity.

2.3 Gas-phase CO_2ER with LDH-loaded GDE in different electrolytes

To investigate the potential CO_2ER activity of Zn-Al LDH, the gas-phase CO_2ER activities of Zn-Al LDH under neutral to strong basic conditions (pH of 1.0 M aqueous electrolyte solutions: 6.5 for KCl, 8.2 for KHCO_3 , 14 for KOH) were compared. Although KOH cannot be used as an electrolyte in liquid-phase CO_2ER because it forms carbonate salts with dissolved CO_2 in an electrolyte solution, it is known that the gas-phase CO_2ER with Ag and Au nanoparticle catalysts was boosted under strong alkaline conditions than the neutral condition: a strong alkaline condition causes lower overpotential and higher current density and FE .^{14,15,45}

Figures 6, S10, S11 and S12 show the applied potential dependence of current density (j) and FE for CO_2ER with Zn-Al LDH in each 1.0 M aqueous solution of KCl, KHCO_3 , and KOH. As shown in Fig. 5 (upper row), as the pH of electrolytes increased, the onset potentials for the partial current density of CO formation (j_{CO}) decreased (KCl: 0.90 V vs. RHE, KHCO_3 : 0.80 V vs. RHE, KOH: 0.50 V vs. RHE), and the maximum $|j_{\text{CO}}|$ for the KOH electrolyte (25 mA cm^{-2}) was higher than that for the KCl and KHCO_3 (17 mA cm^{-2} and 15 mA cm^{-2} , respectively). However, the $|j_{\text{CO}}|$ for all electrolytes was less than 30 mA cm^{-2} even at relatively negative potentials and, as the pH of electrolytes increased, the maximum FE of CO (FE_{CO}) decreased (KCl: 69 %, KHCO_3 : 67 %, KOH: 64 %), as shown in Figs. 6c, S10a, S11a and S12a. Since a trace amount of formic acid was also detected but no other products were detected in the KCl and KOH conditions as well as in the KHCO_3 condition, the main cause of the slight decrease in FE_{CO} with increasing the pH of electrolytes could be the loss of CO by dissolution into the electrolyte, which is more likely to occur in alkaline electrolytes.

The effect of electrolyte type on the CO_2ER activity of Zn-Al LDH was studied in more detail using the Tafel analysis. As shown in Fig. S13a, the Tafel behavior of the j_{CO} plotted with overpotentials showed that the slopes were almost identical for all electrolytes (KCl: 121 mV dec^{-1} , KHCO_3 : 140 mV dec^{-1} , KOH: 115 mV dec^{-1}). Furthermore, the near overlap was observed in the Tafel plots converted with the applied potential vs. standard hydrogen electrode (SHE) for all electrolytes as shown in Fig. S13c, indicating that the rate-determining step (RDS) was not affected by pH of the bulk solution. This behavior is consistent with the previously reported behaviors for Ag and Au nanoparticle catalysts,⁴⁵ deriving from the phenomenon that the local pH of the cathode surface under CO-forming CO_2ER remains basic (pH > 8) even under the KCl condition.^{9,15} Therefore, the CO_2ER by Zn-Al LDH is also considered to depend on the local pH of the cathode surface.

Table S1 showed the summary of $|j_{\text{CO}}|$ and FE_{CO} in the case of gas-phase and liquid-phase CO_2ER by Zn-Al LDH. As expected, it was revealed that the gas-phase CO_2ER showed 1.4, 1.3, and 2.1 times higher $|j_{\text{CO}}|$ than the liquid-phase CO_2ER at -1.4 V vs. RHE for KCl, KHCO_3 , and KOH, respectively. However, these increases of $|j_{\text{CO}}|$ were not as much as a typical gas-phase CO_2ER , since gas-phase CO_2ER by highly active catalysts such as Ag and Au nanoparticle was reported to give the current density of 100 mA cm^{-2} or more.³³ The low $|j_{\text{CO}}|$ in the case of gas-phase CO_2ER by Zn-Al LDH could be derived from high overpotential due to the low electrical conductivity,²⁸ low stability of the key $\text{CO}_2^{\cdot -}$ intermediate (one-electron-reduced CO_2 state), the high affinity for CO_2 , or the high basicity of LDH. Considering that the Tafel slope for Zn-Al LDH was comparable to that for Ag and Au nanoparticle catalysts (110 to 230 mV dec^{-1}).^{15,45} Theoretically, a Tafel slope of 118 mV dec^{-1} means that RDS is the first one-electron transfer to CO_2 , while a Tafel slope of 59 mV dec^{-1} implies that RDS is a chemical reaction occurring after the first one-electron reduction of CO_2 .^{11,46} The Tafel slopes for Zn-Al LDH for all

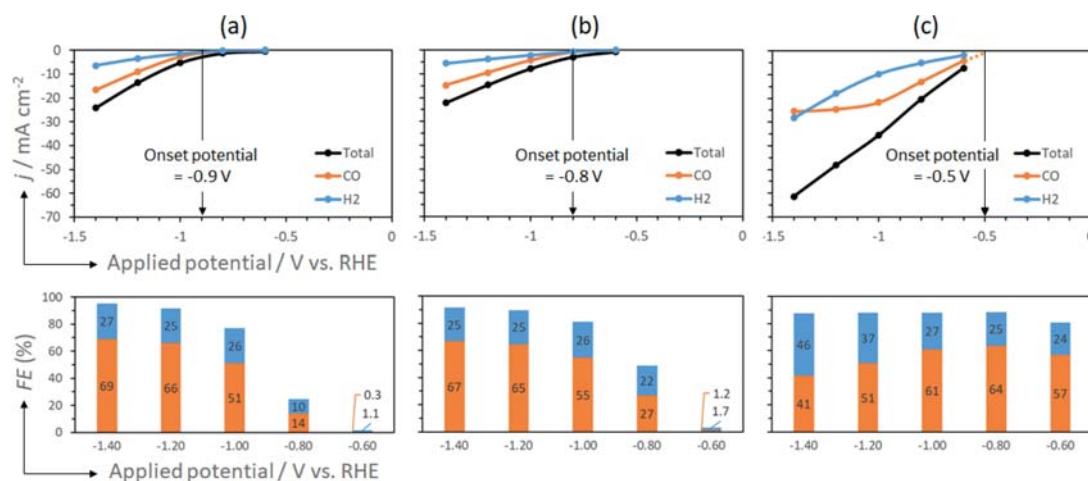


Figure 6. Applied potential dependence of current density (j), onset potentials for the partial current density of CO formation (upper row figures) and Faradaic efficiency (FE, lower row figures; orange bar: CO, blue bar: H_2) for CO_2ER with Zn-Al LDH in each 1.0 M aqueous solution of (a) KCl, (b) KHCO_3 and (c) KOH.

electrolytes were comparable to 118 mV dec^{-1} , indicating that the first one-electron transfer reaction to CO_2 was RDS regardless of the types of electrolytes, and the low electrical conductivity or low stability of the key $\text{CO}_2^{\cdot -}$ intermediate of Zn-Al LDH caused the low $|j_{\text{CO}}|$. On the other hand, the high affinity for CO_2 or the high basicity of LDH could cause the slow diffusion of CO_2 or proton donors onto the LDH surface, leading to the limitation of $|j_{\text{CO}}|$ at the high overpotential. As shown in Fig. S13b, when the overpotential increased beyond the electron transfer rate-determining range, the Tafel plot curved and the current density saturated at a certain value (approximately 30 mA cm^{-2}) for all electrolyte types, suggesting the existence of a slow RDS in the mass transport process.

Regarding the stability of Zn-Al LDH during CO_2ER under the KCl and KOH electrolytes, a constant current density at all applied potential was observed for 10 min of total reaction time in the chronoamperogram as shown in Fig. S14. However, the longer-term stability test has not been studied because of leaks of electrolyte solution into the gas-phase chamber about 1 hour after starting the reaction. While this problem has been reported to be solved by adjusting the CO_2 supply pressure,⁴⁷ it can also be solved by using a membrane electrode assembly (MEA).^{48,49} Reaction cells using MEAs are called zero-gap cells, where the cell voltage can be minimized by direct contact of GDE with a polymer electrolyte membrane without electrolyte solution in between. Because the zero-gap cell is the most practical reaction system, the application of Zn-Al LDH for MEAs could be a promising future challenge.

3. Conclusions

Gas-phase CO_2ER activity of M^{2+} - M^{3+} LDH was studied using Ni-Al, Ni-Fe or Zn-Al LDHs. The in-situ ATR-IR measurements highlighted that the three LDH samples formed, upon CO_2 adsorption, different families of bidentate carbonates with different strength and stability which are leading to a different reactivity of the samples. The Zn-Al LDH, which showed a different carbonate evolution in in-situ ATR-IR measurements, exhibited the highest CO -forming CO_2ER activity. By using different potassium salt electrolytes affording neutral to strongly basic conditions, such as KCl, KHCO_3 and KOH, the gas-phase CO_2ER with Zn-Al LDH-loaded GDE showed 1.3 to 2.1 times higher partial current density

for CO formation than the liquid-phase CO_2ER . However, the general advantages expected in the gas-phase CO_2ER did not seem to work effectively for CO_2ER by Zn-Al LDH. From the above results, the following prospects are expected to lead to the further development of Zn-Al LDH as a CO_2ER catalyst: control of Zn-Al LDH particle size and exfoliation of laminated Zn-Al LDH for the optimization of its electronic conductivity, affinity for CO_2 , and the high basicity.

Acknowledgments

This research was supported through 4AirCRAFT project under the strategic international cooperation between Europe (Horizon2020, No. 101022633) and Japan Science and Technology Agency (JST) with reference number JPMJSC2102. 4 AirCRAFT project is also supported by The Sao Paulo Research Foundation (FAPESP). We acknowledge the Hercules fund 'Direct electron detector for soft matter TEM' from Flemish Government for the purchase of the K2 DED.

CRedit Authorship Contribution Statement

Ryosuke Nakazato: Formal analysis (Lead), Investigation (Lead), Visualization (Lead), Writing – original draft (Lead)
 Keeko Matsumoto: Investigation (Supporting), Visualization (Supporting)
 Noboru Yamaguchi: Investigation (Supporting)
 Margherita Cavallo: Formal analysis (Supporting), Investigation (Supporting), Visualization (Supporting)
 Valentina Crocellà: Formal analysis (Supporting), Investigation (Supporting), Visualization (Supporting)
 Francesca Bonino: Writing – review & editing (Supporting)
 Matthias Quintelier: Investigation (Supporting), Visualization (Supporting), Writing – review & editing (Supporting)
 Joke Hadermann: Writing – review & editing (Supporting)
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Data Availability Statement

The data that support the findings of this study are openly available under the terms

of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

Funding

EU HORIZON 2020: 101022633

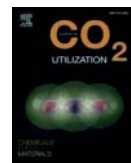
Japan Science and Technology Corporation: JPMJSC2102

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Contents lists available at ScienceDirect

Journal of CO₂ Utilizationjournal homepage: www.elsevier.com/locate/jcou

Insight on Zn-Al LDH as electrocatalyst for CO₂ reduction reaction: An *in-situ* ATR-IR study

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ARTICLE INFO

Keywords:

In-situ ATR-IR spectroscopy
Layered Double Hydroxide
CO₂ reduction reaction
Electrocatalysis

ABSTRACT

Electrochemical reduction of CO₂ (CO₂RR) is expected to play a key role among the various strategies being explored to limit global warming. In this scenario, Layered Double Hydroxides (LDHs) are emerging as a promising class of electrocatalysts to replace the most used noble metals. In this work three Zn-Al LDH with different Zn²⁺/Al³⁺ ratio were synthesized and characterized by means of XRD, STEM-EDX and HR-TEM. Their suitability for CO₂RR to CO was assessed by means of a custom-made three-compartment cell, showing an increase in CO selectivity by decreasing the Zn²⁺/Al³⁺ ratio. The CO₂ interaction with the samples was firstly characterized by means of volumetric adsorption measurements, exhibiting an increase in capture capacity by decreasing the Zn²⁺/Al³⁺ ratio. The evolution of the samples in interaction with a CO₂-saturated liquid flow was then deeply investigated by means of *in-situ* ATR-IR spectroscopy. The samples displayed a different evolution in the vibrational region of the carbonate-like species (1800–1200 cm⁻¹). To better discriminate the different carbonate cyclohexane was also employed. A definitive assignment of the main IR bands of the carbonate was carried out by studying the spectral behavior of the different bands observed in the ATR-IR experiments and by comparing these results with the existing literature. Interestingly, Zn-Al 1:2 LDH, the most efficient electrocatalyst for CO₂RR, is also the sole sample exhibiting a higher monodentate to total bidentate carbonates ratio, suggesting that the existence of a higher content of low coordination oxygen anions with stronger basic character can influence the final catalytic activity.

1. Introduction

In the last centuries, there has been a steady increase in carbon dioxide (CO₂) emissions due to anthropogenic activities. Atmospheric CO₂ concentrations have risen from 277 ppm in 1750 to 410 ppm in 2019, leading to an increase in the global temperature of more than 1 °C [1]. Among the various strategies being explored to limit global warming, Carbon Capture and Utilization (CCU) technologies are expected to play a crucial role, offering the potential not only to mitigate emissions, but also to convert CO₂ into a source of fuels and chemicals [2,3].

Various methods, including thermochemical, biological, photochemical and electrochemical conversion, have been investigated to reduce CO₂ [4]. The thermochemical route, despite being the most

widely used and the most mature technology, requires also the highest heat and pressures [5]. On the other hand, biological and photochemical systems minimize the energetic impact, but the efficiency and selectivity are usually far from large-scale application [6]. In this context, the electrochemical reduction of CO₂ (CO₂RR) presents important advantages, such as easy control of the reaction product and rates by changing the overpotential, mild reaction temperatures and easy separation of the reaction products, by placing the electrodes into individual chambers [7, 8]. Depending on the catalyst and other parameters involved in the reaction, the electrochemical reduction of CO₂ can lead to the formation of various products such as formic acid (HCOOH), methane (CH₄), methanol (CH₃OH), ethylene (C₂H₄), ethanol (CH₃CH₂OH) and carbon monoxide (CO) [8]. Among them, CO is of great interest as it is the

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<https://doi.org/10.1016/j.jcou.2024.102804>

Received 16 February 2024; Received in revised form 3 May 2024; Accepted 10 May 2024

Available online 19 May 2024

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starting point to produce various hydrocarbons and an intermediate for further reduced products [9,10]. The most active electrocatalysts for the selective reduction of CO₂ to CO are Au and Ag, but their high cost and scarcity are drawing attention to the study of lower-cost systems using earth-abundant elements [11,12]. In recent years, layered double hydroxides (LDHs) have been widely studied as promising electrocatalysts, due to their interesting characteristics such as low cost, easy synthesis procedure, tunability of composition, good ionic conductivity, and high alkaline tolerance [13–15]. LDHs or hydrotalcites (HT) structures are characterized by layers of divalent and trivalent cations in octahedral coordination with hydroxyl ions, causing an overall positive charge density which is balanced by the presence of divalent anions which are present in the interlayer along with water. The general molecular formula is $[M(II)_{(1-x)}M(III)_x(OH)_2]^{x+}[A^{n-}]_x mH_2O$ where M(II) and M(III) are respectively the divalent and the trivalent cations, A^{n-} is the anions and x is the fraction of M(III) cation ($x = M(III) / (M(II) + M(III))$). As the temperature is increased, the layered structure slowly collapses to form a mixed oxide configuration (layered double oxide, LDO) and finally a spinel structure. Interestingly, the LDH exhibits a memory effect which allows the original structure to be easily restored by rehydrating the LDO [16]. This feature, together with the versatility of the structures that can be easily modified by changing the metals and the interlayer anions, contribute to making this material suitable for a variety of applications in addition to electrocatalysis [17].

Over the years, LDHs with different metal compositions were proven to be potential electrolytes for alkaline type fuel cells thanks to their high ionic conductivity [18,19] as well as promising catalysts for CO₂ photoreduction [20] and an alternative to IrO₂ and RuO₂ as electrocatalysts for oxygen evolution reaction (OER) [21–24]. More recently, Cu-Al LDH and Cu-Mg-Al LDH were employed for CO₂ reduction to CO/HCOOH and CH₃COOH respectively [25,26]. The potential use of LDHs for the selective reduction of CO₂ to CO was recently evaluated by comparing three Zn-Al LDHs with increasing Zn²⁺/Al³⁺ molar ratios (2:1, 3:1 and 4:1) [27]. The Zn-Al 2:1 LDH was proven to be a promising electrocatalyst for CO₂RR showing a CO selectivity of 77% at 1.4 V vs. RHE in a potassium bicarbonate (KHCO₃) solution. Afterward, keeping the M²⁺/M³⁺ molar ratio constant, the activity of Ni-Al, Ni-Fe and Zn-Al LDHs was compared showing for the latter one the highest CO evolution [28].

Although many studies have been carried out over the years on the composition and preparation of the electrocatalyst, modifications in the electrolyte, variations of the cell design with the ultimate aim of improving the electrochemical activity, little attention has been paid to the detailed characterization of the active sites present in the electrocatalysts and to a deep understanding of the interfacial region. Since the electrochemical reactions take place at the interface between the catalysts and the electrolytic solutions, a deep understanding of the initial structure and of the species formed at the surface is expected to play a central role in the comprehension of the reaction mechanism [29]. Many papers investigated the type, and the strength of the different basic sites present in LDHs by means of IR spectroscopy, distinguishing between the different carbonate-like species formed upon CO₂ interaction [30–34]. However, the pre-treatment of the sample, which modifies the original LDH structure, and the measurement conditions usually employed, lead to a characterisation of the materials in a state far away from their real application. On the other hand, the experimental techniques able to couple electrochemical and IR spectroscopic, which have been widely employed recently [29], still have some limitations in application, in particular: (i) ensuring good conductivity of the system in poorly conducting samples without affecting the actual performance of the catalyst (ii) difficulty in reproducing the results obtained in classical electrochemical cells.

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) demonstrated over the years to be particularly suitable for the study of samples interacting with a liquid interface [35–38]. The strength of this technique compared to other spectroscopic approaches lies in some key

features such as (i) the intrinsically low penetration depth of the IR beam in the sample allows investigating mostly the interfacial region, thus largely avoiding the contribution of the bare liquid phase to the spectrum (ii) the possibility to optimize the signal to noise ratio with multiple reflections [39].

In the present study, three different as-synthesized Zn-Al LDHs having progressively lower M²⁺/M³⁺ molar ratios (2, 1 and 0.5) were electrochemically tested for CO₂RR to CO. The interaction of a CO₂-saturated liquid flow with the three samples was deeply investigated by means of ATR-IR spectroscopy to disclose the existence of different active sites and correlate them with the catalytic activities of the different LDHs.

2. Material and methods

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6 H₂O, 99.0%), aluminum nitrate nonahydrate (Al(NO₃)₃·9 H₂O, 98.0%), sodium carbonate (Na₂CO₃, 99.8%), potassium bicarbonate (KHCO₃, > 99.5%), and sodium hydroxide (NaOH, 97.0%) were purchased from FUJIFILM WAKO PURE CHEMICAL Co. Ethanol (EtOH, > 99.5%) was purchased from Kanto Chemical Co., Inc. Water was purified by a distilled water production system (SHIMIZU SCIENTIFIC INSTRUMENTS MFG Co., Ltd.). An anion exchange membrane (AHA) was purchased from ASTOM Corp. CO₂ gas (>99.5%) was purchased from TAIYO NIPPON SANSO HOKKAIDO Corp. All other solvent and chemicals in reagent grade were purchased and were used without further purification. CO₂ gas (99.995%) was purchased by SAPIO group SRL for the volumetric and spectroscopic measurements, N₂ gas (99.999%) was purchased by SAPIO group SRL and C₆H₁₂ ACS reagent, ≥99%, provided by Sigma-Aldrich were used for spectroscopic measurements.

2.2. Synthetic procedure and fundamental characterization

Zn-Al LDHs (Zn-Al 1:2, Zn-Al 1:1, and Zn-Al 2:1) were prepared using a facile and traditional coprecipitation process [27,28]. Zn(NO₃)₂·6 H₂O and Al(NO₃)₃·9 H₂O were dissolved in deionized water with Zn²⁺/Al³⁺ = 2.0, 1.0, 0.50 mol%. The mixture was dropped into 0.30 M Na₂CO₃ solution with stirring at 353 K. The drop rate was adjusted to 2 mL min^{−1} by using a syringe pump (SPE-1, AS ONE Corp.). The pH of the reaction mixture was adjusted to 10 by adding 2.0 M aqueous NaOH solution with a pH meter (pH700, Eutech Instruments Pte. Ltd.). The obtained solution was aged at room temperature for 24 h. The resulting white precipitate was filtered, washed with distilled water, and dried at 323 K for 24 h. The products were labeled as Zn-Al 1:2, Zn-Al 1:1, and Zn-Al 2:1, corresponding to the starting composition ratio of Zn and Al.

The products were characterized by powder X-ray diffraction (XRD) to identify the crystalline phase. XRD patterns (CuKα) were taken using an XRD diffractometer (Mini Flex 600, Rigaku Corp.).

To check the morphology and the experimental Zn:Al ratio STEM-EDX measurements were performed. The samples were dissolved in ethanol and sonicated for 10 minutes before being drop-casted on a standard TEM grid. STEM-EDX experiments were performed using a ThermoFisher Osiris microscope operated at 200 kV and equipped with a SuperX detector. BF-TEM experiments were performed using a ThermoFisher Tecnai G2 microscope operated at 200 kV and equipped with a Gatan US1000XP CCD camera. HR-TEM images were taken using an image corrected ThermoFisher Titan microscope operated at 300 kV and equipped with a Gatan K2 direct electron detector.

2.3. Electrocatalytic CO₂RR experiment

On the three synthesised samples, the electrocatalytic CO₂RR experiments were carried out by using a custom-made three-electrode setup composed of a three-compartment cell (see Figure S1) [28]. The

cathodic and anodic compartments were separated by a piece of the anion exchange membrane to avoid the unexpected influence of the oxidation reaction taking place on the counter electrode. The LDH-loaded gas-diffusion electrode (GDE) and a platinum mesh electrode (35 × 25 mm, LAKE SHORE CRVOTRONICS Inc.) were used as working and counter electrodes, respectively. The LDH-loaded GDE was prepared by simple drop-casting of the catalyst ink on a gas-diffusion layer (GDL: Sigracet 36BB, SGL CARBON JAPAN Ltd.). The catalyst inks were prepared by mixing 4 mg of LDH ground for 5 min with 1 mg of the conductive aid (carbon black: Vulcan XC72, CABOT Corp.) and 30 μL of the binder (Nafion solution, SIGMA-ALDRICH Co. LLC) in 570 μL of ethanol and sonicating for 10 min. The catalyst ink was drop-casted to the GDL on a hot plate pre-heated at 353 K. The ink coating area was 1.89 cm², whose shape was a 1.55 cm diameter circle and the loading level of the LDH was 2.1 mg cm⁻². The LDH-loaded GDE was further dried at 353 K for at least 30 min to remove the solvents. Ag/AgCl (3.0 M KCl, BAS Inc.) electrode was used as a reference. An aqueous solution (0.10 M) of KHCO₃ was used as an electrolyte. The CO₂ gas flowed with a 50 mL min⁻¹ flow rate and 0.10 MPa inlet pressure to the cathodic compartment, while the solution in the reference electrode compartment was stirred at 600 rpm with a PTFE stirring bar. Under the above conditions, CO₂ electrolysis for 10 min was performed by applying a voltage with an electrochemical analyser (IviumStat, IVIUM TECHNOLOGIES B.V.). Gas-phase products were detected by gas chromatography techniques (GC-2014, SHIMADZU Corp.; carrier gas: nitrogen, flow rate: 10 mL min⁻¹, pressure: 53.2 kPa, vaporization chamber temperature: 393 K). For the detection of hydrogen (H₂), Molecular Sieve 5 A (GL SCIENCES Inc.; column temperature: 323 K, injected sample volume: 1 mL) and a thermal conductivity detector (TCD, SHIMADZU Corp.; detector temperature: 393 K) were used. For the detection of CO and gaseous hydrocarbons, PoraPak N (GL SCIENCES Inc.; column temperature: 323 K, injected sample volume: 1 mL) for a flame ionization detector (FID, SHIMADZU Corp.; detector temperature: 393 K) were used. Electrode potentials in the study were converted to the reversible hydrogen electrode (RHE) according to the following equation (Eq. 1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.222V + 0.059 \quad \text{xpH} \quad (1)$$

All potentials and voltages in this work were evaluated without IR calibration. The Faradaic efficiency (FE) for CO and H₂ was calculated based on the Eq. 2 [40]:

$$\text{FE} = \frac{2Vp \text{ rF}}{\text{IRT}} \quad (2)$$

Where *V* was the volume concentration of CO or H₂ in the produced gas from the reaction cell. *I* (mA) was the average current during the reaction, and *r* was the CO₂ flow rate (m³ s⁻¹) at ambient temperature and pressure. For the other constants in the formula, *p* was 1.013 × 10⁵ Pa, *F* was 96485 C mol⁻¹, *R* was 8.3145 J mol⁻¹ K⁻¹, and *T* was 298 K.

2.4. Advanced Characterization

A deep spectroscopical investigation was performed on the three Zn-Al LDHs to identify possible differences in active sites on the different samples.

A first preliminary investigation of the materials affinity for CO₂ was performed by evaluating the CO₂ capture capacity, by collecting adsorption/desorption isotherms. The measurements were performed at 308 K using a Micromeritics 3Flex sorption analyzer. The temperature was kept constant thanks to a Thermoelectric Cooled Dewar (ISO Controller) provided by Micromeritics. This measurement temperature was chosen due to the better temperature stability observed with this setup under these conditions. The samples were previously pre-treated under vacuum at 353 K for 4 h. This activation temperature was carefully chosen to preserve the LDH original structure, by examining the

variable temperature X-ray diffraction (VT-XRD) pattern of the Zn-Al 2:1 sample. The VT-XRD was performed between room temperature and 723 K using a SmartLab diffractometer (Rigaku, CuK1, λ = 1.541 Å). The temperature ramp was set at 5 K min⁻¹ and the diffractograms were collected in isothermal condition every 10 K. Raman spectra were collected on a Renishaw inVia Raman microscope spectrometer. A diode laser emitting at 785 nm was used while photons scattered by the sample were dispersed by a 1200 lines/mm grating monochromator and simultaneously collected on a CCD camera. The collection optic was set at 50X objective, and the spectral collection consisted of 10 acquisitions, each of 10 s. The spectra of the three LDH samples were obtained by summing up three different spectra.

In-situ ATR-IR measurements were performed with a Bruker Invenio Fourier transform spectrometer to investigate the effect of the interaction of CO₂ with the LDH samples. The spectrometer is equipped with a MCT cryo-detector (Mercury Cadmium Telluride) which operates at liquid nitrogen temperature (~77 K). During the test, each collected spectrum consists of an average of 32 scans (64 for the background spectrum). The ATR-IR measurements were carried out using a commercial horizontal ATR mirror unit and cell (HATR, Horizontal ATR accessory provided by Pike Technologies) equipped with an AMTIR single crystal (internal reflection element 80 × 10 × 4 mm, 45°, Specac). Prior to each measurement, LDH samples were suspended in deionized H₂O (~10 mg per 0.5 mL), deposited on the crystal and dried overnight at room temperature. The ATR-IR spectra of the dried samples were collected before each experiment. The structural interlayer carbonates were identified, and the underlying area was used to normalize the following LDH spectra.

The ATR cell was then flushed with liquid H₂O saturated with N₂ which was supplied through a mass flow controller with a flow rate of 15 mL min⁻¹. H₂O and N₂ were circulated over the deposited LDH at room temperature for 30 minutes to verify the stability of the sample deposition. The circulation was controlled through a peristaltic pump operated at 2.0 mL min⁻¹. The inlet gas was then switched to CO₂ and a CO₂-saturated liquid H₂O flow was circulated over the sample for another 30 minutes (a schematic representation of the setup is reported in Scheme 1).

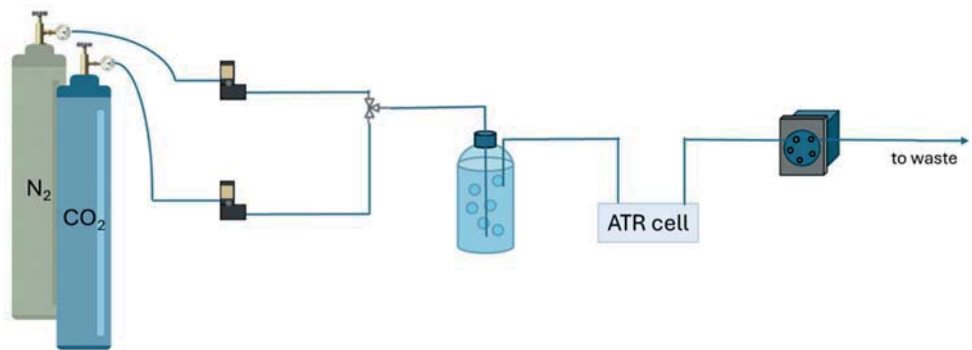
The same experiment was repeated with cyclohexane instead of H₂O to further characterize the sample. Based on those results, a band fitting of the carbonates-like species formed on the LDH structure was performed by means of the FIT routine by Bruker, which allows the interactive search for the best fit to the examined experimental spectral segment based on several spectral components imposed by the operator. Once the spectral position and all the major spectral parameters (half-bandwidth, percent of Gaussian profile) have been fixed, the remaining ones were allowed to float freely. Lastly, the carbonates evolution in time was studied by making a fitting of the carbonates originated from the CO₂-saturated H₂O flow at 0,7,5,15, 22.5, 30 minutes. The underlying area of each couple of carbonates was calculated and reported in histograms.

3. Results and discussion

XRD patterns were first collected to check the crystalline structure of the synthesized LDHs (Figure S2). For all the samples, the (003) and (006) plane reflections, characteristic of the layered structure, were observed and were assigned to the previously reported XRD pattern of Zn-Al LDH with carbonate (CO₃²⁻) as interlayer anions [41], without other impurity peaks.

In Fig. 1 BFTEM, HRTEM and STEM-EDX maps are shown. The BF TEM analysis (Fig. 1a-c) revealed the typical hexagonal particles morphology in all LDH samples. The three samples show differences in particle size and mean particle thickness, HR-TEM also revealed variations in the mean basal spacing (see Table S1 for the values).

STEM-EDX elemental analysis (Fig. 1g-i) yielded mean Zn:Al ratios of 1.96(25), 1.56(20), and 1.19(38) for Zn-Al 2:1, Zn-Al 1:1, and Zn-Al 1:2,



Scheme 1. Schematic representation of the set-up used during the in-situ ATR-IR measurement.

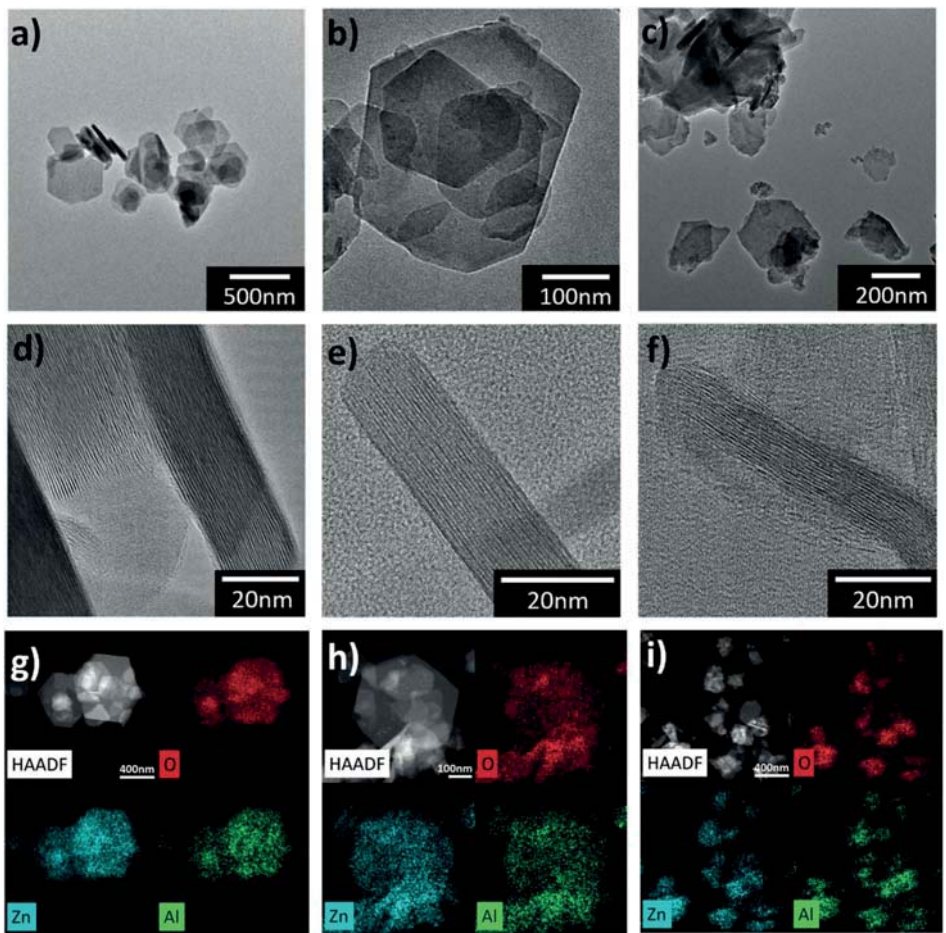


Fig. 1. (top) BF-TEM (middle) HR-TEM images and (bottom) HAADF-STEM elemental maps of Zn-Al 2:1 (a,d,g), Zn-Al 1:1 (b,e,h) and Zn-Al 1:2 (c,f,i). All maps are given in counts.

respectively. In the Zn-Al 1:1 and Zn-Al 1:2 samples there were also smaller particles present that contained only aluminum. This could explain the deviation of the measured mean Zn:Al ratio from the

expected value. Considering that no impurity peak was observed in the XRD pattern, the particles containing only aluminum were ascribed to amorphous alumina.

The potential application of Zn-Al LDHs as electrocatalysts for CO₂RR to CO was then evaluated by means of a three-compartment cell (see Figure S1). The electrocatalytic CO₂RR was performed at the applied potentials of -0.60 to -1.40 V vs. RHE in 0.1 M aqueous KHCO₃ solution as a typical electrolyte. The applied potential dependence of current density (j) and Faradaic efficiency (FE) are shown in Fig. 2.

Fig. 2 shows that the catalytic currents were observed and increased with more negative applied potentials in all the samples. The main gaseous products for all the Zn-Al LDHs were CO and H₂, and the partial current densities of CO evolution tended to be larger in the case of Zn-Al 1:1 and Zn-Al 1:2 than in the case of Zn-Al 2:1 while the total current density and the partial current density of H₂ evolution were larger in the order Zn-Al 2:1 > Zn-Al 1:1 > Zn-Al 1:2, thus H₂ evolution tended to be suppressed for smaller Zn/Al ratios. The suppression of H₂ evolution mainly contributed to the increase of FE of CO evolution (FE_{CO}) with decreasing Zn/Al ratios, which were 11, 37, and 40% at -1.4 V vs. RHE for Zn-Al 2:1, Zn-Al 1:1, and Zn-Al 1:2, respectively. On the other hand, the FE of H₂ evolution (FE_{H_2}) decreased with decreasing Zn/Al ratios, which were 73, 48, and 42% at -1.4 V vs. RHE for Zn-Al 2:1, Zn-Al 1:1, and Zn-Al 1:2, respectively. These results show a progressive suppression of H₂ evolution in favor of CO by decreasing the Zn/Al ratio, reaching the best performances for Zn-Al 1:2. Additionally, the STEM-EDX elemental analysis suggests that amorphous alumina detected in Zn-Al 1:1 and Zn-Al 1:2 could contribute to the suppression of H₂ and to the parallel promotion of CO evolution. Even if alumina itself is basically inert to electrochemical reactions, [42,43] low alumina content in oxide matrices or as a catalyst surface modifier has proven to be also beneficial

since tuned properties such as active chemical sites enhancement and oxidation capacity can be achieved [42–46]. In this sense, stronger oxidation capacity could accelerate the production of reactive oxygen species (O^{2-} , O_2 and O^-) [46]. Therefore, amorphous alumina contained in Zn-Al 1:1 and Zn-Al 1:2 could also contribute in the enhancement of CO evolution

The three LDHs were then deeply characterized to investigate possible differences in their active sites.

The CO₂ adsorption capacities of the Zn-Al LDHs was investigated by collecting volumetric CO₂ adsorption isotherms at 308 K (Figure S3). Prior to the measurements, the samples were activated at 353 K for 4 h in vacuum. To prove that the original LDH structure is still preserved under those activation conditions, a VT-XRD experiment was performed on the Zn-Al 2:1 sample (Figure S4). The reflections associated to the LDH structure disappeared between 373 and 423 K. However, since the activation prior to the volumetric measurements is performed under more severe conditions (i.e., in vacuum and not under inert gas flow), the selected safety temperature for the pretreatment was lower than 373 K.

Although the overall CO₂ uptake at 308 K is low (< 0.5 mmol/g) for all samples, the three LDHs exhibit the following CO₂ adsorption trend: Zn-Al 1:2 >> Zn-Al 1:1 > Zn-Al 2:1. Even if the volumetric measurements are performed with pure CO₂ in gas phase (i.e. far from the real catalytic conditions), they provide a first insight into the different affinity of materials for CO₂. It is worth noting that Zn-Al 1:2, displaying the best catalytic performances, has also the highest CO₂ capture capacity. This behavior suggests that a peculiar CO₂ adsorption

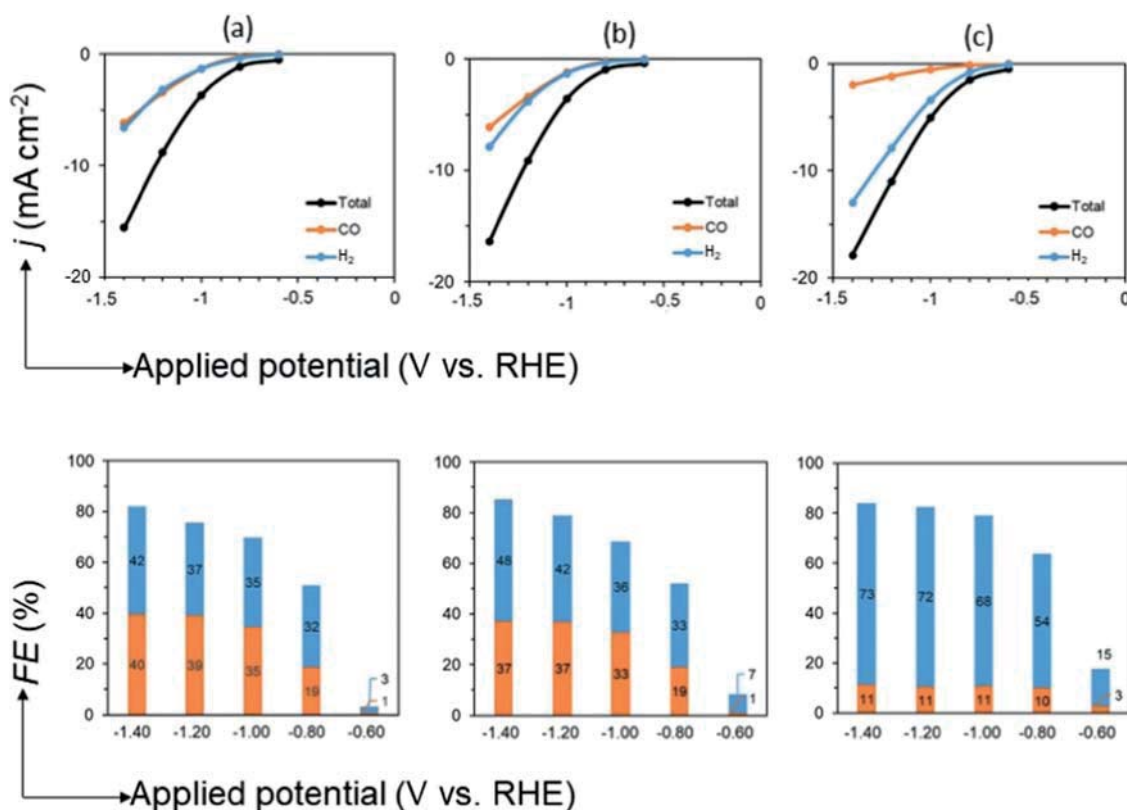


Fig. 2. Applied potential dependence of current density (j , upper row figures) and Faradaic efficiency (FE , lower row figures; orange bar: CO, blue bar: H₂) for CO₂RR in 0.10 M aqueous KHCO₃ solution with (a) Zn-Al 1:2, (b) Zn-Al 1:1, and (c) Zn-Al 2:1.

mechanism occurs in Zn-Al 1:2 sample. Therefore, a further investigation of the CO₂ interaction mechanism in conditions closer to the electrocatalytic ones was carried out by means of in-situ ATR-IR spectroscopy.

To have a clear overview of the different species involved, the spectra of the dried depositions (i.e. obtained on the ATR-IR crystal after solvent evaporation, as reported in the experimental section) were first collected and analyzed (Fig. 3).

All the samples exhibit a broad band at high wavenumbers (3900–2500 cm⁻¹) ascribable to the hydroxyl stretching vibrations. In this spectral region three main contributions could be identified: i) the -OH stretching vibration of structural M-OH (M = Zn or Al) species (3500–3400 cm⁻¹); ii) OH stretching vibrations of the interlayer H₂O molecules (3300–3100 cm⁻¹); and iii) OH stretching vibrations perturbed by the bridging mode of CO₃²⁻ - H₂O species located in the interlayer (3050–2950 cm⁻¹) [47,48].

In the low frequency region (1000–650 cm⁻¹), another broad band can be identified in all the LDH samples. This signal results from the overlapping of the ν_2 out of plane stretching mode of structural interlayer CO₃²⁻ carbonate anions (at ~860 cm⁻¹) and of the lattice HO-M-OH and M-OH (450–800 cm⁻¹) vibrations [49,50].

Lastly, in the intermediate spectral region (1800–1200 cm⁻¹), a band at 1640 cm⁻¹, attributed to the bending vibrations of the structural interlayer water molecules and physisorbed water, and a band at about 1400 cm⁻¹, corresponding to the asymmetric stretching ν_3 mode of the

structural interlayer CO₃²⁻, were observed [51]. Interestingly, there is lower wavenumber component (~1365 cm⁻¹) in this last band. As reported by Labajos and al., [52] the interaction of the carbonate ions with water in the interlayer is responsible for a decrease in symmetry compared to the free carbonate ion leading to a splitting of the ν_3 asymmetric stretching bands. The different components just described are highlighted in the band fitting of the 1800–1200 cm⁻¹ region, shown in Figure S5. A further proof of this phenomenon is the clear appearance of the ν_1 symmetric stretching band at 1060 cm⁻¹ in the spectrum of Zn-Al 1:2. This signal is usually IR inactive, but it could be activated by the symmetry change of the interlayer carbonates.

The other bands in the 1550–1480 cm⁻¹ range originate from the formation of surface (non-structural) carbonate-like species, due to the exposure of the material to the atmospheric CO₂. These signals could be removed by performing a high temperature pre-treatment, but as mentioned above, the original LDH structure is only preserved if the temperature does not exceed 373 K.

The mid-IR spectral range of the three samples perfectly match with the Raman spectra (Table S2 and Figure S6), where the ν_1 CO₃²⁻ symmetric stretching is clearly visible at 1061 cm⁻¹, while the other two less intense Raman-active carbonates vibrations at 680 cm⁻¹ (ν_4 in-plane deformation) and 1415 cm⁻¹ (ν_3 asymmetric stretching) were not observed due to their weak nature and the partial fluorescence of the samples [51]. At lower wavenumbers, two narrow bands were observed at 553 cm⁻¹ and at 480 cm⁻¹, attributed to the Al-O-Zn and Al-O-Al

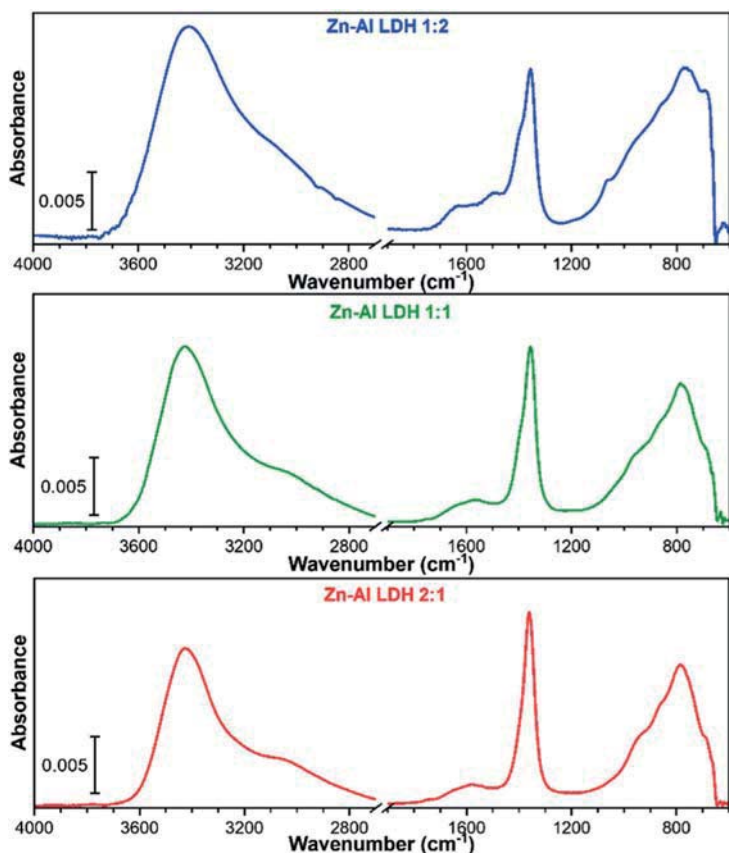


Fig. 3. ATR-IR spectra of the dried samples of Zn-Al 1:2 (blue curve), Zn-Al 1:1 (green) and Zn-Al 2:1 (red curve). The spectra were normalized by the underlying area of the structural interlayer carbonates (Fig. S5).

vibrational modes, respectively, [53]. The signal at 153 cm⁻¹, previously observed by Palmer et al., can be assigned to vibration modes involving the hydrotalcite OH units and the water molecules in the interlayer [53]. At higher wavenumbers, the fluorescence is preventing a clear identification of the main components.

After investigating the main bands present in the different spectra of dried Zn-Al LDHs depositions, the interaction of the samples with a CO₂-saturated H₂O flow was examined by means of ATR-IR spectroscopy, following the methodology described in Section 2.2 (Fig. 4a-c).

The interaction of CO₂-saturated liquid H₂O leads to the appearance of a variety of signals in the 1800–1200 cm⁻¹ spectral region, usually associated with carbonate-like species originating from the interaction of CO₂ with the basic LDH sites [51]. As previously mentioned, when the symmetry of the free carbonate ions is lowered, the original ν_3 asymmetric CO₃²⁻ stretching band at around 1415 cm⁻¹ present in the LDHs spectra (Fig. 4) splits in two distinct components (the symmetric $\nu_{3\text{sym}}$ and the asymmetric $\nu_{3\text{asym}}$ vibrations). Depending on the type and strength of the surface sites, different carbonate-like species are formed resulting in a complex carbonate evolution spectral profile.

The spectrum of Zn-Al 1:2 shows a rapid increase of the bands at ~1340 cm⁻¹, followed by a gradual increment of the signal at 1520 cm⁻¹. This latter band probably overlaps to another signal at lower wavenumbers (approximately 1450 cm⁻¹), rising with a similar trend. Additionally, the broadness of the band related to the HOH bending

vibrations at 1640 cm⁻¹ also suggests the existence of other spectral components superimposed at higher wavenumbers. The spectra collected at higher CO₂ coverage (colored curves) display an unusual minimum at 1363 cm⁻¹, which further complicates the identification of the different components, especially for Zn-Al 1:1 and Zn-Al 2:1 LDHs. This downwards band will be discussed in detail later on.

The Zn-Al 1:1 sample shows, similarly to Zn-Al 1:2, a first increase of the 1340 cm⁻¹ band followed by the rise of a broad band in the 1580 and 1400 cm⁻¹ spectral region. Unfortunately, this sample exhibits an important minimum at 1363 cm⁻¹ which partially hides a probable second component at around 1450 cm⁻¹ and leads to a difficult identification of the real maxima of the different spectral components. For Zn-Al 1:1 and even more for Zn-Al 2:1, the carbonates evolution seems to be lower compared to Zn-Al 1:2, especially for the bands between 1580 and 1400 cm⁻¹ which are nearly absent for Zn-Al 2:1. Indeed, for this sample the prevalent band is the HOH bending at 1640 cm⁻¹, together with the presence of the minimum at 1363 cm⁻¹.

Notably, all samples show a decrease in intensity at 1363 cm⁻¹, leading to the appearance of negative bands for Zn-Al 1:1 and Zn-Al 2:1. Since the vibrational frequency of this negative signal coincides with that of the structural interlayer carbonates (see comparison in Figure S7), it is likely due to a loss of deposition by the crystal, generated by the CO₂-saturated H₂O flow. To minimize the risk of deposition loss and to better appreciate the carbonates bands hidden by the presence of

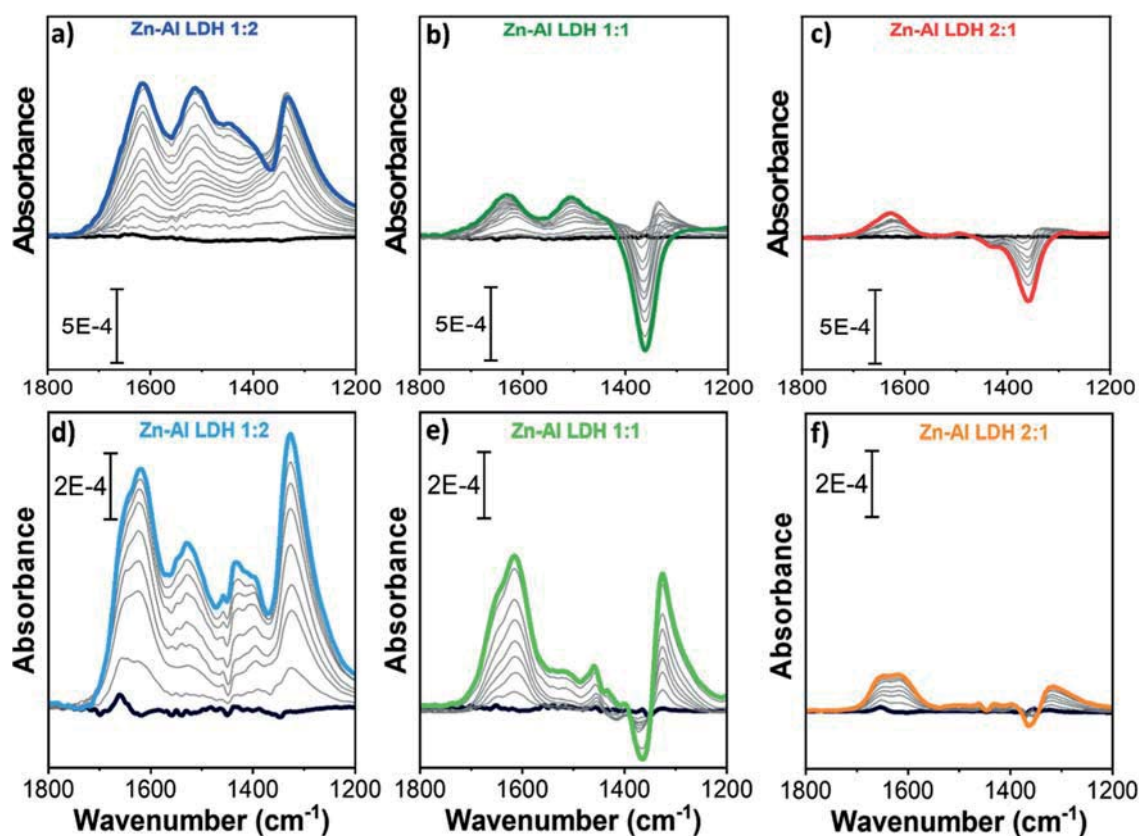


Fig. 4. *In-situ* ATR-IR spectra in the carbonate-like region (1800–1200 cm⁻¹) of Zn-Al 1:2 (a, d), Zn-Al 1:1 (b, e) and Zn-Al 2:1 (c, f) under a CO₂-saturated H₂O flow (a, b and c) and under a CO₂-saturated C₆H₁₂ flow (d, e and f). The spectra are reported by subtracting the spectra of the wet N₂-saturated sample to that of the wet (H₂O) CO₂-saturated one (a, b and c) or wet (C₆H₁₂) CO₂-saturated one. The black and coloured curves represent the wet (H₂O/C₆H₁₂) N₂-saturated and wet (H₂O/C₆H₁₂) CO₂-saturated samples, respectively. The curves of intermediate CO₂ coverages are shown in grey. The spectra were normalized by the underlying area of the structural interlayer carbonates (Fig. S5).

the intense HOH bending mode at 1640 cm^{-1} , a different solvent was used.

Even though water was chosen as the solvent closest to the reaction conditions, to further investigate the formation of carbonates upon CO₂ adsorption, the same tests were repeated in C₆H₁₂ (experimental procedure reported in Section 2.2 and Fig. 4d-f).

The three samples show a carbonates spectral evolution coherent with what was previously observed for CO₂-saturated H₂O flow (see comparison in Figure S8) but with a higher spectral resolution. The IR spectra collected in C₆H₁₂ are characterized by a band at 1448 cm^{-1} ascribed to the CH₂ scissoring bending mode [54]. However, considering the medium-weak intensity of this signal, it does not preclude the investigation of the carbonates spectral region. As previously observed in H₂O, upon contact with CO₂-saturated C₆H₁₂ flow, the spectrum of Zn-Al 1:2 sample (Fig. 4d) shows an increase of the band at $\sim 1340\text{ cm}^{-1}$ along with an increment of the signals in the $1700\text{--}1600\text{ cm}^{-1}$ range, now clearly displaying the presence of two distinct and well-resolved components at 1616 cm^{-1} and 1660 cm^{-1} . The band at 1340 cm^{-1} is characterized by a tail at low frequencies, confirming the existence of an additional component. The $1600\text{--}1370\text{ cm}^{-1}$ region also gradually increases in intensity, revealing the presence of two distinct components, although the presence of the CH₂ bending mode prevents a clear identification of the maxima. Similarly, Zn-Al 1:1 shows a first increase of the bands at 1616 and 1340 cm^{-1} followed by the increment of the bands at 1660 cm^{-1} . The latter can probably be coupled with a component falling between 1340 and 1200 cm^{-1} , as suggested by the asymmetric shape of the band with apparent maximum at 1340 cm^{-1} . An increase of the bands in the $1600\text{--}1370\text{ cm}^{-1}$ spectral region is also observed, although less pronounced than in Zn-Al 1:2. Lastly, the Zn-Al 2:1 spectrum is characterized by a scarce evolution of the carbonates bands.

For all samples, a spectral minimum at 1363 cm^{-1} was detected, but less pronounced than that observed in the water stream, suggesting a higher stability of the sample deposition when in contact with a C₆H₁₂ solution.

By looking at the whole carbonate spectral profile, Zn-Al 1:2 displays a greater carbonates evolution than Zn-Al 1:1 and Zn-Al 2:1 in both H₂O and in C₆H₁₂. Interestingly, this result agrees with the volumetry data collected at 308 K, where Zn-Al 1:2 LDH shows a CO₂ capture capacity at 1 bar higher than for Zn-Al 1:1 and Zn-Al 2:1 (50% and 75% respectively). Another interesting finding is the possibility to better appreciate the existence of two IR components when the experiment is carried out in C₆H₁₂ flow: one with an apparent maximum at 1660 cm^{-1} and another between 1340 and 1200 cm^{-1} , which were weakly detectable in the tests performed in H₂O. These bands can be associated to a basic oxygen, which preferentially interacts with H₂O rather than CO₂. For this reason, the interactions with these sites are only distinguishable when the experiments are carried out in C₆H₁₂. It is worth noting that the increase of those new spectral components is associated with a decrease of the signals in the $1580\text{--}1370\text{ cm}^{-1}$ range, suggesting that a family of carbonates forms at the expense of another.

After the spectroscopic study of the interaction of the CO₂-saturated H₂O and C₆H₁₂ flows with the three samples (Fig. 4), the main carbonate-like species generated by CO₂ adsorption were tentatively assigned (Fig. 5 and Figure S9 and section S6 for the fit parameters). A fit of the main families of carbonates was performed, keeping the position of the structural interlayer H₂O and CO₃²⁻ components fixed (see Figure S5 and Figure S9 for the resulting fit and section S6 for the fit parameters in the SI).

As reported above, CO₂ can interact with basic sites or acid-base couples forming carbonate-like species, whose main signals are detected in the $1800\text{--}1200\text{ cm}^{-1}$ spectral range and originate from the decoupling of the original ν_3 asymmetric CO₃²⁻ signal at 1415 cm^{-1} , related to the free carbonate ion, into two stretching bands (symmetric and asymmetric carbonate components) [51]. The distance between those two “new” stretching components ($\Delta\nu_3$) is usually inversely proportional to the basic strength of the sites available in the material. Indeed, the monodentate carbonates, which have low coordination oxygen anions and account for the strongest basic sites, usually display a

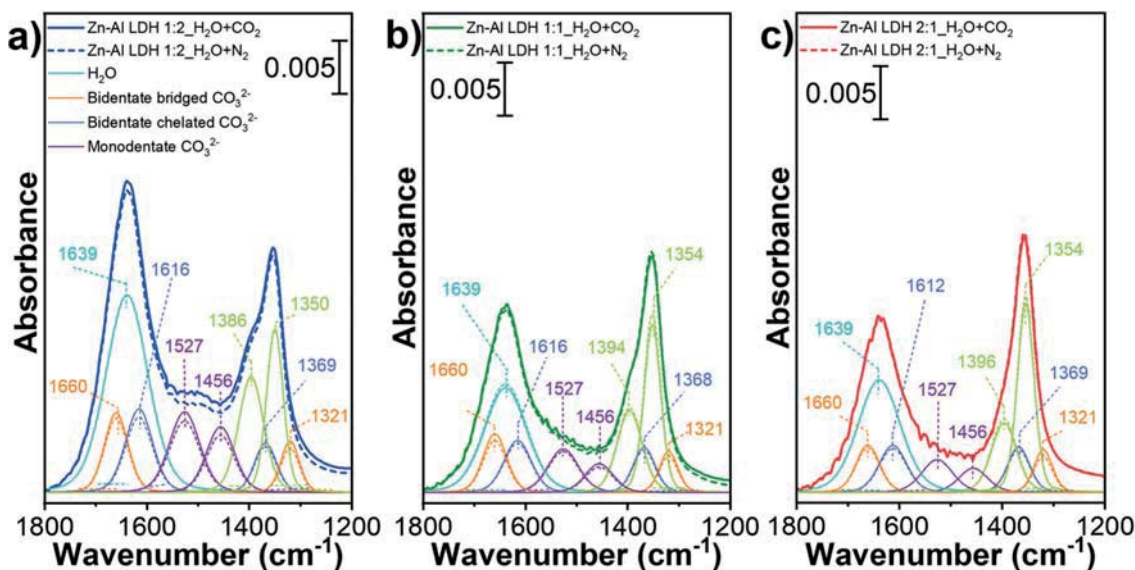


Fig. 5. Band fitting of carbonate-like species species of IR spectra collected under N₂-saturated and CO₂-saturated H₂O flows in the $1800\text{--}1200\text{ cm}^{-1}$ range. The spectral components of distinct carbonates species are evidenced by different colours: orange - Bidentate bridges (Bb), indigo - Bidentate chelated (Bc) and violet - Monodentate (M). The dashed curves refer to the spectrum and relative components of the wet N₂-saturated sample, while the solid curves refer to the spectrum and relative components of the wet CO₂-saturated samples (i.e. the maximum CO₂ loading reached after 30 minutes). The components of asymmetrical vibration of structural carbonates are reported in light green and the component of bending vibrations of structural and physisorbed water is reported in light blue. The resulting fit is reported in Fig. S9 and in section S6 for fit parameters.

$\Delta\nu_3$ of $\sim 100\text{ cm}^{-1}$. The bidentate carbonate-like species, which form on acid–base pairs ($\text{Zn}^{2+}\text{-O}^{2-}$ or $\text{Al}^{3+}\text{-O}^{2-}$) and constitute the intermediate strength basic sites, usually show a $\Delta\nu_3$ of $\sim 300\text{ cm}^{-1}$ for the chelated ones and of $\sim 400\text{ cm}^{-1}$ for the bridged ones (see Table S3 for a sketch of the different carbonate-like species) [30,34,51,53]. Lastly, the other carbonates can form upon CO₂ interaction as bicarbonates or polydentate species. Bicarbonates are easily discernible due to the presence of the characteristic, sharp C–OH bending (δ_{OH}) mode in the 1225–1240 cm^{-1} spectral range and are usually weakly bonded, while polydentate species in gas phase are usually strongly resistant to degassing conditions [51,55].

The assignment of carbonate species based on $\Delta\nu_3$ is not always straightforward, since the band frequencies can be affected by the polarizing power of the metal cations, the composition of the material, the presence of water and/or cations external to the metal coordination sphere, and many other factors [51,56,57]. However, the identification of the main carbonate species formed on LDHs reported in the literature is reasonable following the values of $\Delta\nu_3$ reported above (See Table S2) [31–34,58,59]. Di Cosimo et al. [31], who investigated the interaction of CO₂ with Mg–Al mixed oxides having different molar ratios (0.5–9.0), reported the presence of unidentate carbonates at 1510–1560 cm^{-1} (asym $\nu\text{O-C-O}$) and at 1360–1400 cm^{-1} (sym $\nu\text{O-C-O}$) with a $\Delta\nu_3$ in the range of 200–110 cm^{-1} . The bidentate carbonates were detected at 1630–1610 cm^{-1} (asym $\nu\text{O-C-O}$) and at 1340–1320 cm^{-1} (sym $\nu\text{O-C-O}$) with a $\Delta\nu_3$ of 310–270 cm^{-1} , while bicarbonate species show two bands at 1650 cm^{-1} and at 1480 cm^{-1} together with the appearance of the C–OH bending mode at 1220 cm^{-1} . Comparable frequencies were reported in a similar system by León et al. [32] where, unlike to Di Cosimo et al., two different families of unidentate carbonates and both chelated and bridged bidentate species were detected. Perez-Ramirez et al. [33] reported the presence of monodentate and bidentate chelated carbonates having a $\Delta\nu_3$ lower than the previously mentioned authors, while Coenen et al. [34], who investigated a K promoted Mg–Al mixed oxide in the presence of wet CO₂, mainly reported the appearance of bidentate species. Although the literature data reported above could be a good starting point for the assignment in this paper, all of them deal with the study of the carbonates formation in the gas phase on pre-calcined LDH samples, and are therefore far from the conditions reported here (contact with a CO₂ saturated liquid phase). To develop a consistent identification of the carbonate bands of this work, a correlation between the evolution of the bands observed upon CO₂ contact in both H₂O and C₆H₁₂ was found (Fig. 4).

Consequently, the main bands have been assigned, mainly referring to the work of Debecker et al. [30], in the following way: (i) signals at 1527/1456 cm^{-1} to asymmetric and symmetric O–C–O stretching of monodentate carbonates (Md), (ii) components at 1616–1612/1368–1369 cm^{-1} to asymmetric and symmetric O–C–O stretching of bidentate chelated (Bc) carbonate and (iii) bands at 1660–1321 cm^{-1} to asymmetric and symmetric O–C–O stretching of bridged (Bb) carbonates. The absence of the characteristic δ_{OH} in the 1225–1240 cm^{-1} spectral range suggests the non-presence of bicarbonates even if the presence of the liquid phase complicates their identifications [60]. This assignment agrees with the bands evolution observed in the differential spectra (Fig. 4a–c). In particular, the couple of bands assigned to Md carbonates (orange components at 1527 and 1456 cm^{-1} in the band fitting of Fig. 5) exhibits a similar spectral behaviour in the differential spectra, which in contrast, differs from the evolution of the components associated with Bc carbonates (indigo signals at 1616–1612 and 1368–1369 cm^{-1} in the band fitting of Fig. 5). The Bb carbonates bands (violet bands at 1660 and 1321 cm^{-1} in the band fitting of Fig. 5) are in the same position at which new components were observed in the C₆H₁₂ tests. It is worth recalling that the same signals were hardly detected in the presence of H₂O. This is consistent with the fact that bidentate carbonates formation requires a coordination vacancy to be available in the same coordination sphere of a basic

oxygen. This circumstance is favoured only at higher degree of dehydration [55].

As previously pointed out, due to the low intensity of the signals, the carbonate evolution in the samples could be noticed only by subtracting the spectra of the wet N₂-saturated sample from the wet CO₂-saturated one. Indeed, the not-subtracted ATR-IR spectra show only few differences in the intensity of the various components (see difference between solid and dashed spectra in the whole range of Fig. 5). To better appreciate the evolution of the carbonate species over time, the band fitting of the spectra at intermediate CO₂ coverage (collected each 7.5 minutes after the switch of N₂ to CO₂) was performed and the area of the different carbonates spectral components was evaluated (Fig. 6 and Table 1). Even if a comparison of the carbonates evolution among the three samples would probably lead to a wrong interpretation, the change over time within the same sample could be better evaluated. In particular, contrary to what is observed in the other two LDHs, the Zn–Al 1:2 LDH shows a higher amount of Md carbonates compared to Bb and Bc. However, the sum of bidentate species (Bb+Bc) it is always higher than the Md carbonates in all samples. For this reason, to really highlight the differences among the various LDHs in carbonate species formed upon CO₂ interaction, an evaluation of the monodentate to total bidentate carbonates ratio (Md/(Bb+Bc)) must be carried out. Interestingly, the Md/(Bb+Bc) ratio of Zn–Al 1:2 is higher than for the other two samples (0.680 for Zn–Al 1:2 LDH versus 0.466 and 0.416 for Zn–Al 1:1 and 2:1 respectively), testifying a larger contribution of monodentate species in Zn–Al 1:2. By looking at the bidentate species individually, all samples show a higher content of Bc species compared to the Bb carbonates (Bb/Bc ratio of 0.840, 0.857 and 0.811 in Zn–Al 1:2, 1:1 and 2:1, respectively).

With the same criteria, the band fitting was performed to the experiments performed in C₆H₁₂ (Figure S10 and Figure S11 and Section 6 for the fit parameters), showing a behavior comparable to the one observed in the presence of water. Even if the ratios of the intensity of the different carbonate components are different compared to the test in water, the amount of carbonate-like species, and in particular of Md carbonates, of the Zn–Al 1:2 sample is significantly higher than for the other two LDHs (Table S4).

Since the different carbonate species are strictly connected with the strength of the basic sites, the relative intensities of the IR bands of the various carbonates families provides a powerful tool to discriminate among materials with different basic nature. In particular, the prevalence of the Md carbonates in Zn–Al 1:2 is probably related to the presence of a higher content of low coordination oxygen anions having a strong basic character. On the other hand, Zn–Al 1:1 and 2:1, with a lower Md/(Bb+Bc) ratio, are probably characterized by a higher content of acid–base pairs with intermediate basic strength. Interestingly, Zn–Al 1:2 also exhibits a more pronounced difference between the spectra of the CO₂-saturated and N₂-saturated sample, (see solid and dashed spectra of Fig. 5a in the whole range), together with a higher CO₂ adsorption capacity displayed in the volumetric measurements (Figure S3). Those results ultimately suggest not only the presence of stronger basic sites in Zn–Al 1:2, but also an overall higher affinity of this sample towards CO₂.

The different basic sites are expected to play a crucial role in the overall reaction during the electrocatalytic tests. For this reason, the results derived from the spectroscopic investigation of the different species involved in the CO₂ interaction could explain the highest performances of Zn–Al 1:2 in the CO₂RR.

4. Conclusion

In this work, three different Zn–Al LDHs having a Zn²⁺/Al³⁺ ratio of 2.0, 1.0 and 0.50 were synthesized by means of a co-precipitation method and characterized. The possible applicability of those materials for the electrochemical CO₂RR to CO was tested in a custom-made three-compartment cell, using KHCO₃ as electrolytic solution. The two

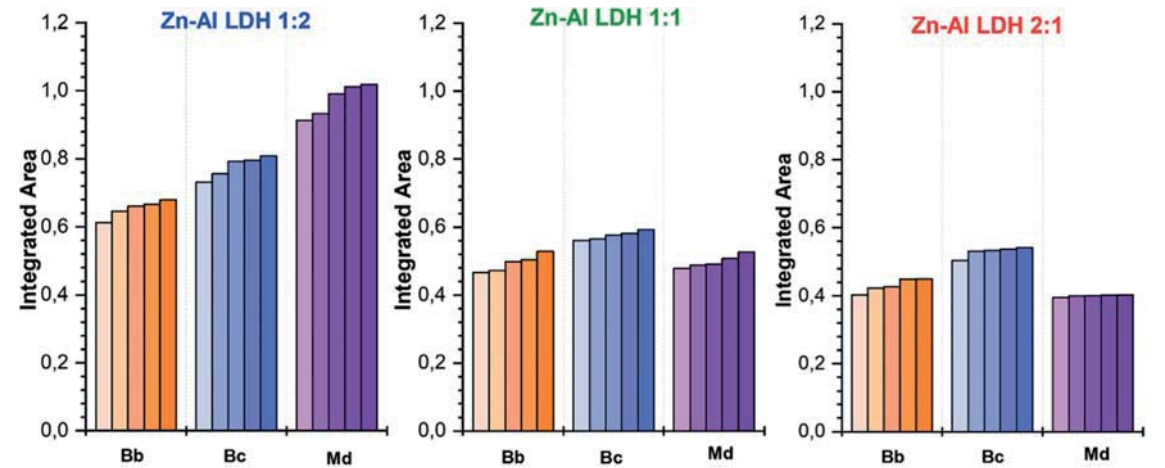


Fig. 6. Evolution of the carbonate species over time. The band fitting of the spectra at intermediate CO₂ coverage (0,7,5,15, 22.5, 30 minutes) was performed (as reported in Fig. 5 for the 0 and 30 minutes coverage) and the area of the carbonates components was evaluated by summing the asymmetric and the symmetric contributions of the same carbonate species. The numbers reported are normalized to the area of the fit of the interlayer carbonates.

Table 1
Evaluation of the carbonate species formed upon the interaction of the samples with a CO₂-saturated H₂O flow. For each sample, the average of the intensities of the histograms in Fig. 6 (Average), the sum of bridged and chelated bidentate (Total Bidentate Bb+Bc), the Monodentate to Bidentate ratio (Md/(Bb+Bc)) and the ratio between the two bidentate species (Bb/Bc) was reported.

	Carbonate species	Average	Bb+Bc	Md/(Bb+Bc)	Bb/Bc
Zn-Al LDH 1:2	Bidentate bridged (Bb)	0.652	1.430	0.680	0.840
	Bidentate chelated (Bc)	0.776			
	Monodentate (Md)	0.973			
Zn-Al LDH 1:1	Bidentate bridged (Bb)	0.493	1.069	0.466	0.857
	Bidentate chelated (Bc)	0.575			
	Monodentate (Md)	0.498			
Zn-Al LDH 2:1	Bidentate bridged (Bb)	0.429	0.959	0.416	0.811
	Bidentate chelated (Bc)	0.529			
	Monodentate (Md)	0.399			

major products formed during the reaction were CO and H₂, which are competitively generated. The selectivity for CO increased by reducing the Zn/Al ratio at the expense of H₂ which progressively decreased till reaching, for Zn-Al LDH 1:2, a selectivity of 40% for CO and of 42% for H₂, under the applied potential of 1.4 V vs. RHE.

To investigate the active sites and their evolution upon a CO₂-saturated liquid flow, an extensive ATR-IR spectroscopic characterization was performed. Firstly, the as-synthesized dried samples depositions were studied by means of IR and Raman spectroscopy, confirming the presence of the vibrational modes usually associated with the hydrocalcite structure. The CO₂ affinity was also evaluated by means of volumetric adsorption measurements, showing, for Zn-Al 2:1 LDH, the highest capture capacity (0.36 mmol g⁻¹ at 308 K and 1 bar).

Afterwards, the evolution of the IR bands of samples in interaction with a CO₂-saturated H₂O flow was investigated, showing peculiar differences in the 1800–1200 cm⁻¹ spectral region, possibly associated with the formation of different carbonate families. The same experiment was also repeated using C₆H₁₂ as a solvent, so reducing the deposition

loss and allowing the discrimination of the different IR components. By considering the evolution of the carbonate bands upon CO₂ interaction in both H₂O and C₆H₁₂, and by comparing them with the literature data, the signals ascribed to the different carbonates families were easily identified. Looking at the ratio between Md carbonates and bidentate one (Md/(Bb+Bc)), the Zn-Al 1:2 LDH shows a greater contribution of monodentate species with respect to the others.

The differences observed in the carbonate families provides a powerful tool to discriminate among materials with different basic sites. Considering the Zn-Al 1:2 LDH, where the Md carbonates prevail, a higher content of low coordination oxygen anions with strong basic character is expected. On the other hand, increasing the Zn²⁺/Al³⁺ ratio, the samples are characterized by a higher content of acid-base pairs with intermediate basic strength. Since the CO₂ adsorption is the first step of the CO₂RR, differences in the basic character and, consequently, in the carbonate formation are expected to play a crucial role in the overall reaction. In addition, since the spectroscopic characterization was carried out without any previous treatment of the samples, the present work could be useful for the study of adsorption processes under more realistic conditions, since, to the best of our knowledge, this is the only work dealing with the study of CO₂ adsorption on LDHs in a water environment.

CRediT authorship contribution statement

Silvia Bordiga: Writing – review & editing, Visualization, Validation, Supervision, Methodology, Funding acquisition. **Joke Hadermann:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Kiyoharu Tadanaga:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Nataly Carolina Rosero-Navarro:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Natale Gabriele Porcaro:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ryosuke Nakazato:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Matthias Quintelier:** Writing – original draft, Visualization, Validation, Methodology,

Investigation, Formal analysis, Data curation. **Matteo Signorile**: Writing – review & editing, Visualization, Validation, Supervision, Methodology, Data curation, Conceptualization. **Valentina Crocellà**: Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Conceptualization, Funding acquisition. **Melodj Dosa**: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Francesca Bonino**: Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Margherita Cavallo**: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

This work was supported by 4AirCRAFT project under the strategic international cooperation between Europe and Japan. 4AirCRAFT has received funding from the European Union's Horizon 2020 research and innovation programme (No 101022633) and Japan Science and Technology Agency (JST) (No JPMJSC2102). We acknowledge the Hercules fund "Direct electron detector for soft matter TEM" from Flemish Government for the purchase of the K2 DED. MC, MD, NGP, MS, SB, VC and FB acknowledge support from the Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023–2027" (CUP: D13C22003520001)

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2024.102804](https://doi.org/10.1016/j.jcou.2024.102804).

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APPENDIX B

Appendix B contains the papers published during my PhD but not discussed in the thesis.

In particular the following publications are related to the topic but not discussed in the PhD thesis:

- “Maruccia, E.; Piovano, A.; Lourenço, M. A. O.; Priamushko, T.; Cavallo, M.; Bocchini, S.; Bonino, F.; Pirri, F. C.; Kleitz, F.; Gerbaldi, C. Revealing the Competitive Effect of N₂ and H₂O towards CO₂ Adsorption in N-Rich Ordered Mesoporous Carbons. *Mater. Today Sustain.* **2023**, *21*, 100270.”
- “Prévot, M. S.; Finelli, V.; Carrier, X.; Deplano, G.; Cavallo, M.; Quadrelli, E. A.; Michel, J.; Pietraru, M.-H.; Camp, C.; Forghieri, G.; Gagliardi, A.; Seidel, S.; Missemmer, A.; Reuillard, B.; Centrella, B.; Bordiga, S.; Salamanca González, M. G.; Artero, V.; Birkelbach, K. V. A.; von Wolff, N. An Anthropocene-Framed Transdisciplinary Dialog at the Chemistry-Energy Nexus. *Chem. Sci.* **2024**, *15* (24), 9054–9086.”
- “Cavallo, M.; Signorile, M.; Köferstein, R.; Crocellà, V.; Taddei, M. Unusual Adsorption-Induced Phase Transitions in a Pillared-Layered Copper Ethylenediphosphonate with Ultrasmall Channels. *Mater. Adv.* **2024**, *5* (1), 183–198.”
- “Pugliesi, M.; Cavallo, M.; Atzori, C.; Garetto, B.; Borfecchia, E.; Donà, L.; Civalleri, B.; Tuci, G.; Giambastiani, G.; Galli, S.; Bonino, F.; Rossin, A. Selective Carbon Dioxide versus Nitrous Oxide Adsorption in Cerium(IV) Bithiazole and Bipyridyl Metal-Organic Frameworks. *Adv. Funct. Mater.* **2024**, *34* (39).”

The following publication is not related to the topic, but results from some of the work carried out during the PhD:

- “Perez Bravo, J. J.; Valverde, A.; Peralta Ramos, M. L.; Cavallo, M.; Bonino, F.; Fernández de Luis, R.; Copello, G. J. MIL-125-NH₂ Functionalized Chitin Scaffold as Dual Sorbent and Photocatalyst Filter for Degradation of Trimethoprim. *J. Environ. Chem. Eng.* **2024**, *12* (3), 113005.”



Revealing the competitive effect of N₂ and H₂O towards CO₂ adsorption in N-rich ordered mesoporous carbons

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ARTICLE INFO

Article history:

Received 21 July 2022

Received in revised form

25 October 2022

Accepted 26 October 2022

Available online 12 November 2022

Keywords:

Ordered mesoporous carbon

N-rich carbon

Nanocasting

CO₂ capture

Gas separation

Renewable feedstock

ABSTRACT

The incorporation of heteroatoms improves CO₂ adsorption on carbon-based materials, but it can also provide some hydrophilic character to the bare-carbon frameworks, making the hypothesis of competitive CO₂/H₂O adsorption not negligible. In this respect, the CO₂ capture is here evaluated through a deep characterization of the sorption properties of N-rich ordered mesoporous carbons under dry and moisture conditions, and in CO₂/N₂ gas mixtures. The nanocasting strategy is used to obtain N-rich CMK-3-type carbons in one pot by impregnating D-glucosamine hydrochloride, a carbon/nitrogen source, into an SBA-15 silica template followed by pyrolysis treatment at 600, 750, and 900 °C. The fine-tuning of the pyrolysis treatment aims to find the right proportion of micropores and N content, which are important features for selective CO₂ adsorption. The highest surface amount of N (11.3 at.%), in particular of the pyridinic type, enhances the CO₂/N₂ selectivity (1.03 mmol/g of adsorbed CO₂ from a 20% CO₂ in N₂), but also the undesired increment in the H₂O uptake. CO₂ uptake under competitive CO₂/H₂O conditions is better preserved with 8.3 at.% of surface nitrogen (1.55, 1.52, 0.61, and 0.89 mmol/g of CO₂ at a relative humidity of 0, 25, 50, and 75%, respectively). Interestingly, the N-CMK-3 materials retain their capture properties over repetitive adsorption-desorption cycles in pure CO₂. In this respect, a TGA-FTIR study is performed to monitor the reusability of the sorbents after CO₂ capture from moist flue gases to assess the effectiveness of the reactivation procedure towards the removal of the adsorbed species.

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1. Introduction

Anthropogenic greenhouse gas (GHG) emissions are the main reason for the climate change phenomena that Earth is experiencing nowadays. GHG effect already caused an increase of 1.09 °C (0.95–1.20) of the global surface average temperature in the period

2011–2020 compared to pre-industrial times [1]. Unfortunately, this trend is expected to constantly grow, aggravated by the expansion of human needs consequent to the increase of the world population, unless strict measures are urgently adopted. Hence, new regulations have been recently introduced to guide the necessary climate actions, since the international agreement in Paris in 2015 to commit the 196 involved countries to keep the average increase in the global temperature well below 2 °C, preferentially below 1.5 °C, with respect to pre-industrial levels [3]. These targets have been renewed during COP26, which took place in Glasgow in 2021. The new targets include also the drastic reduction of emissions by 2030, aiming to reach net-zero emissions by the middle of the century.

Currently, the attention is mainly directed toward CO₂, which among the GHGs plays the main role in the alteration of the energy balance of the Earth-atmosphere system. Nowadays, Carbon Capture and Storage (CCS) technologies represent a robust strategy for

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tackling CO₂ sequestration, and post-combustion capture has the advantage of being easily retrofitted in existing plants. At present, solvent-based CO₂ absorption by aqueous amine solutions is the most mature technology [4,5]. However, amine scrubbing processes are affected by some drawbacks. Particularly, amine degradation generates products that are corrosive to the equipment and toxic to human beings and the environment [6]. Moreover, the energy penalty due to amine-based sorbents regeneration hampers the extensive implementation of this technology [7,8]. Carbon capture strategies based on the adsorption process using porous materials are attractive due to reducing the energy consumption on sorbents regeneration and also overcoming the issues related to corrosion and toxicity [7,9]. Zeolite [10], metal-organic frameworks (MOFs) [11], amino-functionalized porous silicas [12], and carbon-based materials [13] are among the most exploited sorbents for CO₂ capture. An interesting analysis regarding the technical-economic aspects of post-combustion CO₂ capture was carried out by Subraveti et al., who investigated the main attributes of an ideal adsorbent and compared it with monoethanolamine-based adsorbents, revealing that an optimized adsorption process has the potential to be more convenient than absorption, not only from an energetic but also from an economic point of view [14].

The typical composition of post-combustion flue gases is approximately 73–77% N₂, 15–16% CO₂, 5–7% H₂O and 3–4% O₂ in coal-fired power plants [15] and 67–72% N₂, 8–10% CO₂, 18–20% H₂O and 2–3% O₂ in natural gas-fired power plants [16]. The separation of CO₂ from a mixture containing N₂ and H₂O vapor requires the development of adsorbents with characteristics such as high selectivity for CO₂ capture and robustness in humid environments [17]. Generally, the effect of the presence of water vapor in flue gas mixtures has to be carefully taken into consideration, since most sorbents based on silica [18], zeolites [9,19,20], and MOFs [21], undergo a reduction in their CO₂ capture performances, due to structural instability under humid conditions and/or competitive adsorption caused by their strong affinity for H₂O. In this case, a pre-condensation of water was recommended by Ben-Mansour and coworkers [22], who investigated the CO₂ adsorption by a MOF sorbent from dry and humid CO₂/N₂ mixtures through both numerical simulations analysis and lab experiments. On the contrary, CO₂ adsorption by amine-functionalized carbon sorbents benefits from the presence of a proper amount of water, as demonstrated by Lourenço et al. [23] and Wu et al. [24]. For these kinds of sorbents, it is believed that water plays a crucial role in the formation of carbamate ions by the reaction of CO₂ molecules with the amine groups of the sorbents [25]. Moreover, the formed carbamate ion or the amino group itself can subsequently react with CO₂ and H₂O molecules to form bicarbonate ions [26].

Many recent works addressed the problem of the preservation of good CO₂ adsorption performances from wet flue gases by water-sensitive sorbents like MOFs [22,27–32] and zeolites [33,34]. On the contrary, the problem of water presence in post-combustion flue gases is usually considered less crucial for carbon materials, due to their intrinsic hydrophobic nature and remarkable tolerance toward moisture [35]. However, the absence of polar groups in hydrophobic carbons limits the efficiency of selective CO₂ removal in real flue gas mixtures [9]. Hence, O and N are often introduced into the bare-carbon frameworks to enhance the affinity for CO₂, increasing at the same time the surface polarity and providing some hydrophilic character to the carbon surface [36], interacting with water via hydrogen bonding [37,38].

In this work, the influence of water contamination on the selective CO₂ capture from simulated post-combustion flue gases by nitrogen-doped carbonaceous adsorbents was investigated. Sorbents with a high affinity toward CO₂ were prepared through a direct route that avoids post-synthesis functionalization methods. Hence, a nanocasting synthesis procedure was here employed as a

handy and affordable method for the preparation of mesoporous carbons with well-defined porous characteristics. Precisely, SBA-15 ordered mesoporous silica was used as a hard template and D-glucosamine (an abundant component in biomass residues) was chosen as a sustainable, concurrent carbon/nitrogen (C/N) source, to produce CMK-3-type N-containing ordered mesoporous carbons (named, NOMCs). The adsorption performances of the adsorbents were studied, focusing firstly on the evaluation of single component CO₂ and H₂O adsorption, and subsequently, on the evaluation of the selective CO₂ capture from dry (CO₂/N₂ = 20/80 v/v) and wet (CO₂/H₂O, a relative humidity (RH) ranging from 0 to 75%) simulated flue gas mixtures, respectively. Finally, the reusability of the sorbents was also considered to provide a thorough evaluation of the potential applicability of the synthesized materials in industrial applications.

2. Experimental

2.1. Synthesis

The SBA-15 silica hard template was synthesized following the procedure described by Guillet-Nicolas et al. [39]. Precisely, 8 g of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO₂₀PO₇₀EO₂₀, P123, Sigma-Aldrich MW-5800) was dissolved at 35 °C in 150 mL of 0.3 M hydrochloric acid (HCl, VWR, 37%) aqueous solution. When P123 was completely dissolved, 13 g of tetraethyl orthosilicate (TEOS, Sigma-Aldrich 98%) was added to the mixture and let stir at the same temperature. After 24 h, the mixture was hydrothermally treated at 100 °C for 48 h under static conditions. The hot solution was filtered and dried in an oven at 140 °C. P123 was removed by solvent extraction in ethanol/HCl solution (C₂H₆O, EtOH, Brenntag, 96%) and then by calcination at 550 °C. The nitrogen-containing N-CMK-3-type carbons were prepared following the procedure described in our recent work [40]. Briefly, the SBA-15 silica template (degassed overnight at 150 °C under vacuum) was impregnated with an aqueous solution of D-glucosamine hydrochloride (C₆H₁₃NO₅·HCl, Alfa Aesar, >98%) and sulfuric acid (H₂SO₄, VWR, 95%) using a two steps procedure. Precisely, for 1 g of SBA-15, 1.58 g of D-glucosamine hydrochloride, 0.097 mL of H₂SO₄, and 6 g of deionized water were impregnated in the first step, while in the second step, 0.96 g of D-glucosamine hydrochloride, 0.06 mL of H₂SO₄ and 3.66 g of H₂O were used. The slurry was stirred for 1 h at room temperature until a homogeneous gel-like consistency was obtained and then thermally treated in a calcination furnace at 100 °C for 6 h, 140 °C for 2 h, and 160 °C for 6 h (heating rate 150 °C/min) during the first impregnation, and at 100 °C for 6 h, and 140 °C for 2 h during the second impregnation step. The resulting powders were moved into a quartz reactor with a capillary cap design [41,42] and pyrolyzed at 600, 750, or 900 °C (heating rate 3 °C/min) for 4 h in a calcination furnace in the air under atmospheric pressure. The two intermediate steps at 200 °C for 6 h and at 655 °C for 4 h (except for the sample pyrolyzed at 600 °C) were introduced before reaching the final pyrolysis temperature (T_p). The silica removal step was made by dissolving the silica in a 2 M sodium hydroxide (NaOH, 98%, flakes) water/ethanol solution (H₂O:ethanol = 1:1, v/v) at room temperature and overnight. This step was repeated more than two times. The samples underwent several repetitive washing steps in water and ethanol and were finally dried overnight at 70 °C. The obtained materials had been denominated N-CMK-3_X, where X is the pyrolysis temperature (i.e., 600, 750, or 900 °C).

2.2. Characterization

The experimental methodology adopted to characterize the synthesized samples is described in detail in the Supporting Information (SI) and summarized in Table 1.

Table 1
Summary of the experimental methodology adopted to characterize the synthesized samples.

Technique	Equipment	Characterization details
LAXRD ^a	EMPYREAN diffractometer + PIXcel3D detector (Malvern PANalytical, United Kingdom)	Transmission mode; Cu K _{α1+2} radiation ($\lambda = 0.154$ nm); Operating voltage: 45.0 kV; Tube current: 40.0 mA; 2θ step size: 0.013°; data time per step: 50 s. Acceleration voltage: 200 kV; Sample dispersed in high purity ethanol and drop-casted onto lacey-carbon Cu TEM grids.
TEM ^b /STEM ^c	Tecnai G ² F20 S-twin microscope (FEI Technologies Inc., USA) + BF ^d /HAADF ^e detectors	Degassing in vacuum: 12 h, 150 (silica) or 300 °C (carbons); Models: BET ^f , NLDFT ^h (silica, cylindrical pores) or QSDFT ⁱ (carbon, cylindrical pores).
N ₂ sorption @−196 °C: SSA ^f and mesoporosity	IQ2 instrument + AsiQwin 5.2 software (Anton Paar QuantaTech Inc., USA)	1) T = 0 °C, degassing in vacuum: 12 h, 300 °C; Models: NLDFT (carbon); 2) T = 0 °C, degassing in vacuum: 12 h, 300 °C; Virial isotherm model 3) T = −10, 0, 10 °C; degassing in vacuum: 12 h, 300 °C; Clausius-Clapeyron equation.
CO ₂ sorption: 1) microporosity 2) K _H ^j 3) $\Delta H_{ads,CO_2}^k$	IQ2 instrument + AsiQwin 5.2 software (Anton Paar QuantaTech Inc., USA)	1) T = 0 °C, degassing in vacuum: 12 h, 300 °C; Models: NLDFT (carbon); 2) T = 0 °C, degassing in vacuum: 12 h, 300 °C; Virial isotherm model 3) T = −10, 0, 10 °C; degassing in vacuum: 12 h, 300 °C; Clausius-Clapeyron equation.
XPS ^l	PHI 5000 VersaProbe (Physical Electronics, Minnesota, USA) + OriginPro 2020 software (OriginLab Corporation, USA)	Al K _α radiation (1486.6 eV); Pass energy: 187.75 eV (survey spectrum), and 23.5 eV (HR ^m spectra); X-ray beam diameter: 100 μm. HR ^m spectra fit with Gaussian functions and background subtraction with a spline.
TGA ⁿ -CO ₂ /N ₂ selectivity	TG 209 F1 Libra	T = 35 °C, p = 1 bar; Activation in N ₂ : 300 °C, 30 min (10 °C/min); Gas mixture: CO ₂ /N ₂ = 20/80 v/v.
Adsorption-desorption 4) CO ₂ 5) H ₂ O ($\Delta H_{ads}^o_{H_2O}$) 6) CO ₂ /H ₂ O 7) Cyclic CO ₂	Dynamic Vapor Sorption (DVS) instrument (Surface Measurement System, United Kingdom)	Activation in vacuum: 300 °C, 30 min; Equilibrium criterion: dm/dt = 0.002% min ^{−1} 4) T = 30 °C, p = 90%* $p_{CO_2,sat,T}^p$ 5) T = 30–60 °C, p = 90%* $p_{H_2O,sat,T}^q$ 6) T = 30 °C, p = 0 –90%* $p_{H_2O,sat,T}^q$, RH ^r : 0–75%. 7) T = 30 °C, p = 20%* $p_{CO_2,sat,T}^p$. Regeneration in a vacuum: 150 °C
N ₂ sorption @−196 °C (reusability assessment)	3Flex equipment (Micromeritics Instrument Corporation, USA)	Activation in vacuum: 300 °C; Model: NLDFT ^h (cylindrical pores)
TGA-FTIR ^s spectroscopy	TG 209 F1 Libra + Bruker Tensor II equipped with IR gas	T = 25–800 °C, 20 °C/min, N ₂ flow; Activation in N ₂ : 300 °C,

(continued on next page)

Table 1 (continued)

Technique	Equipment	Characterization details
	cell + FT-IR ^s Coupling Systems (Netzsch, Germany)	30 min (10 °C/min); IR spectra of the evolved gases sampled at 3 °C intervals

- ^a LAXRD: low-angle X-ray diffraction.
^b TEM: transmission electron microscopy.
^c STEM: scanning transmission electron microscopy.
^d BF: bright-field.
^e HAADF: high-angle annular dark-field.
^f SSA: specific surface area.
^g BET: Brunauer-Emmett-Teller.
^h NLDFT: non-local density functional theory.
ⁱ QSDFT: quenched solid density functional theory.
^j K_H: Henry's law constant.
^k $\Delta H_{ads,CO_2}$: isosteric enthalpy of CO₂ adsorption.
^l XPS: X-ray photoelectron spectroscopy.
^m HR: high resolution.
ⁿ TGA: thermogravimetric analysis.
^o $\Delta H_{ads,H_2O}$: isosteric enthalpy of H₂O adsorption.
^p $p_{CO_2,sat,T}^p$: CO₂ saturation pressure at T.
^q $p_{H_2O,sat,T}^q$: H₂O saturation pressure at T.
^r RH: relative humidity.
^s FTIR: Fourier transform infrared.

3. Results and discussion

3.1. Textural properties

The textural properties of the N-CMK-3_X materials were determined by analyzing the samples by LAXRD, TEM, and N₂ physisorption. Fig. S3b presents the LAXRD patterns of the N-CMK-3_X carbon replicas, that seem to possess a similar arrangement of the pores ($p6mm$ hexagonal symmetry) [43] to the parent SBA-15 silica template (Fig. S3a). The parent silica shows the typical three well-resolved peaks indexed as (100), (110), and (200) planes, while the N-CMK-3_X replicas only display the (100) reflection. Noteworthy, the increase of the T_p above 750 °C improved the pore organization. The XRD unit cell size a_{100} was calculated from the (100) reflection using the expression $a_{100} = \frac{2}{\sqrt{3}} d_{100}$ [44], where the interplanar spacing d_{100} was calculated using Bragg's law. The high-temperature treatment causes shrinkage of the mesostructure in a higher magnitude as long as T_p increases [45,46], as observed by the reduction of the interplanar d -spacing and, consequently, of the unit cell size (Table 2). The periodic alignment of the channel-like pores, according to the typical arrangement of N-CMK-3-type materials, is also evident from the TEM/STEM images shown in Fig. 1 and Fig S4, which were obtained using different objectives apertures to optimize the image contrast.

The N₂ adsorption-desorption isotherms (at −196 °C) are type IVa isotherms, which are typically observed for (ordered) mesoporous materials (Figs. S5a–b and Fig. 2a), with some character of type I, for all the samples [47]. At a relative pressure (p/p_0) within the range of 0.4–0.9, capillary condensation inside mesopores occurred, while a further increase of the adsorbed volume at $p/p_0 > 0.9$ can be ascribed to adsorption in larger-sized interparticle voids [48]. The QSDFT model was selected to calculate the specific surface area and the mesopore size distribution of the N-CMK-3_X samples, as it fits well the experimental data (Fig. S6, SM).

Although the Rouquerol criteria partially helped in overcoming the complexity of determining the linear range of relative pressure where BET is applicable, BET surface area calculated with isotherms obtained on microporous materials does not represent the real probe accessible surface, but only an apparent surface area [49]. On the contrary, in our case, the surface area and porosity parameters calculated with the QSDFT method are

Table 2
Physicochemical properties of the N-CMK-3 samples.

	a_{100}^a nm	S_{BET}^b m ² /g	S_{DFT}^b m ² /g	V_p^b cm ³ /g	D_p^b nm	V_{ump}^c cm ³ /g	V_{mp}^c cm ³ /g	D_{mp}^c nm
SBA-15	11.9	719	598	1.0	8.8	—	—	—
N-CMK-3_600	10.2	605	672	0.4	4.1	0.12	0.16	0.5; 0.8
N-CMK-3_750	9.2	656	921	0.6	4.4	0.12	0.19	0.5; 0.8
N-CMK-3_900	9.2	667	818	0.5	4.5	0.14	0.23	0.5; 0.8

^a Unit cell size (a_{100}) calculated using the expression $a_{100} = \frac{2}{\sqrt{3}} d_{100}$
^b Specific surface area (S_{DFT}), pore volume (V_p), and pore width (D_p) in the mesoporous range, calculated by NLDFT and QSDFT methods for silica and carbons, respectively, applied to N₂ isotherms at −196 °C.
^c Ultramicropore volume (V_{ump}), micropore volume (V_{mp}), and pore width (D_{mp}) of N-CMK-3 samples in the microporous range, calculated by the NLDFT method, applied to CO₂ isotherms at 0 °C.

considered more reliable, by taking into account not only the geometry of the pores but also the solid-fluid interaction and surface roughness [49–52]. The mesopore size distribution (PSD) is narrow and centered approximately at 4.5 nm (see inset in Fig. 2a) for the samples N-CMK-3_750 and N-CMK-3_900. Conversely, the sample N-CMK-3_600 shows lower specific surface area and pore volume and a less narrow pore size distribution in comparison to the other samples of the series, in line with the lower quality XRD pattern and TEM image. According to the findings of Zhang et al. [53], the slight collapse of the ordered mesoporous architecture could occur during the drying step in the synthesis procedure of the N-CMK-3_600 sample, which contains a higher surface concentration of heteroatoms (see Paragraph 3.2), therefore presents a higher hydrophilic character in comparison to the other samples of the N-CMK-3 series. The micro- and ultramicroporosity were specifically analyzed via CO₂ adsorption isotherms at 0 °C (Fig. 2b). CO₂ was chosen as the preferred gas probe to benefit from the smaller kinetics diameter and the higher absolute temperature and pressure of analysis than N₂ sorption at cryogenic temperature. Hence, both the gas probe diffusion and accessibility in the very narrow pores ($D_p < 0.4$ nm) increased, as already demonstrated in the literature [47,48,54]. From the observation of Fig. 2b, it is possible to see the presence of microporosity in N-CMK-3 samples, consisting of two populations of micro- and ultramicropores, with the maximum of the populations found at 0.8 and 0.5 nm, respectively. The physicochemical parameters derived from N₂ and CO₂ sorption analysis are summarized in Table 2.

3.2. Physicochemical properties

The CMK-3-type NOMCs samples are mainly constituted by C (78.9, 79.1, and 83.4 at.%), O (8.4, 8.9, and 9.4 at.%), and N (11.3, 8.3,

and 4.4 at. %) elements, for N-CMK-3_600, N-CMK-3_750 and N-CMK-3_900, respectively, as derived from the XPS survey spectra in Fig. S7. The increment of T_p leads to the increase of the surface C relative amount as a consequence of the loss of heteroatoms [55]. Therefore, the highest surface atomic concentration of N was found in the sample N-CMK-3_600. Residual amounts of Na (<2 at.%), S (<0.5 at.%) and Si (<0.7 at.%) were observed in all samples. Both Na and S are derived from the synthesis procedures, while the latter is related to the remaining silica hard template, which is anyhow negligible, thus confirming the successful removal of the template. The adventitious contaminations of S and Na might both positively contribute to CO₂ capture, since S-doping is another strategy proposed in the literature to enhance the efficiency of the process [56–59] and a recent theoretical study envisaged the same effect on carbon models with a high loading of alkali metals (around 10 at.%) [60]. Since in our case the amount of S and Na inclusions is very low and randomly distributed in the series of samples, we can safely neglect their contribution with respect to the more abundant and properly modulated incorporation of N-species. High-resolution (HR) acquisitions were performed in C1s, N1s, and O1s regions to investigate the chemical bonding state of the most relevant elements. From C1s core level peaks, we were able to observe three different carbon species (see Figs. S8a, S9a, and S10a in SM) assigned to C–C sp² (284.3–284.8 eV), CO/C–N (285.9–286.5 eV), and C=O/C=N (286.5–287.6 eV) [61,62]. Oxygen signals (see Figs. S8c, S9c, and S10c in SM) were fitted by using three components assigned to C=O (~531 eV), C–O (~533 eV), and COOH (~534 eV) [62], while the deconvolution of the N1s peak of NOMCs revealed three components assigned to pyridinic (C=N–C, N-6, 397.7–398.9 eV), pyrrolic (C–NH–C, N-5, 399.9–400.7 eV), and graphitic (C–NH–C, N-Q, 401.0–401.8 eV) nitrogen-based structures (Figures S8b, S9b and S10b in SM) [61]. The relative percentages of each component were calculated from the fitted

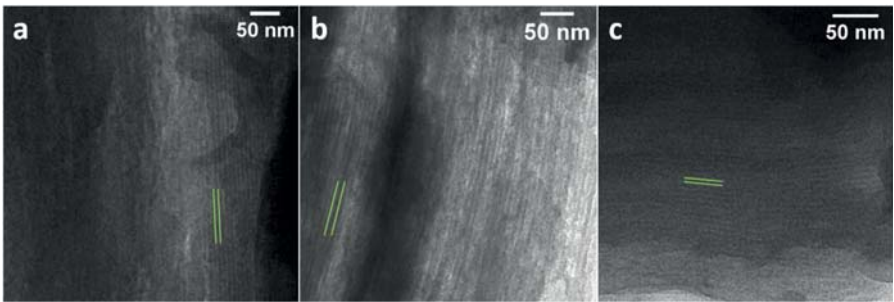


Fig. 1. TEM micrographs of (a) N-CMK-3_600, (b) N-CMK-3_750, (c) N-CMK-3_900 samples.

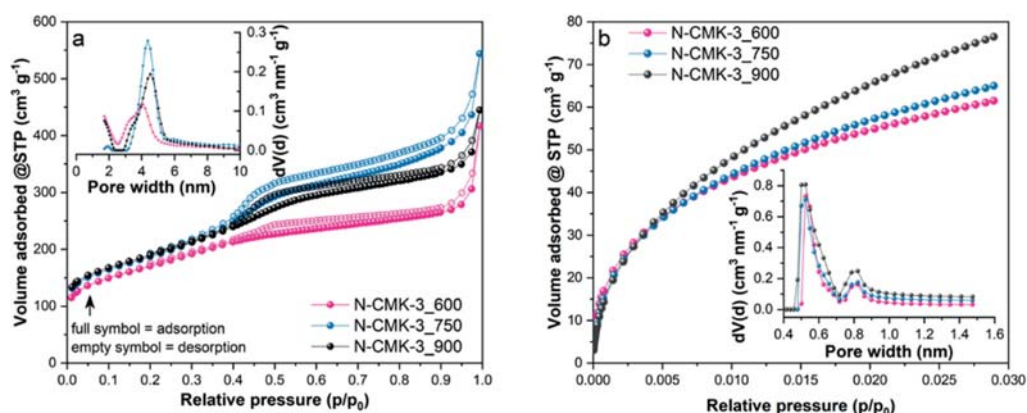


Fig. 2. (a) N_2 adsorption-desorption isotherms at $-196\text{ }^\circ\text{C}$ and in the inset QSDFT pore size distribution in the mesoporous range of NOMC samples, i.e., N-CMK-3_600, N-CMK-3_750, and N-CMK-3_900 (pink, cyan, and black profiles, respectively), and (b) CO_2 adsorption-desorption isotherms at $0\text{ }^\circ\text{C}$ and in the inset the NLDFT pore size distribution in the microporous range of NOMC samples, i.e., N-CMK-3_600, N-CMK-3_750, and N-CMK-3_900 (pink, cyan, and black profiles, respectively).

peak areas quantified by the deconvolution of the HR-XPS signals in the C1s, N1s, and O1s regions. The summary of the quantities derived from the XPS analysis is reported in Table 3.

It is possible to observe that the graphitization degree of the N-CMK-3_X samples increases with the rise of the temperature, observed by the increase of the C–C sp^2 and C=X relative contents. The evolution of nitrogen-containing moieties is related to their different thermal stability. The fraction of N-6 and N-5 decreases with the increase of T_p from 600 to 900 $^\circ\text{C}$ because they are both transformed into N-Q in the pyrolysis temperature range of 600–800 $^\circ\text{C}$ [63]. Accordingly, N-Q is detected in a higher concentration in the sample pyrolyzed at 900 $^\circ\text{C}$. The O-functionalities are less sensitive to the thermal treatment; indeed, their relative percentage was found to be approximately unmodified in all the N-CMK-3 samples under study.

3.3. Pure CO_2 adsorption measurements

The isosteric enthalpy of CO_2 adsorption ($-\Delta H_{\text{ads},\text{CO}_2}$) as a function of the surface coverage (i.e., CO_2 adsorbed amount in mmol/g), is shown in Fig. 3b. $-\Delta H_{\text{ads},\text{CO}_2}$ was calculated for the N-CMK-3-type samples from the adsorption branches of the CO_2 isotherms obtained at -10 , 0 , and $10\text{ }^\circ\text{C}$ in Fig. S11 using the Clausius-Clapeyron approach. The main contribution to $-\Delta H_{\text{ads},\text{CO}_2}$ at low coverage is given by the occupation of the adsorption sites associated with a stronger affinity for CO_2 [64]. At higher surface loadings, $-\Delta H_{\text{ads},\text{CO}_2}$ decreases as a function of the coverage and stabilizes roughly to the heat of liquefaction of CO_2 , i.e., approximately 17 kJ/mol in the considered temperature range, because at this point the system is approaching the pore filling regime, where adsorbate-adsorbate interactions govern the mechanism of adsorption [65]. The values of $-\Delta H_{\text{ads},\text{CO}_2}$ calculated for the N-CMK-3 samples synthesized in this work lay in the range of 30–38 kJ/mol, which is attributable to a physisorption mechanism (from 25 to 50 kJ/mol) [66]. The values of $-\Delta H_{\text{ads},\text{CO}_2}$ stay within an optimal energetic range (30–50 kJ/mol) for achieving concurrently efficient adsorption and easy regeneration [7,67]. Henry's constant (K_H) and the virial coefficients C_1 e C_2 were also calculated from the CO_2 isotherms at $0\text{ }^\circ\text{C}$ (Fig. S12) and listed in Table S1 in SM. K_H values follow the inverse trend of the pyrolysis temperature as a consequence of the loss of heteroatoms during the high-

temperature heat treatment, as was already observed in our previous work [40].

N-CMK-3_600 material better performed in the pure CO_2 adsorption (precisely 7.3 wt%, i.e., 1.66 mmol/g of adsorbed CO_2) at $30\text{ }^\circ\text{C}$ (Fig. 3a). This result is associated with the highest value of K_H (Table S1), which in turn derives from the high amount of N species, especially of the pyridinic type, present in the sample. Conversely, the N-CMK-3_900 sample provided the lowest CO_2 adsorption at $30\text{ }^\circ\text{C}$, equal to 3.7 wt%, i.e., 0.83 mmol/g. The pure CO_2 uptake in the N-CMK-3_900 sample is mainly ascribed to the microporosity, due to the lower contribution derived from the surface N content. Indeed, the positive effect of micro- and ultramicroporosity on the uptake undergoes a more pronounced reduction than surface chemistry by increasing the test temperature [68]. Conversely, this difference is less pronounced in the samples pyrolyzed at lower temperatures, both for the already mentioned N-CMK-3_600 and also the N-CMK-3_750, which showed intermediate performances (6.8 wt%, i.e., 1.55 mmol/g of adsorbed CO_2). This behavior further confirms that N species play a beneficial role in the CO_2 uptake, especially at temperatures close to ambient temperature [69].

3.4. Reusability assessment by multiple CO_2 adsorption-desorption cycles

Ten cycles of adsorption-desorption were performed on N-CMK-3 samples to assess the reusability of the sorbents (Fig. 4). The samples under study showed good reproducibility upon repetitive use under pure CO_2 adsorption measurements at $30\text{ }^\circ\text{C}$ and at 20 kPa (0.2 bar). The regeneration of the sorbents was carried out by heating up to $150\text{ }^\circ\text{C}$ between consecutive cycles (TSA process). The highest efficiency loss (up to ca. 10 and 16% for N-CMK-3_600 and N-CMK-3_900 samples, respectively) occurred between the first and the second cycle. For both samples, a certain amount of CO_2 cannot be desorbed during the regeneration step at $150\text{ }^\circ\text{C}$, likely because the adsorbate is strongly bonded to the high-energy N-sites in the case of N-CMK-3_600, or trapped in the micropores as for the N-CMK-3_900. After the second cycle, all the N-CMK-3 studied samples proved to be stable and the adsorbed amount was almost unvaried. This evidence demonstrated that the sorbents can be reused in multiple adsorption/desorption cycles from dry flue

Table 3
Summary of the XPS analysis on the survey and high-resolution spectra of the C1s, N1s, and O1s region for the N-CMK-3 samples.

Sample name	Peak	Amount ^a at. %	Binding energy eV	Assignment	Fitted peak area counts s ⁻¹	Fitted peak area ^b (%)
N-CMK-3_600	C1s	78.9	284.7	C–C	2835.0 ± 9.3	69.83
			285.8	C–O/C–N	939.2 ± 10.1	23.13
			287.1	C=O/C=N	285.6 ± 10.7	7.04
			398.4	C=N–C	442.9 ± 5.6	46.12
	N1s	11.3	400.4	C–NH–C	454.4 ± 8.2	47.30
			401.3	C–NC–C	63.2 ± 8.3	6.58
			530.9	C=O	698.3 ± 33.3	48.70
			532.5	C–O	560.4 ± 22.0	39.08
			533.5	COOH	175.2 ± 13.1	12.22
			284.8	C–C	4813.3 ± 14.0	71.67
N-CMK-3_750	C1s	79.1	285.9	C–O/C–N	1156.9 ± 16.6	17.23
			286.6	C=O/C=N	745.7 ± 17.9	11.10
			398.4	C=N–C	477.3 ± 8.7	39.00
			400.3	C–NH–C	335.8 ± 19.1	27.44
	N1s	8.3	401.1	C–NC–C	410.8 ± 14.6	33.56
			530.9	C=O	794.9 ± 8.8	48.30
			532.5	C–O	586.4 ± 11.6	35.64
			533.5	COOH	264.3 ± 12.7	16.06
	C1s	83.4	284.8	C–C	4860.8 ± 11.0	70.68
			286.2	C–O/C–N	1202.8 ± 11.9	17.49
N-CMK-3_900	C1s	83.4	287.6	C=O/C=N	813.1 ± 16.0	11.83
			398.5	C=N–C	248.5 ± 6.5	35.94
			399.9	C–NH–C	115.2 ± 8.6	16.66
			401.1	C–NC–C	327.7 ± 28.6	47.40
	N1s	4.4	530.9	C=O	616.2 ± 7.9	46.72
			532.5	C–O	527.1 ± 12.4	39.98
			533.5	COOH	175.4 ± 11.4	13.30
	O1s	9.4				

^a Derived from the XPS survey scan.
^b The percent fitted peak area is here considered as an indication of the relative amount of each species in the sample.

gases without losing their performances and, in addition, be satisfactorily regenerated under mild conditions.

3.5. CO₂/N₂ adsorption measurements

TGA measurements were performed at 35 °C and 1 bar exposing the samples to a mixture that simulates a typical exhaust gas (20 vol% CO₂ and 80 vol% of N₂) [70], to evaluate the competitive adsorption of these two gases (Fig. 5). N-CMK-3_600 sample achieved an improved selectivity in CO₂/N₂ mixture, measured as a 4.52 wt% weight increase (1.03 mmol/g). Indeed, the N-CMK-3_600 sample benefits from the higher surface N content and, particularly, the superior concentration of pyridinic-N inclusions, which allowed for enhanced CO₂ uptake in comparison to the N-CMK-

3_750 and N-CMK-3_900 samples, which achieved 4.36 wt% (0.99 mmol/g) and 3.69 wt% (0.84 mmol/g), respectively. Similarly to what was observed for the pure CO₂ adsorption measurement, the increase of the pyrolysis temperature promotes a decrease in the selectivity towards CO₂ in the N₂/CO₂ separation process, which can be associated with the lower quantity of N-6 species in the materials pyrolyzed at higher temperature (*cf.* XPS quantification in Table 3). Indeed, pyridinic-N inclusions are considered to provide the strongest contribution to CO₂ adsorption among the other types of N-containing functional groups, thanks to the strong basicity, derived from the lone pair electrons of the N atom which establishes a Lewis acid-base interaction with the electron-deficient carbon atom of the CO₂ molecule [40,71,72]. Moreover, the work of Lin et al. [73] also demonstrated the highest difference between

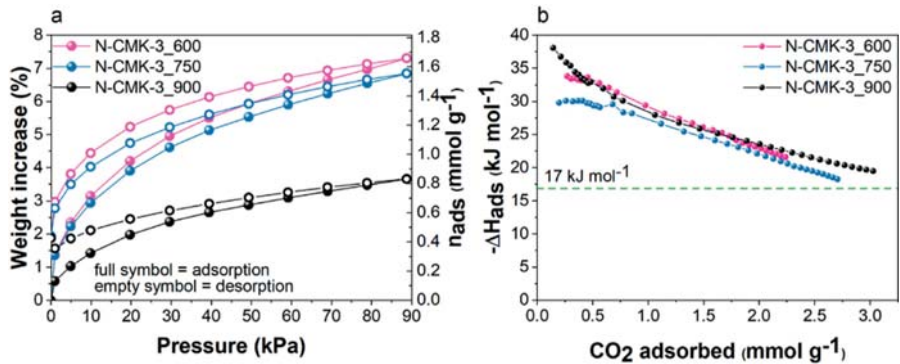


Fig. 3. Pure CO₂ adsorption-desorption isotherms measured at 30 °C up to 90 kPa with a gravimetric sorption analyzer (see Fig. S2a in SM), (b) isothermic enthalpy of CO₂ adsorption calculated in the temperature range between –10 and 10 °C vs. the CO₂ adsorbed for the N-CMK-3 samples under study. The green dashed line describes the heat of liquefaction of CO₂ in the temperature range considered.

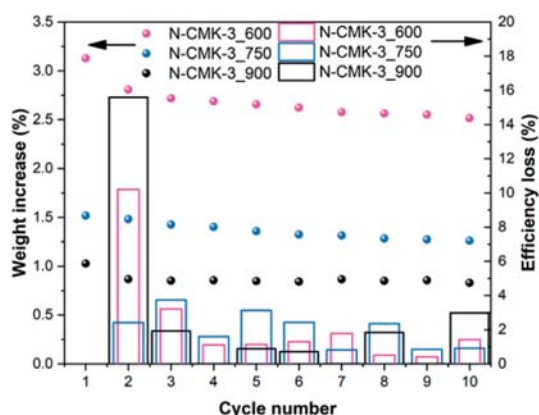


Fig. 4. Reusability tests of the studied N-CMK-3 samples under repetitive adsorption (30 °C) - desorption (150 °C) cycles at 0.2 bar (see Fig. S2d in SM). The efficiency loss is calculated with respect to the previous cycle.

CO₂ and N₂ adsorption energies for the pyridinic group compared to several analyzed N-functionalities, including pyrrolic and quaternary N, thus resulting in improved CO₂/N₂ selectivity [73]. The regenerability of the sorbents was also considered by the quantification of the percentage of released CO₂ in PSA conditions. As for the PSA approach, the promotion of the desorption of CO₂ by simply applying a flow of N₂ is more convenient from an energetic point of view than the TSA condition effectively applied in Paragraph 3.4. It is interesting to observe in Fig. 5a that almost the overall amount of the adsorbed CO₂ is released in PSA conditions (−2.90, −2.68, and −2.55 for N-CMK-3_600, N-CMK-3_750 and N-CMK-3_900, respectively). Then, heating was applied to remove the strongly bounded CO₂. At T < 150 °C, most of the adsorbed CO₂ is released. Also under these conditions, the adsorption capacity and selectivity results are consistent with the trend of the calculated K_H values (see Fig. 5b and Table S1 in SM).

3.6. H₂O adsorption measurements

Single component H₂O adsorption isotherms were performed at 30 °C to compare this result with CO₂ adsorption (Fig. 6a). It is

worth taking into consideration that owing to the relatively unstable H₂O adsorption observed by the as-synthesized samples, which revealed their poor hydrophilic character, the isotherms reported in Fig. 6a are obtained after previous H₂O adsorption measurements at 30 °C. As a result, the carbon-based adsorbents display an increased affinity to water after a previous adsorption of water, as shown in Fig. S13, in agreement with the mechanism of adsorption governed by cluster formation hypothesized by Horikawa et al. [74]. In detail, the H₂O vapor adsorption-desorption curves in Fig. 6 and S14 present a sort of type IV isotherm (IUPAC denomination) [47], characterized by Type I character at very low partial pressure [36], indicative of an onset of water adsorption at very low pressure. A change in the concavity of the adsorption/desorption branches describes a two-stage-adsorption mechanism, which involves firstly the filling of micropores in the low relative pressure regime and subsequently of mesopores at higher pressure. In our case, the growing trend of total adsorbed water while increasing the analysis temperature is ascribable to the higher water vapor saturation pressure (p_{H2O,sat,T}), which allows for conducting the analysis at increased absolute pressure values. Indeed, in the relatively low-pressure regime, the amount of adsorbed H₂O is higher for the isotherms obtained at lower analysis temperatures. From the reported data, it is possible to observe that H₂O adsorption is higher in the N-CMK-3_600 sample than for N-CMK-3_750 and N-CMK-3_900 ones. This evidence is consistent with the predictions since the more abundant incorporation of heteroatoms (namely O and N) in the carbon framework obtained at the lowest T_p provides a stronger hydrophilic character. Indeed, N and O species are considered to promote water adsorption, especially in the low and intermediate pressure region [74,75], and according to the study of Kumar et al. [38], water vapor adsorption is more influenced by the local density of N species than their type. Despite an increased affinity for H₂O given by heteroatoms incorporation inside the pristine carbon surface, the N-CMK-3-type samples studied in this work exhibited still a poor hydrophilic character when compared to other highly hydrophilic N-doped carbons, which achieved 4–5 orders of magnitude higher H₂O uptake in the low relative pressure range [36]. This conclusion is particularly encouraging from the perspective of the original application of the N-CMK-3 sorbents studied in this work as selective CO₂ sorbents from moisture flue gases. Analogous observations are also derived from the quantification of the isosteric enthalpy of water adsorption (−ΔH_{ads,H2O}). In the considered loading range, the ΔH_{ads,H2O} values of all the N-CMK-3 samples (see Fig. 6b) are below the

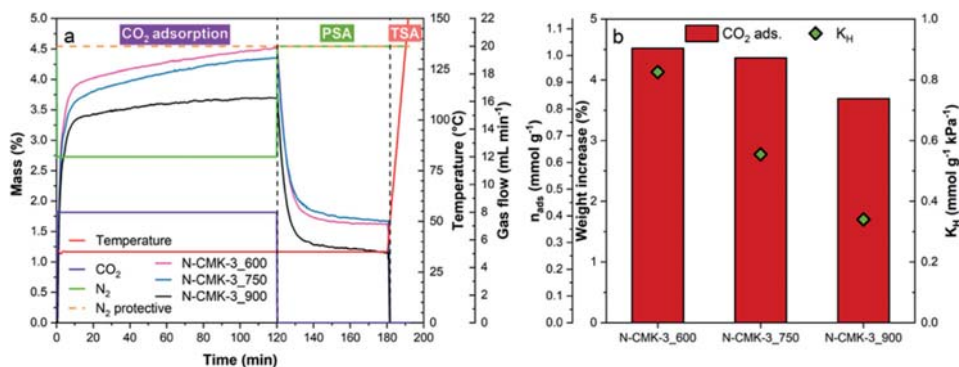


Fig. 5. (a) Adsorption and desorption steps and (b) weight increase due to the CO₂ adsorption in a gas mixture of 20 vol % CO₂ and 80 vol % of N₂ at 35 °C for CO₂/N₂ adsorption measurements by the N-CMK-3 samples under study. Details on setup for CO₂/N₂ selectivity tests by TGA in Fig. S1 in SM.

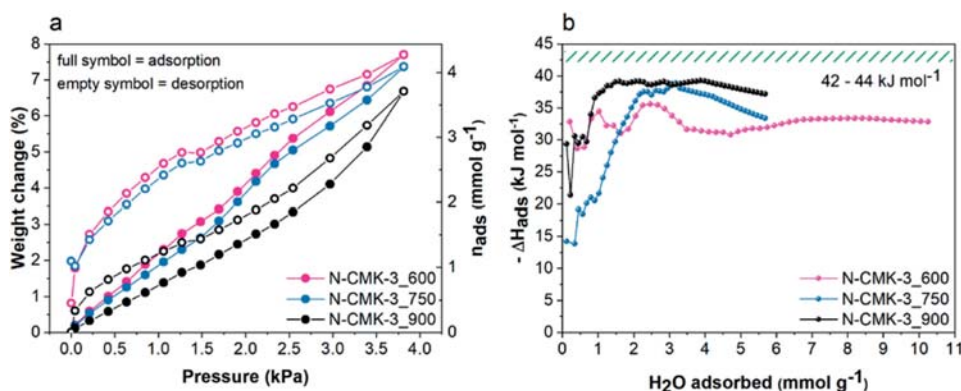


Fig. 6. Pure H₂O vapor sorption isotherms were measured at 30 °C with a gravimetric sorption analyzer (see Fig. S2b in SM). The weight change is plotted against the absolute pressure (kPa): N-CMK-3_600 (pink dots), N-CMK-3_750 (cyan dots), and N-CMK-3_900 (black dots) samples. b) ΔH_{ads,H2O} plotted against the H₂O adsorbed amount was calculated in the 40–60 °C temperature range for N-CMK-3_600 (pink dots), N-CMK-3_750 (cyan dots), and N-CMK-3_900 (black dots) samples. The patterned green area describes the range of values for the water heat of condensation in the considered temperature range.

enthalpy of condensation of water, which lies approximately in the range 42–44 kJ/mol in the analyzed temperature range (30–60 °C) [76]. This indication confirms the hydrophobic nature of the NOMC samples studied in this work. However, despite the average behavior, the samples locally present some specific sites, such as micropores or O- or N- sites, where $-\Delta H_{ads,H2O}$ approaches the enthalpy of condensation of water. Precisely, the adsorbate-adsorbent interactions govern water adsorption at low coverage [77].

Hence, the initial modest values of $-\Delta H_{ads,H2O}$ for the N-CMK-3_750 sample likely derive from the lower N content, which causes a weaker affinity for the H₂O, with respect to the N-CMK-3_600 sample. In the case of the N-CMK-3_900 sample, the high content of micropores likely compensates for the low concentration of N-species. As the adsorption progresses, the energy involved in the water cluster formation becomes dominant and mostly influences ΔH_{ads,H2O} values.

3.7. CO₂ adsorption under humid conditions

Three consecutive H₂O/CO₂ adsorption-desorption cycles (the method used is schematically described in Fig. S2c) were performed at 30 °C on the two most promising samples (N-CMK-3_600 and N-CMK-3_750) to study the ability of the samples to capture CO₂ under humid condition. Fig. 7 shows the weight change of the samples resulting from the exposition to different mixtures of H₂O and CO₂. During the 1st cycle (Fig. 7a and b), RH was kept constant at 25% (i.e., $p_{H2O} = 1.06$ kPa), while CO₂ partial pressure (p_{CO2}) was varied from 0 to 65% (i.e., from 0 to 2.76 kPa), in the assumption that H₂O adsorption remains constant at the same absolute H₂O pressure. An increment of p_{CO2} at constant RH corresponds to an increase in the weight of the samples which is attributable to CO₂ adsorption. It is worth noticing that a certain amount of the adsorbed species did not desorb during the 1st cycle, thus occupying part of the available pore volume and, in turn, hindering the utilization of the maximum capacity of the sorbents during the subsequent cycles. The same adsorption behavior is observed during the 2nd cycle (Fig. 7c and d) when RH was kept constant at 50% and p_{CO2} gradually increases from 0 to 40%.

However, it is promising to observe that the samples are still able to capture CO₂ even if water is previously adsorbed in the porosity of the samples and this increment of the sample weight is directly proportional to p_{CO2} . During the 3rd cycle (Fig. 7e and f), RH gradually increased and stabilized at 75%. Subsequently, 15% of p_{CO2} was added. The introduction of CO₂ caused a remarkable increment of the weight correspondent to 2.9 and 3.9 wt% for N-CMK-3_600 and N-CMK-3_750 samples, respectively. Generally, the sample N-CMK-3_750 adsorbs a lower amount of H₂O, as observed also in single-component isotherms (see Fig. 6a and Fig. S14), and a higher amount of CO₂ in comparison to the sample N-CMK-3_600 under humid conditions.

Table 4 reports the amounts of CO₂ adsorbed under different conditions of humidity. The maximum amount of adsorbed CO₂ at RH = 25% is comparable to the one under pure CO₂ (reported in Fig. 3a), which means that a moderate presence of moisture does not affect the ability of the adsorbents to capture CO₂, especially for the N-CMK-3_750 sample. However, by rising the RH up to 75%, the amount of CO₂ adsorbed was significantly reduced. Nonetheless, this behavior is not linear. For instance, the quantity of the CO₂ adsorbed decreases after the increase of RH from 25% to 50%, but on the contrary, the adsorbed CO₂ amount increases from RH 50–75%. Similar behavior has already been reported in the literature [24–26], demonstrating that the effect of H₂O on CO₂ adsorption is a balance between the competition towards the occupation of the adsorption sites and the promotion of side reactions at the N-species that consume CO₂ (e.g., bicarbonate formation). Considering the two examined samples, the lowest affinity for H₂O shown by the N-CMK-3_750 sample, allowed higher retention of satisfying CO₂ capture capabilities in presence of water. This result makes it the most suitable sorbent among the studied ones for CO₂ capture under moisture conditions.

3.8. Assessment of sorbents reusability after H₂O adsorption

The adsorption in pure CO₂ at 30 °C was repeated after the tests under humid gas mixtures (see Fig. S15), observing a considerable reduction in the CO₂ uptake after the exposition to water (–45% for N-CMK-3_600 and –65% for N-CMK-3_750). This might be related

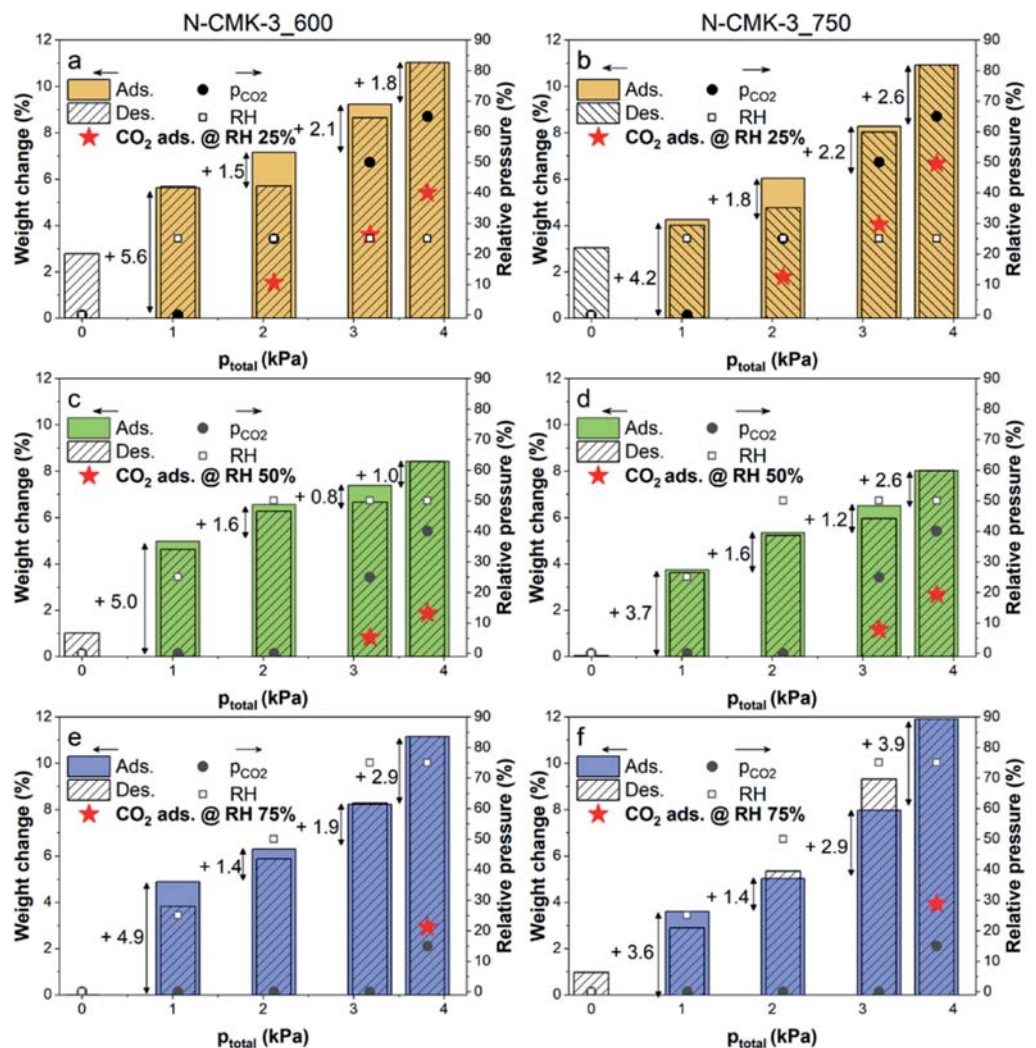


Fig. 7. Weight increase vs total pressure derived from cyclic H₂O/CO₂ adsorption-desorption tests performed at 30 °C at a different relative pressure of H₂O and CO₂ according to the scheme in Fig. S2c. The data refer to the sample N-CMK-3_600 (a, c and e are for the 1st, 2nd, and 3rd adsorption/desorption cycle, respectively) and to the sample N-CMK-3_750 (b, d, and f are for 1st, 2nd, and 3rd adsorption/desorption cycle). For the 2nd and 3rd cycles, the residual adsorbed species from the previous cycles are counted in the initial weight. The arrows indicate the weight increase between two consecutive adsorption cycles and the star symbol indicates the weight increase due to CO₂ adsorption with respect to the weight increase achieved under pure H₂O at the target RH.

either to the incomplete desorption of the adsorbates from the previous tests, even upon reactivation at 300 °C under vacuum, or to a structural collapse during the reactivation, promoted by the same trapped gases. Indeed, some irreversibility between adsorption and desorption was observed during the CO₂/H₂O adsorption tests in Fig. 7, presumably not desorbed H₂O, since this species is more difficult to remove, owing to the higher isosteric enthalpy of water adsorption in respect to CO₂ [78]. As a matter of fact, at the end of the desorption branch of the 1st cycle, the final weight of the sample was around 3 wt% of the initial weight (see Fig. 7a and b). Further analysis of the textural features before and after the exposition to H₂O on the N-CMK-3_600 sample was performed by N₂ adsorption-

Table 4
Maximum CO₂ adsorption at 30 °C under different humidity percentage for the N-CMK-3-type samples under study.

Sample name	CO _{2,ads} @ RH 0% mmol/g	CO _{2,ads} @ RH 25% mmol/g	CO _{2,ads} @ RH 50% mmol/g	CO _{2,ads} @ RH 75% mmol/g
N-CMK-3_600	1.66	1.23	0.42	0.66
N-CMK-3_750	1.55	1.52	0.61	0.89

desorption isotherms at -196°C , to verify the more convincing hypothesis of unsuccessful regeneration as the main cause of the decrease of CO_2 uptake, even after the usual activation process at 300°C preceding each measurement. This sample was chosen among the others of the N-CMK-3 series for its more marked hydrophilic character, derived from the higher content of N-species. The samples were activated at 300°C in a vacuum for 1 h before the analysis, in line with the procedure used for the measurements under $\text{CO}_2/\text{H}_2\text{O}$ atmosphere. A further attempt was considered by extending the activation treatment up to 12 h to evaluate the potential beneficial effect of a longer treatment in improving the evacuation of the adsorbed species. The isotherms obtained in Fig. 8a of the fresh sample and the same sample treated in H_2O and subsequently activated for 1 h or 12 h are the same original combination of type I plus IV, confirming the retention of the characteristic CMK-3 mesostructure. Similarly, the pore size distributions in the inset in Fig. 8b are all roughly comparable, except for the population of the smallest micropores ($\varnothing < 1\text{ nm}$, reasonably the most effective in CO_2 capture) that are completely disappeared, together with a specific family of quite small mesopores ($\varnothing \approx 2\text{--}2.5\text{ nm}$). The fact that some pores populations remain totally unaffected while others completely disappeared unequivocally supports the hypothesis of pore occlusion by non-desorbed H_2O molecules, rather than structure collapse during water adsorption tests and/or reactivation treatment.

As a consequence of pore occlusion, the sample treated in H_2O shows a sizable reduction of the BET surface area, total pore volume, and micropore volume, even after the activation procedure, with a stronger deterioration, as predictable, in the case of the shortest regeneration treatment of 1 h. Precisely, a reduction of 60.6% of S_{BET} , 47.1% of V_p , and 89.6% of V_{mp} was recorded in the case of the activation at 300°C for 1 h. The longer treatment carried out at 12 h only slightly helped in restoring the initial textural features. The dramatic decrease of the micropore volume is the most remarkable information deduced from this analysis since this characteristic is important for CO_2 adsorption. Therefore, it is reasonable that the considerable reduction of the number of these preferential sites of adsorption is the cause of the inability to restore the initial uptake capability by the considered sample. To further investigate this phenomenon, a thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) on the N-CMK-3_600 sample was performed after H_2O adsorption and compared with the fresh sample (see Fig. 9a and b). The TGA profile of the fresh sample (Fig. 9a) shows a first degradation peak

at 70°C , corresponding to a weight loss of about 8 wt%, then a constant limited loss of 6 wt% for temperatures varying from 100 to 600°C and a final step of weight loss equal to ca. 10 wt% from 600 to 800°C . The evolved gases are composed mainly of H_2O , CO_2 , CO, NH_3 , and HCN; their relative intensities change during the test, as shown in Fig. 9c. During the first step (Figs. S16a–b), the fresh sample mainly released H_2O that was adsorbed from the atmosphere; in the second step (Fig. S16c), the main component of the evolved gas mixture is CO_2 , while from temperatures higher than 600°C , the weight loss slowly increases as expected from carbonaceous materials prepared at 600°C . Indeed, in this phase (see Fig. S16d), the fresh carbon sample slowly evolves producing HCN and NH_3 , thus reducing the quantity of nitrogen incorporated in the carbon framework, as expected based on the XPS analysis, and producing CO and CO_2 from material graphitization. The TGA-FTIR analysis on the sample tested in H_2O adsorption, here labeled as “treated”, shows several differences in comparison to the fresh sample. First, the thermodegradation curve exhibits a new step with a maximum at around 235°C and a weight loss of ca. 20 wt% (Fig. S16e). In this range of temperatures, the IR spectra (see Figs. S16f–g) clearly show the presence of CH_2 moieties and carbonyl groups typical of ketones, carboxylic acids, etc. [79]. In addition, it is worth noticing that, differently from the fresh sample, at temperatures higher than 300°C , the IR spectra of the treated sample show the release of H_2O (see Fig. S16h), with a continuous increment of the intensity of the signal as long as the temperature increases (Fig. 8d).

In conclusion, the volumetric and thermogravimetric analyses considerably helped in extrapolating useful information regarding the optimal regeneration conditions for the studied sorbents after their exposition to moist environments. In detail, the usual activation process carried out at 300°C was revealed to be not completely successful in evacuating the previously adsorbed species during H_2O or $\text{H}_2\text{O}/\text{CO}_2$ adsorption tests. The attempt of keeping the same temperature (i.e., 300°C) while prolonging the activation time was not fully successful to restore the initial properties of the sorbents so that to justify a longer time for the regeneration procedure, which is a collateral step of the capture process. On the contrary, the increase of the activation temperature, as suggested by the thermogravimetric analysis, could be more effective in totally restoring the initial adsorption capacity, but the feasibility of the process is still questionable in terms of energy consumption for a real application.

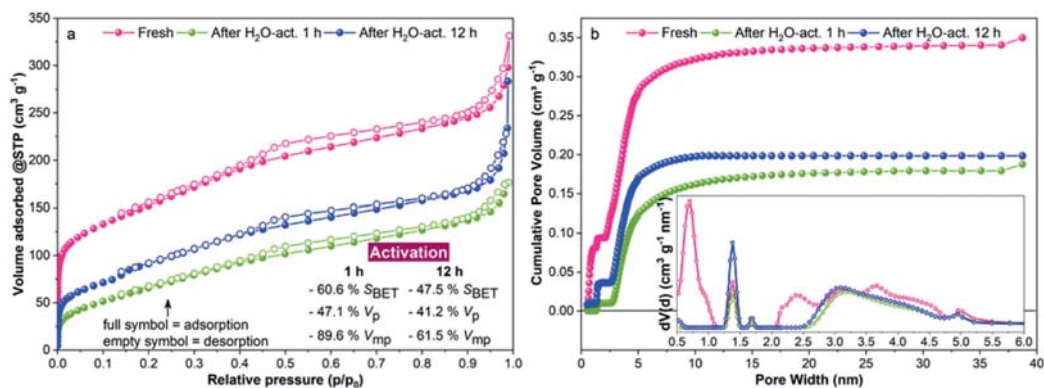


Fig. 8. Investigation of the change in the porosity properties of the N-CMK-3_600 sample before and after H_2O adsorption: a) N_2 adsorption-desorption isotherms at -196°C and, b) DFT cumulative pore volume and pore size distribution (inset) in the micro- and mesoporous range. The activation treatment was carried out at 300°C in a vacuum for 1 h, in the case of the fresh sample and at 300°C in a vacuum for 1 h or 12 h in the case of the same sample previously treated in H_2O .

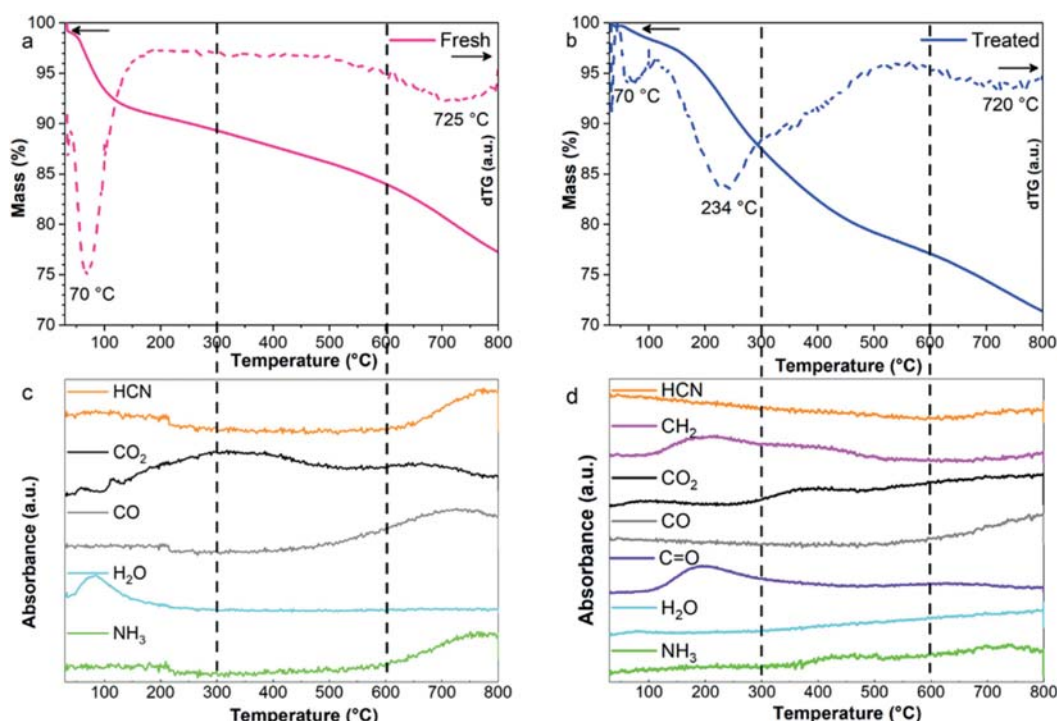


Fig. 9. TGA-FTIR analysis: a,b) mass change vs. temperature (wt.% vs. °C) and differential weight (dTG) vs. temperature (d%wt./d°C vs. °C) profiles of fresh N-CMK-3_600 sample and the same sample after H₂O adsorption; c) intensity vs. temperature of the peaks relative to NH₃ at 965 cm⁻¹, H₂O at 1505 cm⁻¹, CO at 2179 cm⁻¹, CO₂ at 2349 cm⁻¹, HCN at 3735 cm⁻¹ for fresh N-CMK-3_600 sample, and d) intensity vs. temperature of the peaks relative to NH₃ at 965 cm⁻¹, H₂O at 1505 cm⁻¹, CO at 2179 cm⁻¹, CO₂ at 2349 cm⁻¹, HCN at 3735 cm⁻¹, paraffin by -CH₂ at 2925 cm⁻¹, oxidized paraffin by -C=O at 1715 cm⁻¹ for the same sample after H₂O adsorption [80–82].

4. Conclusions

This work investigated the CO₂ capture ability and selectivity over N₂ and H₂O gases in simulated post-combustion flue gases by N-containing carbonaceous adsorbents. Three different N-containing ordered mesoporous carbons of the CMK-3-type were successfully synthesized through the nanocasting method of D-glucosamine on SBA-15 silica template. The pyrolysis temperature was adjusted to tune both the porosity features and the surface chemistry (e.g., N content) in a single step. It was observed that a higher N content improved both the CO₂ adsorption at a temperature close to room temperature and atmospheric pressure and the selectivity toward CO₂ in CO₂/N₂ gas mixtures. In this work, D-glucosamine was chosen as the nitrogen-rich carbon source, being sustainable and renewable, as extractable from chitin, the second most abundant natural polymer present in several biomass residues (e.g., insects, arachnids, or crustaceans) [83]. Furthermore, nanocasting from broadly available SBA-15 silica template worked as a standardized procedure for tuning both the porosity features and the surface chemistry in a single step, thus bypassing post-synthesis modification aimed at increasing micropore content and heteroatoms doping.

Specifically, a maximum CO₂ adsorption capacity of 1.66 mmol/g for pure CO₂, and 1.03 mmol/g for 20% CO₂ in N₂ was obtained for the sample with the highest N content (N-CMK-3_600, with 11.3 at.% of N). However, N species enhanced also the affinity for H₂O, so that the N-CMK-3_600 sample experienced a higher reduction in CO₂/H₂O selectivity in comparison to the sample N-CMK-3_750,

which contains a lower amount of nitrogen (8.3 at.%). Generally, despite an unavoidable reduction in the CO₂ uptake in humid gas mixtures, due to the competitive adsorption between CO₂ and H₂O, the studied samples still retained good CO₂ capture capability. As mentioned above, the N-CMK-3_750 sample better preserved the selectivity for CO₂ uptake in moist gas compositions with a CO₂ uptake of 1.52, 0.61, and 0.89 mmol/g at RH 25, 50, and 75%, respectively. However, the repetition of the CO₂ adsorption tests after H₂O adsorption revealed a considerable reduction in the uptake, owing to the incomplete desorption of water mainly from very narrow micropores ($\varnothing < 1$ nm), thus making these binding sites unavailable for the subsequent capture of CO₂. Conversely, the retention of the CO₂ capture properties under repetitive sorption-desorption cycles was assessed by reusability tests in pure CO₂ flow, revealing almost unvaried performances even after 10 cycles. Only a slightly appreciable efficiency loss was registered between the first and the second cycle, but it is ascribed to irreversible sorption of CO₂ molecules, which stayed bound at the most energetic sites after the regeneration step at 150 °C. The hypothesis of the degradation of the samples was excluded because, after the second cycle, the CO₂ adsorption remained reproducible upon multiple cycles.

In summary, the obtained sorbents displayed good characteristics in terms of adsorption capacity, cyclability in pure CO₂, and selectivity in CO₂/N₂ and CO₂/H₂O binary mixtures, in comparison with other materials reported in the literature (as in Table S2) [23,24,30,84–86]. Furthermore, this study satisfies the original aim to explore the competition between H₂O and CO₂ from simulated

post-combustion flue gas mixtures onto N-rich carbons, to identify their potentiality and limits from a real application perspective. Therefore, in a future perspective, the identification of the ideal reactivation conditions for fully restoring the specific CO₂ adsorption sites from accidentally adsorbed H₂O might be the decisive solution, to assure complete reusability of the sorbents applied for CO₂ capture from moist flue gases.

Author contributions

The manuscript was written with the contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding sources

The RECODE project received funding from the EU's H2020 (R&I) programme under GA 768583. E.M., T.P., and F.K. acknowledge the funding support of the University of Vienna (Austria).

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Claudio Gerbaldi reports financial support was provided by European Commission.

Data availability

Data will be made available on request.

Acknowledgment

The RECODE project received funding from the EU's H2020 (R&I) programme under GA 768583. E.M., T.P., and F.K. acknowledge the funding support of the University of Vienna (Austria). The authors are thankful to Dr. Salvatore Guastella for XPS measurement in the core facility (Department of Applied Science and Technology, Politecnico di Torino), Dr. Marco Fontana for TEM images (Center for Sustainable Future Technologies (CSFT), Istituto Italiano di Tecnologia (IIT)) as well as to Dr. Giuseppe Ferraro Center for Sustainable Future Technologies (CSFT), Istituto Italiano di Tecnologia (IIT)) and Dr. Rémy Guillet-Nicolas (Department of Inorganic Chemistry – Functional Materials, University of Vienna) for technical support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtsust.2022.100270>.

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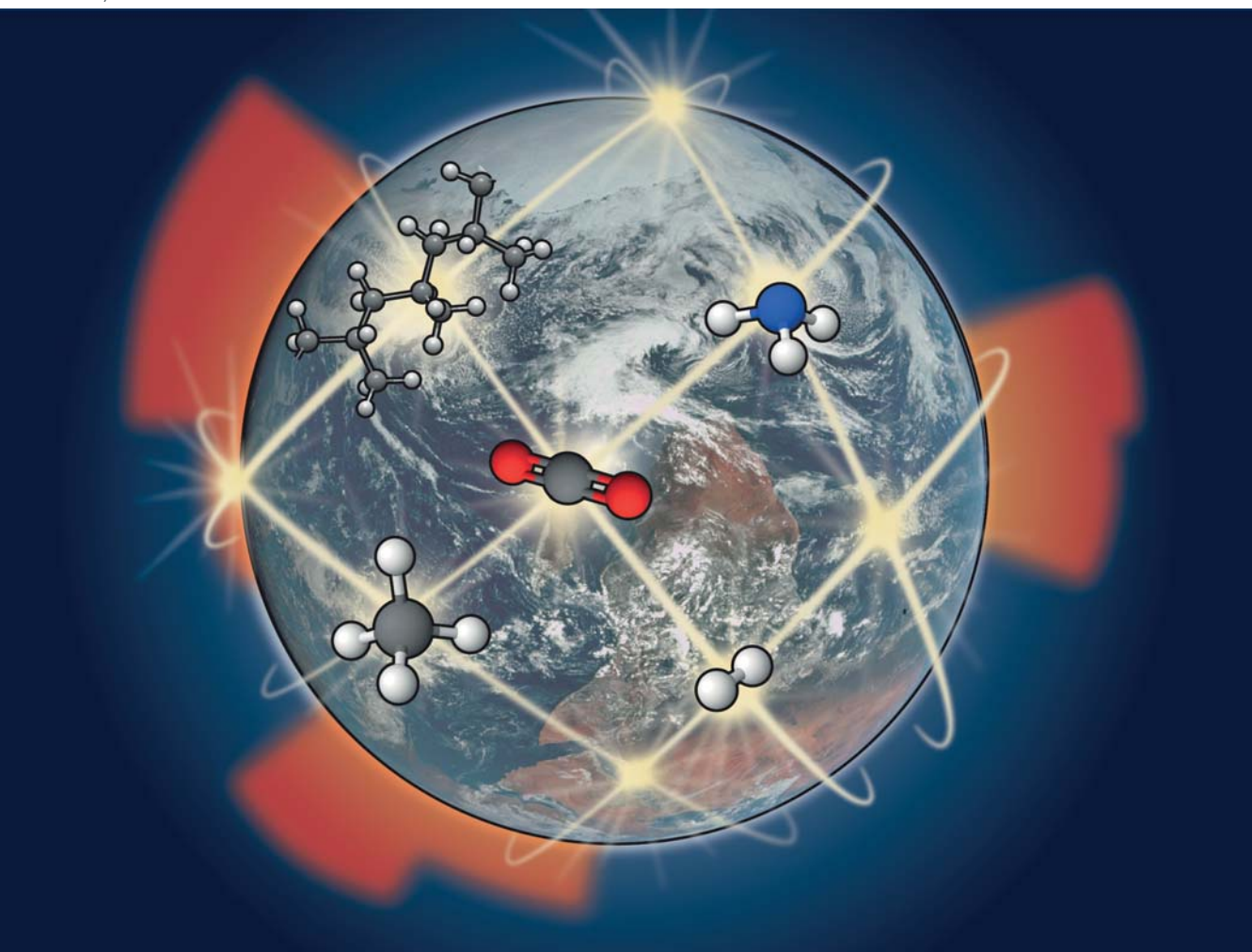
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Chemical Science

Volume 15
Number 24
28 June 2024
Pages 9003–9378

rsc.li/chemical-science



ISSN 2041-6539



EDGE ARTICLE

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An anthropocene-framed transdisciplinary dialog at the chemistry-energy nexus

Cite this: *Chem. Sci.*, 2024, 15, 9054

All publication charges for this article have been paid for by the Royal Society of Chemistry

An anthropocene-framed transdisciplinary dialog at the chemistry-energy nexus†

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At the energy-chemistry nexus, key molecules include carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄), and ammonia (NH₃). The position of these four molecules and that of the more general family of synthetic macromolecular polymer blends (found in plastics) were cross-analyzed with the planetary boundary framework, and as part of five scientific policy roadmaps for the energy transition. According to the scenarios considered, the use of some of these molecular substances will be drastically modified in the coming years. Ammonia, which is currently almost exclusively synthesized as feedstock for the fertilizer industry, is envisioned as a future carbon-free energy vector. "Green hydrogen" is central to many projected decarbonized chemical processes. Carbon dioxide is forecast to shift from an unavoidable byproduct to a valuable feedstock for the production of carbon-based compounds. In this context, we believe that interdisciplinary elements from history, economics and anthropology are relevant to any attempted cross-analysis. Distinctive and crucial insights drawn from elements of humanities and social sciences have led us to formulate or re-raise open questions and possible blind-spots in main roadmaps, which were developed to guide, *inter alia*, chemical research toward the energy transition. We consider that these open questions are not sufficiently addressed in the academic arena around chemical research. Nevertheless, they are relevant to our understanding of the current planetary crisis, and to our capacity to properly assess the potential and limitations of chemical research addressing it. This academic perspective was written to share this understanding with the broader academic community. This work is intended not only as a call for a larger interdisciplinary method, to develop a sounder scientific approach to broader scenarios, but also – and perhaps mostly – as a call for the development of radically transdisciplinary routes of research. As scientists with different backgrounds, specialized in different disciplines and actively involved in

Received 5th January 2024
Accepted 10th April 2024

DOI: 10.1039/d4sc00099d

rsc.li/chemical-science

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4sc00099d>

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contributing to shape solutions by means of our research, we bear ethical responsibility for the consequences of our acts, which often lead to consequences well beyond our discipline. Do our research and the knowledge it produces respond, perpetuate or even aggravate the problems encountered by society?

1. Introduction

1.1. Anthropocene: the overarching context

The term Anthropocene, popularized by Paul J. Crutzen (an atmospheric chemist) around 2000,¹ is becoming established both among scientists and the wider public. It reflects how Earth's biochemical processes have been profoundly altered by humanity's way of inhabiting the environment (housing, agriculture, industry, transportation, *etc.*). The effects extend to the composition of the Earth's crust and its atmosphere. Consequently, our activities have become an Earth-altering force of geological magnitude. The term was devised to refer to our current age, considering that the Earth had moved beyond the stable periods of the Holocene (the temperate period of the last 12 000 years, following the last Pleistocene glaciation) and the striving age of humanity (with the beginning of agriculture around 11 000 years ago). The Anthropocene age is characterized by fluctuations and uncertainty, which are further exacerbated by the "great acceleration" suggested by the analysis of several socio-economic and Earth Systems trends performed by scientists from the Stockholm Resilience Center.² With others, P. J. Crutzen and W. Steffen contributed to the definition of the "planetary boundaries"-framework aiming to assess the extent and consequences of our impact on nine Earth system processes.^{3–14}

The challenges posed by the Anthropocene will need to be addressed, and science, including chemistry, is expected to be part of this process. Indeed, options for change, and their implementations to help either avoid or mitigate the multidimensional ecological crisis humanity faces will need to be scientifically informed. Among the pressing open questions, scientists must provide new knowledge to help the deployment of solutions to achieve an equilibrium between our energy and resource consumption and the planet's human habitability. Several sustainability-driven systemic frameworks have been proposed for chemistry, *e.g.*, the green and sustainable periodic table,¹⁵ one-world-chemistry,¹⁶ or "circular chemistry for circular economy".¹⁷ Implementing sustainability has also been advocated for in chemistry education, through the teaching – among other principles – of systems thinking.^{18–20}

In this paper, we particularly explore the importance of Anthropocene-spurred interdisciplinary connections between the social sciences, chemistry and the humanities as part of the search for the sustainability-driven balance at the chemistry-energy nexus.

1.2. About the authors

Chemistry's connections with ethical, social, economic, and political aspects have always been present, since chemistry both shapes and is being shaped by them. At the same time, these connections become more explicit in the Anthropocene, since

the Anthropocene questions the roles of human societies in natural dynamics. The Anthropocene therefore explicitly calls for a dialog between, and even an interweaving of, the social and natural sciences in order to scientifically consider the state of the planet and its future course.

Since interweaving social and natural sciences is a defining stance of this manuscript, it seemed necessary to adopt aspects of the social sciences in our writing, even though they are rarely used in the natural sciences. We will therefore start by stating "from where we write". Indeed, social scientists have demonstrated that scientific discourse – including that in the natural science field – is rarely neutral. Despite all the methodological precautions, all scientific discourse is historically and culturally situated.^{21,22} This contrasts with the idea of science as neutral and objective, which is a recurrent trope in the natural and physical sciences. Therefore, as a prelude to any attempt at interdisciplinarity of chemistry-centered academic research, it seemed necessary to make this teaching our own, and to specify aspects of our own situations and backgrounds (details in ESI, Section SI-1.1†). Briefly, we are a group of scholars with different profiles (age, career trajectory, nationality) and disciplinary backgrounds, including chemistry, economy, history, and ethics. We share a common viewpoint, that a narrow disciplinary approach cannot successfully guide chemistry-centered research in the context of the Anthropocene due to the complexity of the associated interdependencies. This shared viewpoint led us to formulate two questions: do we consider that the way chemists are called upon to work on the energy transition by some, if not most, leading research-shaping authorities satisfactorily aligns with Anthropocene-related challenges? Can interdisciplinarity help us to shape tools to answer this question?

1.3. Outline and scope of the paper

After the introduction, the paper is developed in three sections. In Section 2, elements of the planetary framework are presented through five representative molecular substances: carbon dioxide (CO₂), hydrogen (H₂), ammonia (NH₃), methane (CH₄), and (bio)polymers. For each of these substances, Section 3 presents an analysis of a selection of recently published scenarios produced by leading organizations guiding policy makers in Europe, where most of the authors are based (more details in the ESI, Section SI-1†), and at the global level. These include scenarios by the IPCC (Intergovernmental Panel on Climate Change),²⁵ the IEA (International Energy Agency),²⁴ Dechema,²⁵ Sunergy,²⁶ and Shell.²⁷ Section 4 builds upon a selection of insights provided by other disciplines, in particular drawing in the social sciences and humanities (history, economics, political science, ethics), to highlight some limitations that emerge when attempting to bring together the



elements presented in the two previous sections. We then conclude and share our current perspectives on the topic.

Our focus on the chemistry-energy nexus, which is our main center of academic expertise, necessarily obscures other aspects for which chemistry is central. Indeed, we make no claims to exhaustivity nor to have selected the most important possible subfields. At the same time, this approach allowed us to define a perimeter, the energy transition, which attracts or even monopolizes a large segment of public and scientific discourse, thus justifying the scope, relevance, and timeliness of this manuscript. Our paper is intended to all scientists not familiar with transdisciplinary research: PhD students, early career researchers and more senior scholars, in chemical sciences or trained in other fields and working on the energy transition, who do not regularly have opportunities to experience what substantial integration of other disciplines can bring to their own research. Our aim is to share with our peers some of our thoughts and concerns about the transdisciplinary challenges associated with our research.

2. Five sample molecular substances at the energy/chemistry/planetary boundaries nexus

2.1. Why these five molecular substances?

The nine Earth system processes and their Planetary Boundaries (PB) scientific framework was developed in tight association with the Anthropocene concept in 2009 by authors from the Stockholm Resilience Centre and others. These PB correspond to quantitative limits associated with essential Earth system processes.⁴ The framework attempts to define quantitative boundaries within which humanity can continue to evolve safely in the long-term with the stability that characterized the Holocene. PB have been quantified for many years for seven of these nine Earth system processes^{3–11} – freshwater use, land-system change, biosphere integrity, climate change, stratospheric ozone depletion, ocean acidification, and

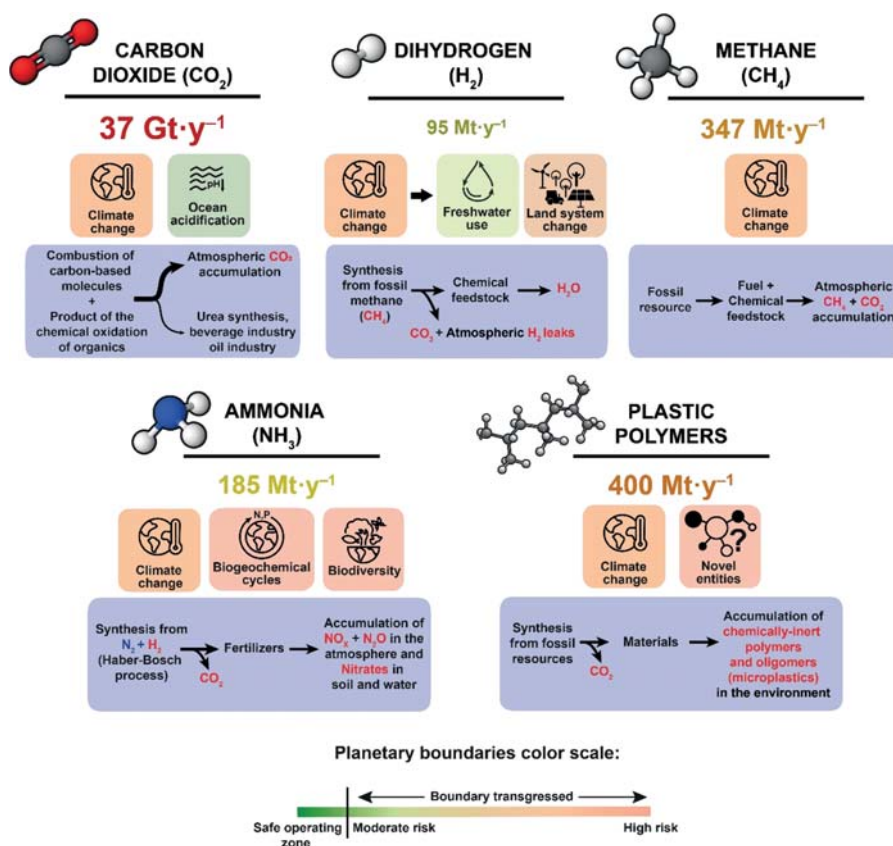


Fig. 1 The four molecules (CO₂, H₂, CH₄ and NH₃) and plastic polymers, chosen here as illustrative molecular substances sitting at the crux of the chemistry-energy nexus. For each of these substances, are reported: their current annual global production (in 2022), and the main Earth system processes with which they interact. In the case of dihydrogen, the shift in affected Earth system processes entailed by a shift towards production of "green hydrogen" (see Scheme 1 for definition) is materialized by an arrow. The current level of transgression of each planetary boundary estimated in literature is represented by its color, according to the caption at the bottom of the figure. Finally, current mode of production, main usage, and issues associated with end-of-life considerations are described in the blue boxes. More details in text and in ESI, Table SI-3.†

biogeochemical flows – and are updated regularly,^{12,13} whereas estimation of the remaining two – atmospheric aerosol loading and novel entities – has only started recently.^{12,14} All these Earth system processes have aspects which are at the heart of the chemical-energy nexus and are therefore closely related to the chemical sciences.

Here, we have chosen four molecules to focus on: carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄), and ammonia (NH₃). We selected these molecules not only because their consumption and production are central to the fabric of modern society, but also because they have been repeatedly identified as key pieces of the global transition needed to wane from excessive fossil resources consumption. They are projected to fill crucial niches in alternative carbon-free or carbon-neutral processes. As such, they appear central to most energy-driven transition scenarios proposed by governments, scientific consortia, and companies in their roadmaps for the coming three decades, all of which emphasize the objective of “Net-Zero-Emissions by 2050”, as called for by the COP2021 Paris agreement,²⁸ and the United Nations.²⁹ We have added to the four molecules listed above the broader family of synthetic macromolecules represented by polymer blends found in plastics. According to the IEA, “petrochemicals are rapidly becoming the largest driver of global oil demand”,³⁰ and nowadays, 90% of these petrochemicals are used for the synthesis of polymers.³¹ Plastics are thus currently tightly dependent on fossil resources: their inclusion in our scope aimed at introducing an indicator of fossil-based chemical production not directly embedded in energy-driven scenarios (Fig. 1).

Below, we present an overview of the space occupied by these five molecular substances in the current global chemical landscape, in particular in relation to energy, and how they can be linked to the Planetary Boundaries framework.

2.2. Carbon dioxide

Anthropic CO₂ overwhelmingly remains a waste product of oxidative fossil fuel use as a heat source, or for other energy generation. Four sectors were responsible for 94% of the 36.8 Gt of CO₂ released worldwide in 2022: power generation (14.65 Gt), industry (9.15 Gt), transportation (7.98 Gt), and building (2.97

Gt).³² Among industrial processes, most emissions are linked to the production of cement, iron, and steel. In 2022, 4.16 Gt of cement were produced,³³ releasing 2.4 Gt of CO₂ into the atmosphere (0.58 t of CO₂ produced per ton of cement).³⁴ During the same year, 1.88 Gt of steel and iron were produced,³⁵ associated with 2.6 Gt of CO₂ (1.41 t of CO₂ per ton of steel).³⁶ Chemical and petrochemical production emitted 1.33 Gt of CO₂ in 2022.³⁷ This included the production of ammonia (419.80 Mt of CO₂ emitted), methanol (261.25 Mt of CO₂ emitted), and other high-value chemicals (*i.e.*, ethylene, propylene, benzene, toluene, xylenes, 255.29 Mt of CO₂ emitted in total).³⁸ Although the chemical sector ranks third in terms of direct CO₂ emissions (25% due to processes, 75% due to fuel combustion), it is the primary consumer of energy: 50% of primary petrochemicals are used as actual energy-source to fuel the processes, and 50% are used as feedstock – and are thus no longer available for energy generation.

The current main uses of CO₂ as a feedstock are for food and beverage purposes (230 Mt per year),³⁹ enhanced oil recovery (80 Mt per year),³⁹ and in the synthesis of key compounds: urea (130 Mt per year), methanol (2 Mt per year), salicylic acid (30 kt per year), and cyclic carbonate (40 kt per year).³⁶ Overall, these processes consume up to 422 Mt per year, which is only slightly more than 1% of the annual anthropogenic CO₂ emissions.

2.2.1 Link to Earth system processes and their planetary boundaries. The concentration of carbon dioxide in the atmosphere has increased from 277 ppm in 1750 to 417 ppm in 2022 (+51%).⁴⁰ This accumulation has led directly to an increase of the global mean surface temperature of more than 1 °C.⁴¹ The PB associated with climate change is an atmospheric CO₂ concentration of 350 ppm, which has thus been crossed.⁴² Any further increase in CO₂ emissions adds to the ocean acidification as well: the associated planetary boundary is set at a minimum level of aragonite saturation of 80% of the pre-industrial level, whereas the current value amounts to 81%.^{42,43} Over the period 1980–2016, a decrease of pH from 8.11 to 8.06 was reported, which is 100 times faster than any change in acidity experienced during the previous 55 million years.⁴⁴ Crossing both of those PB has cascading consequences, such as rising sea levels or extreme weather events, and endangers many species. The rise in atmospheric CO₂

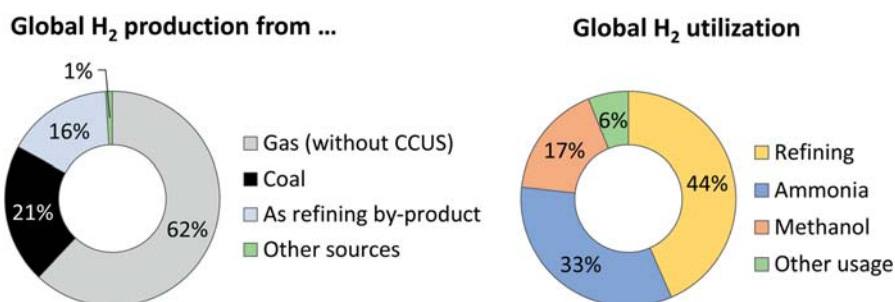


Fig. 2 Production (left) and utilization (right) of H₂ in 2022, according to IEA.⁴⁸ “Other sources” in the H₂ production panel include oil (0.5%), fossil fuels coupled to CCUS (0.6%), and water electrolysis (0.1%). “Other usage” in the H₂ utilization panel is mostly linked to the iron and steel industry (DRI, Direct Reduced Iron).



concentration results from CO₂-emissive anthropogenic activities: fossil fuel combustion and industrial activity were responsible for around 5 Gt of CO₂ in 1950, around 15 Gt in 1970, and more than 37 Gt in 2023.^{32,41,45,46}

2.3. Hydrogen

Historically, large-scale hydrogen use was first developed in the 18th century with aerial transportation (Zeppelin airships). It expanded in the 20th century as part of massive industrial processes (mainly ammonia and methanol production and oil refining, Fig. 2, right), and also found niche applications in space propulsion or lubrication. Some consider the end of the 1990s as the period when the idea of a hydrogen-based society emerged, with applications expected in both transportation and energy.⁴⁷

Global hydrogen production reached 95 Mt in 2022⁴⁹ of which less than 0.7% is low-emission hydrogen, *i.e.*, mostly from fossil fuel coupled to carbon capture, utilization and storage (CCUS) technologies (0.6%), or through water electrolysis (0.1%): in 2022, only 100 kt of H₂ was produced by electrolysis.⁴⁸ The remaining >99% was produced through fossil fuel-based industrial processes, primarily from natural gas through steam reforming (Fig. 2, left). The demand for hydrogen is mainly related to refining processes (*e.g.*, for the removal of sulfur from crude oil) and base chemical production, like key small molecules (*e.g.*, ammonia), chemical

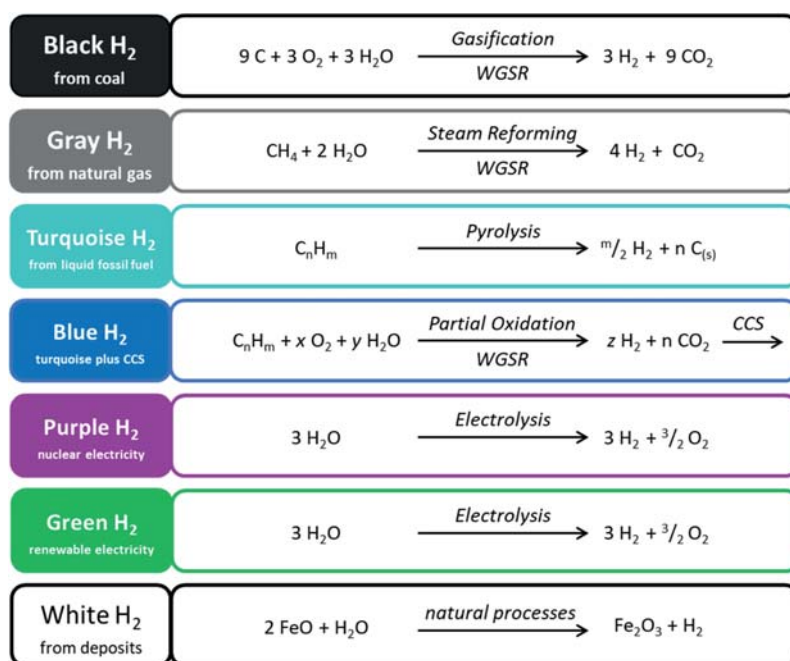
intermediates (*e.g.*, methanol), and fine chemicals (*e.g.*, for the food and pharmaceutical industries). These numerous applications reveal how hydrogen connects fossil resources to several global production processes.

2.3.1 Link to Earth system processes and their planetary boundaries. Since more than 99% of current hydrogen is produced using fossil fuels, its production bears a considerable planetary burden. In 2022, H₂ production was responsible for 1.144–1.291 Gt of CO_{2eq.} emissions.^{48,49} The well-to-gate greenhouse gas (GHG) emissions from natural gas-powered steam reforming were 9 kgCO_{2eq.} per kgH₂.⁴⁸

2.4. Methane

Most of the methane currently used in the industry and energy sector is of fossil origin, as it is a major component of natural and shale gas. Between 2010 and 2021, worldwide methane consumption rose by 28% to 4038 billion cubic meters (bcm) (132 EJ, 4.3×10^{13} kW h).⁵⁰ Methane is mainly used as an energy source through combustion. Compared to coal and oil, the combustion of methane is more carbon efficient: natural gas-powered plants emit about 50% less CO₂ than coal-powered plants⁵¹ (see Scheme 1 for a relative comparison based on hydrogen production rather than fuel combustion).

About 15% of methane is used as a chemical feedstock.⁵² Current upgrading routes of methane progress *via* steam methane reforming and the water-gas shift reaction (CO₂/CO/



Scheme 1 Simplified chemical reactions (only one possible representative reaction is shown) associated with current fossil-based and projected hydrogen syntheses, with CO₂ emissions decreasing top to bottom and the corresponding "color" scheme used in literature. WGSR: water–gas shift reaction. CCS: carbon capture and storage.^{78–80}



H₂ mixtures). Direct routes for methane upgrading (either under oxidative or non-oxidative conditions) have been proposed as alternatives, yet limited advances have been made in converting methane into chemicals other than syngas. Given methane's important role in the current energy infrastructure, biomass methanization processes are being developed, and other biological, photo-, electro- or photoelectrochemical routes are explored (power-to-methane, either *via* direct electrolysis of captured CO₂ or *via* the intermediate production of green H₂, for example; see Scheme 1 for the definition of "green H₂").

2.4.1 Link to Earth system processes and their planetary boundaries. Methane is a potent GHG, with a Global Warming Potential over a 100 years period (GWP-100) estimated to be between 27 and 30 (vs. GWP-100 = 1 for CO₂). Methane emissions may arise from its production or transportation.

In 2021, 144 bcm (4.7 EJ, 1.5×10^{12} kWh) of natural gas were flared: besides being a waste of fuel, flaring also releases CO₂, soot, and other greenhouse gases in the atmosphere. In 2022, a 3% decrease in flaring was recorded.⁵³ More ambitiously, the World Bank's Zero Routine Flaring by 2030 initiative,⁵⁴ which is in line with the Net-Zero Emissions by 2050 scenario²⁴ calls for a complete stop to this practice.

Large distances often separate up- and downstream processing sites of methane, necessitating extensive and vulnerable infrastructures, particularly pipelines and tankers to transport liquefied natural gas (LNG). For instance, methane emissions from local distribution in the United States have been estimated at 0.69 Mt per year.⁵⁵ Methane leaks at various points in the natural gas supply chain can have detrimental environmental consequences.⁵⁶

2.5. Ammonia

The Haber-Bosch process is at the root of industrial ammonia production. It converts atmospheric N₂ to NH₃, while consuming about 1.2% of the world's energy (about 39.3 GJ required per ton of ammonia produced). Current annual industrial ammonia production is 185 Mt.⁵⁷ This represents the amount of anthropogenic elemental nitrogen that enters the reactive nitrogen (Nr) pool every year: 75–80% in the form of fertilizers and 10% as explosives. Fertilizers include urea (NH₂)₂CO, ammonium sulfate (AS), diammonium phosphate (DAP), monoammonium phosphate (MAP), ammonium nitrate (AN), and calcium ammonium nitrate (CAN). The nitrates among these can be further combined with phosphates to generate NPK (nitrogen, phosphorus, potassium) fertilizers. When used, urea (~60% in N mass) will eventually release CO₂ back into the atmosphere.

15% in N mass of ammonia is converted to nitric acid (HNO₃) through the Ostwald process, *en route* to nitrates.^{58,59} During the Ostwald process, 6–9 kg of N₂O, a potent GHG (298 CO_{2eq}), are produced along each ton of nitric acid, although abatement measures may reduce this value down to 0.12 kg.⁶⁰ This main route to nitrates which starts with dinitrogen reduction *via* Haber-Bosch to ammonia followed by oxidative Ostwald process is a chemical detour and thus energy intensive.

Further down the "value chain" of ammonia utilization as fertilizer, the ammonia-to-eaten food arc has a deplorable nitrogen use efficiency.⁶¹ Overall, between 86 and 96% of the nitrogen fixed as ammonia is not eaten, which represents a significant waste of energy and excess CO₂ emissions during NH₃ manufacturing, transformation, transport, and dispersal.⁶² A significant fraction of losses occurs through denitrification of NH₃ to N₂: the non-denitrified "run-off" nitrogen excess contributes substantially to major pollution events such as eutrophication, marine anoxia, and fine particle emissions (PM_{2.5}, particulate matter <2.5 μm), leading to loss of biodiversity. Among these run-off nitrogen compounds, 3 to 5% of ammonia degraded through biological denitrification is released as the GHG N₂O.⁶³ In fact, if only 10% of annual ammonia production were biologically denitrified, the CO₂-equivalent footprint of N₂O byproducts would be comparable to that of the whole Haber-Bosch process, thus doubling the carbon footprint of ammonia synthesis.

2.5.1 Link to Earth system processes and their planetary boundaries. Because of this massive anthropogenic flux of Nr, the nitrogen geochemical cycle is among the most severely transgressed planetary boundaries. In the PB framework, the safe operating space has been estimated at 62 Mt per year of Nr:⁸ the current anthropogenic Nr is 190 Mt per year, that is five-fold above the considered safe operating space limit (see Fig. 1 and Table SI-3†).¹² Current agricultural practices are reliant on the use of ammonia-based fertilizers and on other chemicals, which also require ammonia during their production: these include, but are not limited to, the herbicides metolachlor, glyphosate, or atrazine, and neonicotinoid insecticides like imidacloprid. These chemicals or their decomposition products are expected to negatively impact freshwater use and biosphere integrity.⁶⁴ Moreover, since – unlike ammonia – most of these synthetic chemicals do not belong to natural biochemical degradation manifolds, they contribute to current transgression of the planetary boundary associated with "Novel entities".¹² However, their impact remains to be quantified given no identification of a unique control variable for the Earth system process.

In summary, ammonia is produced, dispersed, and chemically transformed in quantities and ways that are difficult for Earth Systems to "metabolize" without entailing severe effects on Earth system processes, causing most planetary boundaries to be transgressed.

2.6. Plastics

The definition of term "plastics" varies depending on the source.⁶⁵ The term generally refers to materials which contain an essential ingredient synthetic polymers of high molecular mass. Plastics include some of the most widespread synthetic carbon-based materials. The roughly 400 Mt of plastics produced in 2022 are mainly constituted of the following polymers: polypropylene (PP) counts for 18.9% of the production, followed by low density and linear low-density polyethylene (PE-LD, PE-LLD) with 14.1%, polyvinyl chloride (PVC) at 12.7% and high density and medium density polyethylene (PE-HD, PE-MD)



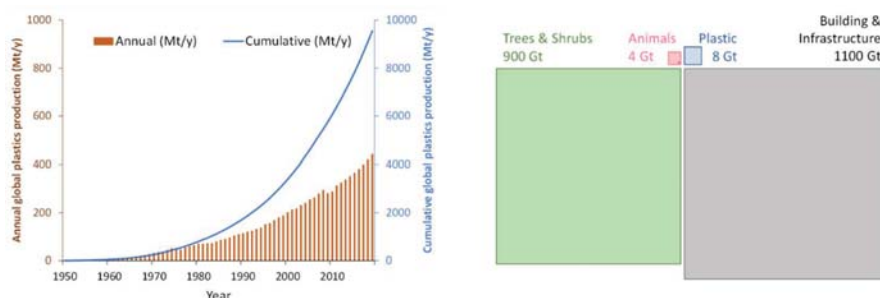


Fig. 3 Left: annual (brown bars) and cumulative (blue line) global plastic production between 1950 and 2019 (data by OurWorldinData, Licence CC-BY).⁶⁹ Right: comparison between the mass of animals (pink), trees & shrubs (green), plastic (blue), and building & infrastructure (gray). The areas of the squares are proportional to the total mass estimated for each group.⁶⁸ The red dot in the "Animals" square represents at scale the mass of all human beings (ca. 0.06 Gt of carbon).⁷⁰ Assumptions in mass accounting made in different studies explain the differences in absolute numbers between the left and right parts of the figure; the overall message remains the same in the two parts of the figure, with respect to the general trend discussed here.

at 12.2%.⁶⁶ The remainder share of production is mainly constituted by polyethylene terephthalate (PET), polyurethanes (PUR), and polystyrene (PS), together with the contribution of other less common polymers. More than 90% of the total amount of polymers is obtained from the polymerization of petrochemicals and are therefore fossil-based. "Circular" plastic (*i.e.* recycled or bio-based) is estimated to account for the remaining 10%.⁶⁶ The vast majority of plastics produced are used in the packaging industry (44%) followed by the building and construction industry (18%).⁶⁷

Global plastics cumulative production has risen exponentially from 1950 to 2019 (Fig. 3, left), to the point where the total amount of plastics now accounts for twice as much as the total mass of animals on the planet,⁶⁸ contributing to 2020 being a landmark year: it is the date when the combined weight of man-made elements started exceeding that of all living biomass (Fig. 3, right).

2.6.1 Link to Earth system processes and their planetary boundaries. It was estimated that the global life-cycle GHG emissions of plastics were 1.8 Gt of CO_{2eq.} worldwide in 2019, that is 3.4% of global GHG emissions, and 90% of these emissions are caused because plastics are manufactured from fossil resources.⁷¹ These facts link plastics life-cycle to the "climate change" Earth system process.

Furthermore, synthetic polymers traditionally combine high chemical stability with the absence of any natural biogeological cycle, leading to long residence times in most environments. As such, their massive introduction at accelerating rates has recently been presented as the main evidence of transgression of the "Novel Entity" Earth system process.¹⁴ Despite difficulties in accurately quantifying the PB related to this process, the claim that the boundary has been transgressed is linked to the fact that the rate of production and release of plastics is so rapid that it has outstripped our ability to assess safety and monitor adverse environmental effects. To support this, there is increasing evidence that plastic and microplastic ingestion and accumulation can lead to environmental and health damage,⁷² affecting the biosphere integrity and the freshwater use Earth system processes.

3. Selected scenarios and projections through the prism of these molecular substances

3.1. Selected scenarios

The five molecular substances under discussion in this article are among key levers of the energy transition. Strategies for their production or management have been the subject of modelling efforts by a wide range of institutions ranging from intergovernmental, international, national, and private bodies to industry leaders.

These institutional and private stakeholders provide data and advice to policy makers, so that they can implement actions to meet the objectives and define regulations surrounding the production and use of chemicals on their territory and, by extension, globally. It is clear that many factors can influence the vision presented in these roadmaps, starting with the identity of the authors. Given our Europe-centered composition, using representative European examples, we will explore the visions most often presented to political leaders and policy makers, resulting in policy programs shaping the research objectives chemists are expected to meet.

Among the available scenarios, we selected five bodies that cover a part of this institutional diversity while largely maintaining a focus on United Nations-level, trans-Atlantic and Europe-centered institutions, organizations, and companies.

- The Intergovernmental Panel on Climate Change (IPCC):²³ the United Nations body assessing the science of climate change from a global perspective. IPCC reports are based on a diverse array of data and research from member countries and aim to provide policy makers with scientific assessments of climate change and to propose appropriate mitigation and adaptation approaches.

- The International Energy Agency (IEA):²⁴ this intergovernmental organization provides reports, data, and analyses of the global energy sector. In particular, it publishes policy recommendations to reach targets set by the political leadership of its



members. It has 31 member-countries and 13 association countries, which overall represent 75% of the global energy demand. As an autonomous body under the umbrella of the Office of Community Economic Development (OECD), spurred from post-world war II Marshall plan, its membership reflects this trans-Atlantic barycenter. The current members, for example, do not include Africa, Russia, most of Asia and Middle East (Japan, South Korea, Turkey, and Israel are members).

- Dechema, the German Society for Chemical Engineering and Biotechnology:²⁵ a German non-profit organization representing over 5000 chemists, biotechnologists, and engineers, working at the interface between academic science, industry, economics, and the general public. Dechema has notably published several roadmaps for the use of chemicals in the European Union in the coming years.

- The Sunergy Initiative²⁶ powered by the EU-funded SUNER-C coordination and support action: this community groups together more than 300 academic and industrial stakeholders, with the aim of studying and promoting the development of breakthrough technologies to allow circular energy models at the European level.

- Private stakeholders, whose businesses involve the use or production of the substances of interest here, have regularly published data and perspectives on their activities. As a representative example, we selected the British-Dutch oil company Shell,²⁷ which is one of the largest multinationals. Shell regularly publishes reports on the future of fossil fuel and frequently lobbies policy makers regarding regulations on fossil fuel resource extraction, management, and use.

As summarized in Table 1, these scenarios are not synoptic. Their authors have vastly different roles in society, which results in a multitude of approaches and ultimately different individual goals. At the same time, we posit that a dominant picture for each of the five molecular substances described above can be proposed from a comparative analysis of these scenarios. While nuances or even differences exist between these scenarios, our goal is precisely to explore the possibility that a shared picture can be extracted, which surpasses the fragmented vision offered by focusing on the specificities of each scenario.

3.2. Dominant projected future for carbon dioxide

All scenarios consider anthropogenic CO₂ emissions to be the main cause of climate change, and share common views of future CO₂-related technologies. To reduce the concentration of CO₂ in the atmosphere it should be captured either from air (Direct Air Capture, DAC) or from point sources, where CO₂ is very concentrated (e.g., industrial exhaust fumes). The captured CO₂ should then either be used as a starting material to produce fuels and primary chemicals (CCU, Carbon Capture and Utilization), or stored through geological storage or mineralization (CCS, Carbon Capture and Storage). All published scenarios share a demand for large-scale and low-cost “green energy” to power these processes, “green energy” ranging from energy from renewable sources (solar, wind, ...) to energy production routes with lower carbon impact with respect to current dominant ones.

Potential solutions (carbon storage vs. carbon utilization) vary between the different authors involved – academia, policy makers or industry. As CO₂ is the key driver of climate change, the IPCC proposes a 2030 goal of a 45% reduction in CO₂ emissions. Shell sees CO₂ as an unavoidable byproduct of energy generation: to maintain the level of production of (petro-sourced) energy, Shell suggests that the emitted CO₂ should therefore be captured and kept in geological storage by the (petro)chemical industry itself. The required CCS (Carbon Capture and Storage) technologies should be powered by wind and solar energy, to decrease total CO₂ emissions by 50% in 2030.²⁷ The other scenarios analyzed here – Dechema and Sunergy – focus on either CO₂ captured from air or sequestered from point sources and its use as a key feedstock in the chemical value chain. To allow the maturation of the novel required processes, the significant emission-reduction goals in their scenarios are set only after 2030.^{25,26}

Below we will discuss technologies directly related to CO₂, although some of them rely on other processes such as the production of “green” hydrogen (see Scheme 1) or the generation of decarbonized electricity. The level of detail available on the technologies to be promoted differs depending on the scenario.

3.2.1 Carbon capture. Carbon capture technologies are quite advanced, and proofs of concept have been established, with some facilities already running.⁷³ However, remaining difficulties are linked to, *inter alia*, high costs and energy consumption, which hamper scale-up and industrial applicability. Broader application will therefore depend on future efficiency gains.

Sunergy has reviewed various solutions for carbon capture. The most mature technology is amine-based CO₂ absorption: large plants are expected to capture from a point source up to 0.4 MtCO₂ per year at an energy cost of about 3.5–3.8 GJ/tCO₂, and an economic cost of less than 50 € per tCO₂. Higher modularity could be achieved by implementing membrane adsorption.²⁶ Direct air capture (DAC) is also possible, but poses the additional problem of separation and purification of the low-abundant CO₂ in air, if it is to be subsequently exploited. Today, each ton of CO₂ treated by DAC costs €300–600 and consumes 5–9 GJ of energy. Nevertheless, the IEA estimates that following scale-up and optimization, DAC costs could fall to less than 100 € per tCO₂.²⁴ Sunergy also proposes a long-term solution based on the direct capture of CO₂ from the air in small-scale, decentralized plants.²⁶ Dechema, in contrast, considers harnessing point sources to be the most appealing strategy as it would allow easier capture of highly concentrated CO₂ streams.²⁵

The scenario proposed by the IEA involves large-scale facilities capable of capturing about 1200 MtCO₂ per year in 2050. In 2022, about 45 Mt of CO₂ were captured, and based on the TRL of future planned plants, the IEA estimates that about 390 Mt year could be captured in 2030, *i.e.*, less than a third of the Net Zero Emissions, NZE, goal.⁷⁴ Carbon dioxide removal technologies would only have a significant impact if emissions could be first reduced to ~10–20% of their current levels.⁷⁵

3.2.2 Carbon storage vs. carbon utilization. The different scenarios promote storage (CCS) and/or use (CCU) of the captured carbon to varying degrees. The IEA highlights the need





Table 1 Overview of the main applications and actions proposed by the energy scenarios considered here (IPCC, DecHEMA, Shell, IEA, Sunergy) for the five molecular substances under review (NH₃, H₂, CO₂, CH₄, plastics)^a

	IPCC	DecHEMA	Shell	IEA	Sunergy
CO ₂	- 1.5–2 °C warming is inevitable, measures should aim to manage this new reality - CCUS is a potential solution but with its own negative environmental impact	- Zero emissions 2050 - Point sources (<i>via</i> CCUS) and biomass as dual feedstocks for industry - 4 scenarios described	- Net-zero 2050, 50% reduction by 2030 - Switch to renewables, geological storage and reforestation - 0.4 Mt CO₂ in CCS in 2021, up to 25 Mt in 2035	- 3 scenarios: (1) STEPS: 32 GtCO₂ per year in 2050, +2.5 °C. (2) APS: 12 GtCO₂ per year in 2050, +1.7 °C. (3) NZE: 0 Gt per year in 2050, +1.4 °C - Need to decouple CO₂ emissions from chemical value chains, requires massive, immediate investments - Notes huge discrepancy between required and realized CCS capacity	- CO₂ as a feedstock for localized on-demand production of chemicals - Sourced from DAC - DAC currently not at CCUS level, low TRL
H ₂	- Low-carbon hydrogen required (<i>e.g.</i>, electrolysis of water) - Low-carbon hydrogen as an energy carrier when electrification not possible	- Hydrogen from different types of electrolyzers - Poor electrolyzer scaling makes direct large-scale industrial use difficult due to land occupancy	- Investment in increased H₂ production - Maritime and terrestrial transportation - Development of refueling stations	- H₂ mostly produced by electrolysis of water, but also from fossil resources, coupled with CCUS - Low carbon H₂: 90 Mt in 2030, and 450 Mt in 2050	- Solar to hydrogen technologies, photo(electro)chemical technologies - Water electrolysis
CH ₄	- CH₄ fugitive emissions from transportation of fossil fuels could be avoided to reduce the GHG emissions linked to CH₄	- Potential use as H₂ vector if methane is green, but CH₄ pyrolysis is low TRL - SNG as potential energy storage for renewables (CO₂ hydrogenation)	- Reduction of methane emissions and methane flaring	- All non-emergency flaring must cease by 2030	- CH₄ as a solar fuel
NH ₃	- Reduction of fertilizer consumption through innovation and best practice - NPK recovery from wastewater	- SNG synthesis has to deal with H₂O byproduct and energy costs - Production in current infrastructure but with green H₂ - Most important lever is cost of “green” (as in CO₂-neutral) energy	- Use as maritime fuel	- Biomethane production to double by 2025, either by biogas upgrading or gasification of biomass - Beneficial to US and Europe with well-established gas grids - Emissions from NH₃ synthesis need to drop despite growth in demand - Envisions NH₃ as low-emission H₂ fuel - Will consume 25% of “greener” H₂ in 2050 - NH₃ and H₂ make up 45% of energy use in shipping 2050 - H₂/NH₃ for seasonal storage of renewables, NH₃ to transport H₂ by sea	- DAC and subsequent upgrading of CO₂ to CH₄ using solar energy - Precision farming to reduce N₂ pollution - Multiple “green” pathways toward NH₃, but all low TRL - Requires significant improvements to Haber–Bosch to become viable - Emphasis on decentralized NH₃



Table 1 (Contd.)

	IPCC	Dechema	Shell	IEA	Sunergy
Plastics	- Switch from fossil to biomass as carbon source	- 4 scenarios for more sustainability: 1) CO ₂ to MeOH. 2) from biomass. 3) circular economy. 4) CO ₂ copolymers - In addition: Improvements in recycling	—	- Switch toward biopolymers to improve footprint - Main emphasis on recycling of existing polymer	- Incorporation of bio-based feedstocks into chemical industry - CO ₂ as building block for polymers - Highly durable biopolymers act as a carbon-negative technology

^a NPK: nitrogen, phosphorus, potassium fertilizer; Nr: reactive nitrogen; TRL: technology readiness level; CCUS: carbon capture, utilization, and storage; STEPS: stated policies scenario; APS: announced pledges scenario; NZE: net-zero-emissions; DAC: direct air capture; SNG: synthetic natural gas. See Scheme 1 and Fig. 4 for definitions of “green H₂” and “green NH₃”.

for negative emissions, and thus the decisive role of long-term carbon storage: 95% of the carbon captured should be geologically stored by 2030, and only 5% should be used.²⁴ In the Shell scenario, the use of “nature-based” CCS is promoted, mostly *via* reforestation in addition to geological undersea storage.²⁷ Conversely, Sunergy discards the option of CCS, estimating that sequestration would be too energy intensive, and that geological pits would be too scarce.²⁶ Rather, they set a goal of finding innovative ways to use CO₂ as a feedstock, an option that is also promoted by Dechema.²⁵ For Dechema, the use of H₂ generated by green water electrolysis (see Scheme 1) constitutes a sustainable pathway toward conversion of CO₂ to methanol, which is a major platform chemical in the production of value-added products such as ethylene, propylene, or benzene/toluene/xylene (BTX), as well as for fuel production.²⁵

While Dechema sees CCU as a technology to be integrated into existing large-scale industrial infrastructure, Sunergy aims to decentralize the entire value chain, thanks to small-scale DAC setups with subsequent valorization *via* microplants producing chemicals for local needs. Sunergy also presents various strategies to exploit CO₂, starting with biohybrid systems, involving biocatalytic conversion (*e.g.*, by bacteria or enzymes), and extending to electrochemical CO₂ reduction, powered by green electrons from solar energy, or, ideally, artificial photosynthesis and photoelectrochemical conversion of CO₂. Once again, the TRLs of the solutions proposed by Sunergy range from low to medium, which means that they may not be ready to implement in time to address the most urgent challenges.²⁶ This concern is shared by the IEA scenario,²⁴ for which more than 60 of the required technologies are at the prototype or demonstration stage. In the long-term, Sunergy aims to harness processes encompassing both CO₂ capture and its conversion. Direct air capture and conversion (DACC) would selectively yield valuable chemicals – such as syngas, hydrocarbons, or methanol – through the formation of carbonate or carbamate intermediates. Thermally-powered DACC to syngas is envisioned by 2030, with a photoelectrochemical process projected by 2040. The ideal processes would be insensitive to oxygen and nitrogen present in captured air, to allow immediate conversion of CO₂ without the need for its purification from the air stream – which would have advantages in energy terms.²⁶

3.2.3 Conclusion on CO₂-related scenarios. Carbon dioxide has been, is and is expected to remain at the crux of the energy-chemistry nexus. CO₂ has been released into the atmosphere mostly because the energy we have used and are still using stems from carbon-intensive chemical processes (burning fossil resources). Today, the paradigm accepted for the future of chemistry focuses on using CO₂ as a feedstock and/or on finding processes that can reduce its release. Although CO₂ is widely accepted as the main GHG responsible for global warming and ocean acidification, its capture, storage and/or use are currently not affordable enough for a wide application. Profitable dissemination of CCS and/or CCU technologies, as well as a CO₂-based economy, is not yet on the cards.

Notwithstanding its possible limitations,⁷⁶ the concept of the carbon footprint – the analysis of the positive or negative emissions caused by chemical processes – has become one of the

major criteria by which the sustainability of chemical processes is assessed. This choice affects the four other molecular substances considered here (H_2 , CH_4 , NH_3 , plastics), and drives research in academia and industry into modifying processes accordingly.

3.3. Dominant projected future for hydrogen

Hydrogen is presented as one of the most promising short-term fossil-free and carbon-free energy carriers in all the scenarios studied. With a stored energy per weight of 120 MJ kg^{-1} , it surpasses all other chemicals (e.g., 50 MJ kg^{-1} for methane). This has led to massive policy incentives for production of so-called green H_2 at individual country and international levels.

The next section will help clarify the chemical definition of the color associated with hydrogen. More broadly, the term “green” will be used hereafter with the same ambiguity found in common literature: while it can, in some context, be associated with the idea of sustainability and absence of detrimental environmental impact, the term green can also more prosaically mean less impactful than current routes (mostly in terms of overall CO_2 emissions, ideally tending toward CO_2 -neutrality). Water electrolysis powered by renewable electricity is the current technology of choice for green H_2 production. Thus, the European Strategic Roadmap envisions a rapid increase in green H_2 production, from 6 GW to 40 GW of available electrolyzer power in the 2024–2030 period.⁷⁷ Some further details on green H_2 production infrastructure technologies are reported in ESI, Section SI-4.† Importantly, beyond its potential role as an energy vector, H_2 remains a central reducing chemical involved in a multitude of large-scale chemical processes (see Fig. 2), for which a switch to green H_2 could directly reduce CO_2 emissions.

3.3.1 The hydrogen production color chart – going for green. While green hydrogen generated by renewable power with no CO_2 emission is the stated target for all scenarios, the path toward large-scale production can take various routes, including a gradual transition or branching through different production methods, often distinguished by color-coding (Scheme 1).^{78–80} Black and gray H_2 refer to CO_2 -intensive coal gasification or Steam Methane Reforming (SMR), and represents most of today's production. Blue H_2 refers to a modification of gray H_2 production using CCS technologies (discussed in Section 3.2) to reduce the associated CO_2 emissions. Turquoise H_2 is produced through fossil fuel pyrolysis, yielding carbon black as a byproduct. Purple hydrogen is obtained from water electrolysis powered by nuclear energy. Last, white hydrogen is a natural form of hydrogen (also called native hydrogen) produced through various phenomena (redox reactions with ferrous ions, water radiolysis...).

As of yet, production of green hydrogen (median cost 3.64 \$ per kg) is more expensive than production of gray hydrogen (median cost 1.66 \$ per kg for steam reforming of methane without CCUS).⁸¹ Several projections phase out gray hydrogen by 2050,⁸² but with non-fossil H_2 production remaining below 50% of total hydrogen production. The scientific literature does not unanimously agree on the benefits of transitioning through blue H_2 due to limitations in CCS technologies (see Section 3.2),

and arguments have been advanced for greater investment in renewables (i.e., green hydrogen) in the midterm.⁸¹

The IEA roadmap²⁴ anticipates an explosive rise in blue and green H_2 demand from about 0.3 Mt in 2021 to about 420 Mt in 2050, with 13% of this demand coming from the energy sector, 30% from industry, 26% from transportation, and 26% for use as feedstock in the production of other low-carbon fuels. In this scenario, hydrogen would represent a 20% share of the yearly global energy supply. This scenario contrasts with another projection set out in the same IEA report, the Stated Policies Scenario (STEPS), which is based on a trajectory modeled on today's global policy settings. The latter predicts a lower demand for blue and green H_2 of only 24 Mt by 2050. This illustrates the gap to be bridged if we are to transition to a green hydrogen economy capable of net-zero CO_2 emissions. For comparison, current demand for H_2 , which is met by gray H_2 , is about 95 Mt.

3.3.2 Hydrogen as an energy vector. While hydrogen has sometimes been presented as a key fuel for the energy transition, recent roadmaps, including the IPCC report, tend to downplay this vision and emphasize the efficiency of using electricity (over H_2 fuel) for buildings energy needs and light-duty vehicles. Hydrogen fuel cell vehicles have been substantially overshadowed by the rise of electric vehicles (EV), the lack of infrastructure for H_2 -based vehicles being a significant obstacle. Indeed, 1.3 million refueling stations were available globally for EV in 2020, compared to just 530 for H_2 -powered vehicles.^{48,83} The market for H_2 -fueled vehicles is also hampered by the price and stability of fuel-cells requiring platinum catalysts. Potentially game-changing innovations could still emerge for H_2 -fueled internal combustion engines, thus providing a significantly extended range compared to EVs: the focus on fuel cell development is shifting towards heavy-duty trucks.⁸⁴ Hydrogen remains a more convincing option than electrification for other heavy-duty transport such as the marine and aviation sectors, either directly or through synthetic fuels (power to liquid technology, ammonia, etc.).⁸⁵

As the electrification of the chemical industry progresses, the IPCC scenarios envisage hydrogen primarily as an energy carrier. The limited development of a hydrogen infrastructure, compared to the electricity grid, supports this trend. Nevertheless, green hydrogen may be adopted by some large industrial sectors, for example as fuel for furnaces in the glass industry, which need very high temperatures and stable operation conditions.⁸⁶

Overall, the role of hydrogen as a fuel in the IEA global energy picture is projected to have a relatively low impact. Thus, in the NZE 2050 scenario, that is “Net Zero Emissions by 2050” scenario (one of the more optimistic scenarios when it comes to fossil resource and H_2 use), H_2 will account for a total share of roughly 6% by 2050.⁸⁷

3.3.3 Hydrogen as a chemical for industry. While its future application as an energy vector is somewhat nuanced, there seems to be a clear advantage of switching out gray H_2 for green H_2 in chemical processes, in particular for the production of steel (through hydrogen-based direct reduced iron), ammonia, methanol, or chemical feedstock from biogenic sources. In one specific example, Dechema presents methanol production from



captured CO₂ and green H₂ as the cornerstone of a low-carbon strategy to synthesize complex organic compounds. This alternative to traditional petrochemical pathways involves mature methanol-to-olefin and methanol-to-aromatics processes.

3.3.4 Green H₂ production infrastructure. The 2050 targets proposed for green hydrogen production require the rapid and large-scale development of a new global park of industrial electrolyzers. According to the IEA, if all projects announced as of September 2022 are completed, the global electrolyzer capacity could rise from 1 GW (currently) to 134–240 GW by 2030.⁸⁸ This estimation is double that from the previous year, which highlights the difficulty in predicting future green H₂ production. To meet this growth, electrolyzer production must reach 65 GW per year by 2030. Various existing and emerging electrolyzer technologies are foreseen to achieve this objective (see ESI, Section SI-4†).

3.3.5 Green H₂ transport infrastructure. Repurposing natural gas pipelines for long-range H₂ transport appears economically viable, with a potential 50 to 80% reduction in initial investment compared to building new pipelines according to IEA. Two conditions must be met: (i) avoiding interference with existing natural gas demand, and (ii) having a market of large hydrogen consumers nearby. Nevertheless, retrofitting poses technological challenges. The IPCC report mentions issues like steel embrittlement and seals degradation: H₂ leakage is likely to be even more prevalent than natural gas leakage, raising safety concerns (although not a GHG, H₂ is explosive). These concerns are further compounded by the expected atmospheric reactivity of leaked dihydrogen with hydroxyl radicals, ultimately leading to a longer atmospheric methane lifetime, enhanced production of tropospheric ozone (GHG with 2000 CO₂ equivalent power over 100 years), increased production of stratospheric water (GHG), and influence on aerosol formation and behavior.⁸⁹ No convincing approach to address this issue, which already plagues the methane infrastructure, has yet been proposed. Repurposing liquefied natural gas (LNG) infrastructure seems even more unlikely due to the high cost of H₂ liquefaction (−253 °C) compared to methane (−162 °C).

3.3.6 Conclusion on H₂-related scenarios. We have attempted to highlight the most salient features for the future of hydrogen, focusing on the economic and technological data available in the open literature. While H₂ is expected to be able to support the defossilization of many industrial processes, from the chemical to the transportation sectors, the development of safe and easy-to-scale infrastructures to allow H₂ transport and storage remains challenging. The ongoing development of electrolyzing technologies makes the evolution of green hydrogen difficult to predict.

3.4. Dominant projected future for methane

Methane is attributed a particular role in energy transition in cases where existing infrastructure can be easily switched from coal to gas.⁹⁰ In the Net-Zero-Emission scenario by 2050, a 75% reduction of energy-related emissions is projected by 2030, down to 30 Mt, and reaching 10 Mt in 2050. Indeed, due to the

increased global warming potential of methane (80 times that of CO₂ in a 20 years timeframe), its emissions must be substantially reduced in the near future by diminishing fossil fuel consumption, applying new emission-reduction measures throughout the fossil technology supply chain,⁹¹ and implementing leak-detection programs impacting on fossil methane's climate footprint.⁹⁰ Measures to reduce these leaks and rapidly phase out all non-emergency flaring are included in all the scenarios, as they address both the strained gas markets (prone to geopolitical tension) and the need to reduce GHG emissions. According to Shell Sustainability Report 2021,⁹² routine flaring contributed to 7% of Shell's global GHG emissions in 2021 (4.5 MtCO_{2eq.}); and it was reduced by 33% from 2020 to 2021 (0.2 Mt).

3.4.1 Technologies for methane use and production. In the context of society's transition towards decentralized technologies, the exploitation of fossil or biomass-derived methane feedstock to produce energy-dense and more easily transportable chemicals (e.g., higher hydrocarbons and methanol) is attractive to maximize efficient use of energy resources. Yet, this remains a scientific and industrial challenge.

Methane could be used as a low carbon-footprint feedstock for hydrogen production during its controlled thermal decomposition.²⁵ Synthetic natural gas (SNG) production from CO₂ could be considered as a means to store energy, if green H₂ is employed to reduce CO₂. Using CO₂ in this way could help with the transition from fossil fuels to sustainable and renewable fuels, in accordance with the Paris Agreement and the SUNRISE Technological Roadmap for the development of negative emissions technologies (NETs), which are supposed to be optimized by the 2030s.²⁶

Methane and fuels in general could also be produced by reducing CO₂ in photoelectrochemical devices, which should allow a more versatile, local, and thoughtful on-demand production. Working with autonomous systems that only depend on sunlight would obviously represent a great advantage.²⁶

3.4.2 Biomethane as a turning point in the energy transition. Biomethane can be defined as renewable methane, and is today mainly produced from biomass, in the form of municipal solid waste, animal manure, crop residues, and wastewater. These materials need to be anaerobically digested to produce biogas (mainly CH₄/CO₂), which can then be converted to biomethane by removing CO₂: 90% of biomethane is currently produced this way.⁹³ The second route produces biomethane by direct gasification of biomass (e.g. forestry residues), followed by methanation.

Even though in 2020 biomethane only accounted for 0.1% of methane demand, sustainable biomethane production could be a turning point in the context of circular use of energy resources. Since it is chemically equivalent to fossil-derived methane, biomethane can be used directly to produce electricity and heat, and is fully compatible with natural gas infrastructures and gas-powered vehicles.⁹⁴ Around 60% of plants are currently operational or under conversion to include biomethane in the gas distribution network.⁹⁴ Biomethane combines the advantages of natural gas with a lower carbon footprint.⁹⁰ It is thus a valuable tool to harness agricultural/



municipal waste, since it can generally be produced in small-scale plants located near the end-use site. Adoption of biomethane could require a drastic modification of the distribution network to allow for the injection of excess biomethane produced in summer into the underground reserves as well as a change in production scale, from large to smaller, in particular for rural and farming communities. Such a change could limit transportation issues and geopolitical tensions. Hence, the benefits of biomethane might extend even beyond the defossilization issue.

Current worldwide bio-LNG and synthetic LNG production is 2.2 bcm per year (0.07 EJ per year, 2.3×10^{10} kW h per year). Biomethane potentials are in fact much higher and, in principle, could provide nearly 60 bcm per year (2 EJ per year, 6.3×10^{11} kW h per year) in the EU-27 for production only through thermal gasification.⁹⁵ This value has almost doubled compared to the data provided for 2019, in line with the REPowerEU 2030 target plans.⁹⁶ Biomethane potentials in EU-27 by 2030 are estimated at 41 bcm per year (1.3 EJ year, 4.3×10^{11} kW h per year), considering both biomethane produced from anaerobic digestion and from thermal gasification.⁹⁶ Even if biomethane is more expensive than natural gas, its cost-effectiveness and competitiveness could increase over time. Nevertheless, it is quite difficult to evaluate the CO₂ footprint of biomethane because it depends on the region, type of biomass and technology used. The IEA Sustainable Development Scenario underlines that consuming biomethane will avoid the emission of around 1000 Mt of GHG in 2040, including CO₂ emissions related to natural gas and CH₄ emissions from biomass decomposition.⁹⁰

3.4.3 Conclusion on CH₄-related scenarios. To conclude, methane emerges as a promising energy and chemical vector due to its lower CO₂-to-energy production compared to fossil fuels, provided that the leaks of this potent green house gas could be limited (see Section 2.4). Fossil methane would need to be completely replaced by green or biomethane to allow defossilization. This will probably entail the development of decentralized infrastructures in most cases – *i.e.*, for agriculture-derived biomethane – and wider development of CCUS solutions. However, the energy transition must be supported by policies coordinating the various aspects involved, namely waste management, environmental issues, and agricultural, energetic and transportation sectors.⁹⁰

3.5. Dominant projected future for ammonia

The amount of anthropogenic reactive nitrogen species (Nr) has increased constantly since the Haber–Bosch process was initially developed in the early 20th century as a result of its use for agriculture (see Section 2.5). Production will accelerate in the near future if NH₃ use is extended to energy applications.

3.5.1 CO₂-mitigation scenarios. Mitigation strategies linked to fossil-based ammonia production strongly focus on CO₂ emissions related to the Haber–Bosch process. Due to an inherent low conversion rate and economies of scale, Haber–Bosch plants are large facilities, typically producing ammonia in the order of kt per day. In addition, latest-generation steam

reforming ammonia plants operate close to the exergy limit. As a result, modern Haber–Bosch plants have a process-related carbon footprint of *ca.* 30% of the total carbon footprint, as reported in eqn (1) of Fig. 4, for total and stoichiometric ammonia production-related CO₂ emissions, respectively, in steam reforming-based Haber–Bosch plants.

Therefore, overall efficiencies do not leave much room for improvement on that front, and indeed they have remained largely constant over the last two decades. In fact, most of the carbon footprint of the Haber–Bosch process is linked to H₂ production *via* natural gas reforming (Fig. 4).⁹⁷ A modern methane-powered Haber–Bosch process generates at best around 0.6 tNH₃/tCO₂. It is less in practice, resulting in effective global emissions of 450 Mt per year of CO₂. This makes current industrial ammonia a fossil chemical in all but name.

Current decarbonation approaches are based on the deployment of carbon dioxide capture and storage technologies at ammonia plants (blue ammonia) or use of decarbonized H₂ from water electrolysis powered by renewable electricity (green ammonia) (Fig. 4).

3.5.2 Ammonia as an energy vector. Ammonia is being advanced as a prime candidate carbon-free energy vector (or hydrogen vector). The 2022 World Energy Outlook⁸⁷ states that to achieve NZE by 2050, NH₃ should be co-fired in coal power plants in the short-term, and later on used as the primary long-distance hydrogen vector (representing 85% of planned hydrogen transportation capacity for projects announced). Furthermore, ammonia is expected to represent as much as 45% of fuel for shipping by 2050 in the NZE framework. Similar projections for industrial ammonia use are included in roadmaps presented by energy suppliers, such as Shell. Many current projections rely on the use of low-carbon hydrogen (green, blue, turquoise, *etc.*, see Fig. 4) as part of a more sustainable Haber–Bosch process and on a reduction in the energy costs of producing ammonia. The advances required to transform ammonia into an energy vector in terms of technology, energy efficiency, and infrastructure are substantial and far from guaranteed for deployment at the proposed massive scales.⁹⁹

3.5.3 Scenario considerations other than the carbon-intensity of ammonia and its use as an energy vector. Little is mentioned with respect to ammonia production for fertilizers other than the need to lower the CO₂ footprint, which is likely due to the fact that most scenarios analyzed are skewed toward energy transition. Instead, the topic is dominated by the potential use of ammonia as an energy or hydrogen carrier. The few scenarios addressing the topic of poor nitrogen use efficiency (NUE) in agricultural practices relying on ammonia focus strongly on variations in agricultural practices (nutrient recycling, agroforestry, cover crops, hydroponics) and very little on chemistry-related levers (*e.g.*, slow-release ammonia fertilizers combined with precision farming).

3.6. Dominant projected future for plastics

In the roadmaps studied here, the impact of plastic production and use in relation to Earth system processes is almost



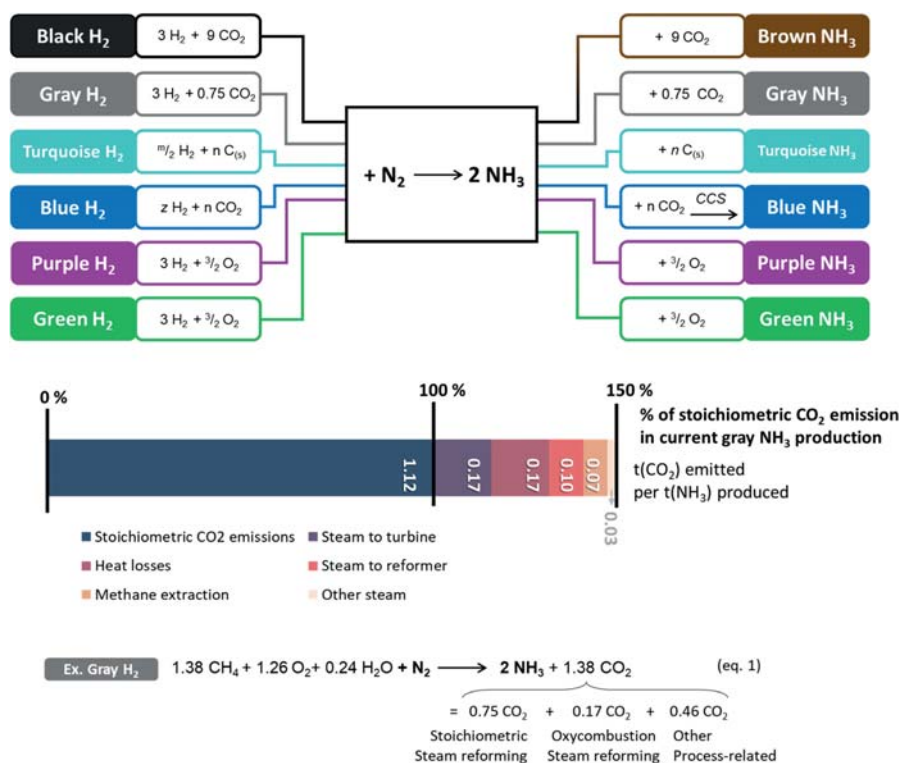


Fig. 4 Upper panel: schematic representation of current fossil-based and projected ammonia synthesis processes with decreasing CO₂ emissions (top to bottom) and respective ammonia "color". The CO₂ reported is only the stoichiometric quantity. See Scheme 1 for hydrogen syntheses. Since in ammonia plants, on-site hydrogen production is integrated with ammonia synthesis, the two hydrogen routes in Scheme 1 and here differ. Lower panel: differences between stoichiometric quantity (blue) and additional process-related CO₂ emissions (other colors) expressed in tCO₂/tNH₃ in modern optimized methane-powered Haber–Bosch processes for gray ammonia, leading to overall eqn (1) (see more on eqn (1) in Scheme S1–1†).⁹⁸

exclusively tied to the high CO₂ emissions generated by the production of monomers by oil cracking in refineries. To mitigate this issue, three main low-carbon-emission circular alternatives are advanced. (i) Producing bioplastics from biomass, the largest reservoir of contemporary carbon, by breaking down and refining biopolymers into biosourced monomers. Dechema suggests that this path should be preferentially followed to obtain monomers that maintain the functional units of the feedstock molecules, (*e.g.*, oxygen-rich and carbonated molecules), rather than hydrocarbons such as ethylene or propylene, due to the low efficiency of biomass use for the production of the latter. Biomass is also recommended for the production of methanol and ethanol for further exploitation. (ii) Using CO₂ and green hydrogen as feedstock to produce syngas, followed by Fischer–Tropsch inspired production of olefins. This route should reduce CO₂ emissions, but can be energy intensive. (iii) Alternatively, CO₂ can be hydrogenated to produce methanol, which can then be converted into light olefins or aromatic compounds through established catalytic "methanol-to-olefins" and "methanol-to-aromatics" processes.

The European Green Deal includes a plan on increased regulations regarding the use and production of microplastics, and highlights the need for risk assessments to include the entire life cycle of materials, which is relevant to remaining within the planetary boundary related to Novel Entities. Importantly, the EU also voiced concerns with the global trade of plastics, and in particular the export of plastic waste. This strategy has led to plastic waste accumulation in landfills in South-East Asia, progressively contaminating freshwater sources, and ultimately large ocean areas in the form of a loosely agglomerated floating mass three times the size of France. This mass was infamously named the "seventh continent".¹⁰⁰ A recent European Green Deal¹⁰¹ act implements stricter measures on plastic consumption, adopting a reduce-reuse-recycle strategy. Attention is drawn to a more transparent labeling system, especially with regard to the use of "bioplastics" terminology, making consumers active players in the energy transition.

Among the scenarios analyzed, the main solutions proposed for the manufacture of sustainable and defossilized plastics

include the macro-topic of bioplastics to replace conventional plastics and the use of CO₂ to produce building blocks as part of a sustainable polymer industry. Less emphasis is placed on end-of-life of synthetic polymers, which is linked to the issue of environmental accumulation. When tackling this aspect, scenarios often encourage investment in the recycling chain, and only touch on biodegradability, even though this is a hot topic in polymer research. Furthermore, replacement of conventional plastics with biodegradable plastics has been proposed or is under implementation in several countries.¹⁰²

3.7. Conclusion on the scenarios section

In summary, the five European/UN/OECD scenarios reviewed share some viewpoints. The existence of climate change and its consequences are central: the aim is to develop energy systems that are more carbon-sober. This system should be scaled to respond to projected increases in demand in most economic and industrial sectors. While all the scenarios generally agree that the energy transition envisioned should be powered by low-carbon electricity, different technical solutions, or distributions over various solutions are proposed. The general consensus is that some new or currently low-maturity technologies will be needed, and must be deployed at scale to reach some of the goals. This vision shapes most research-orienting frameworks and research-funding opportunities at the chemistry/energy nexus.

Open questions remain, as pointed out in the IPCC report, for example: “most models and studies fail to address the systemic impacts of the widespread development of new technology” including “material and resources”. “Systemic solutions are also not being sufficiently discussed, such as low-carbon materials; making buildings, transport, and industrial equipment lighter-weight; promoting a circular economy, recyclability and reusability, and addressing the food-energy-water nexus”.²³

4. Interdisciplinary considerations

The scenarios presented above set out scientific and technological orientations mostly informed by engineering and data processing tools (such as techno-economic analysis, life cycle analysis, *etc.*). In addition, the scenarios have been almost exclusively elaborated to address the transgression of the planetary boundary causing climate change, with little to no mention of possible ripple effects impacting other Earth system processes. In this section, through selected examples, we will attempt to show that extension toward other fields of knowledge (game-theory, history, ethics, ecology, earth systems, *etc.*) can help bring to focus aspects that the scenarios might appear to overlook but that remain relevant when seeking to assess the sustainability of the proposed research directions.

We will showcase six examples related to the substances discussed above and some other underlying concepts mobilized by the energy transition/chemistry/Earth system processes nexus addressed in this manuscript:

- CO₂: how (economics-derived) game-theory considerations moderate the hopes that research into the use of CO₂ with

a view to industrial transfer will substantially contribute to mitigating climate change.

- CH₄ and H₂: how political science can bring forward the tensions and potential conflicts surrounding the use of land and water resources for the deployment of methane- or hydrogen-based “energy transition solutions”.

- NH₃: how Earth system analysis, based on the planetary boundaries framework, raises questions as to the suitability of ammonia as a major contributor to the energy transition.

- Plastics: how decolonial studies can bring into focus the dynamics of waste recycling at a global scale.

- Related issue of the requirement for materials: how cultural studies of science can help deconstruct part of the implicit model in the scenarios proposed, whereby access to natural resources is taken for granted.

- Within the overarching concept of the energy transition: how history raises questions on the use of the term “transition” subsuming the scenarios proposed.

4.1. CO₂ as a raw material: can we really scale up?

The direct catalytic conversion of CO₂ to valuable chemicals has attracted considerable research interest over the past few years.¹⁰³ As detailed above, from a fundamental research perspective, like for many other challenging reactions, there is a curiosity-driven interest in understanding how such a stable and relatively inert molecule can be activated in an energy-efficient way to selectively produce carbon-based molecules.¹⁰⁴ In a more climate-related context, any such process could also theoretically contribute to reducing atmospheric CO₂ concentrations – either by replacing fossil fuels with CO₂-derived “solar” and “e-fuels,” or by producing useful fossil-free carbon-based chemical – thus helping to “close the carbon cycle”.¹⁰⁵ These approaches are often referred to by acronyms such as “CCU”, “CCUS” and “CDU” (for, respectively, “carbon capture and utilization”, “carbon capture, utilization and storage” and “carbon dioxide utilization”). Furthermore, these “emerging” technologies/processes can be viewed as possible contributors to the value chain in the chemical industry.^{75,106} Carbon capture technologies are thus represented both as an economic opportunity and as an environmental solution, with verification of total global warming impact provided by life cycle analysis (LCA).¹⁰⁷

Even if the current technological hurdles could be overcome, substantial economic and social obstacles might arise.¹⁰⁸ Game-theory can be an interesting tool to help analyze and understand how decision-making is influenced on a global scale. In public economics, two criteria are generally used to characterize goods: rivalry and exclusion. Rivalry refers to the fact that a product can only be consumed once. Exclusion refers to the fact that some individuals may not have access to the market. Based on these criteria, four categories of goods are defined: private goods, club goods, common goods, public goods (Table 2).

In this economic framework, the reduction of CO₂ emissions can be considered a public good, as it counteracts a public menace – CO₂ emissions – that has a negative impact on climate stability. The reduction of CO₂ emissions is subject to what



Table 2 Matrix of economic goods and simple examples

	Rivalry	Non-rivalry
Exclusion	Private goods <i>e.g.</i> , open-market products	Club goods <i>e.g.</i> , products accessible only to a restricted group of individuals
Non-exclusion	Common goods <i>e.g.</i> , fish or game stocks in freely-accessible fishing/hunting grounds	Public goods <i>e.g.</i> , public lighting, broadcasted radio programs, open-access scientific literature

economists call free riding: the tendency of individuals to benefit from collective efforts without having to contribute to them. Within this analysis, to mitigate climate change, every country tends to make the minimum effort. In game-theory, economists also refer to a sub-optimal equilibrium, or Nash equilibrium: the resulting strategy is that each country keeps polluting, whereas, the optimal strategy would be to reduce emissions (Table 3).

Research aiming to reduce CO₂ through chemical transformation could be included in these public good-oriented activities. In our current situation, it is difficult to imagine the potential scale-up of CO₂-based industry. Indeed, in the case of free riding, unless the technological solutions found are price-competitive in the current (possibly subsidized, more below) market, they will not be adopted.

Even assuming an absence of free riding (if, for example, a binding international climate agreement were adopted), the success of CO₂-based chemicals would not be guaranteed if fossil-based materials and fuels remained cheaper and widely available. The argument that CO₂-based chemicals have a double advantage – of creating new value and reducing the amount of CO₂ in the atmosphere – could be strengthened by quantifying what economists call the co-benefits of a policy. Co-benefits refer to subsidiary gains from a policy initially targeting a specific objective. In environmental policy, co-benefits are commonplace: *e.g.*, the promotion of active forms of transport (walking, cycling) not only reduces polluting motorized traffic but also has long-term health

benefits.¹⁰⁹ In the case of CO₂-emission reduction, the co-benefits of CO₂-based chemicals could be measured by estimating the values of carbon emissions – there are many estimates of the social value of carbon that reflect the economic and social gains associated with reducing emissions.¹¹⁰ This social value could then be added to the private value of the chemicals, and this might actually reverse the co-benefit comparison relative to fossil-derived chemicals. To achieve this reversal, the co-benefits must not only be theoretically quantified, but strong political measures are needed to support them, *e.g.*, forcing fossil-based products to bear an additional cost through a carbon tax. However, the economics literature shows that the capacity of industrial and political trade-offs to take into account the co-benefits associated with environmental measures remains weak for the moment.¹¹¹ Hindrances and obstacles, including lobbying, are important, and difficult to quantify. It is therefore far from certain that the environmental co-benefits associated with the development of CO₂-based chemicals would tip the balance in favor of these products, especially as a full assessment would also include potential drawbacks or hidden costs of these products, such as the risks of rent capture by a few private actors, like industrial companies capable of deploying the technology at the targeted scale, to the detriment of social welfare.

At the same time, the co-development of waste-handling strategies (*e.g.*, geological storage, CO₂-based carbon cap-and-trade programs, synthesis of stable CO₂-based molecules as a form of long-term chemical storage, *etc.*) are already underway. The emerging players for the most part respond to the dynamics of market economies (large established industrial groups, start-up companies whose business model revolves around CCUS-related services, *etc.*). These players have therefore found solvent markets for their activity. Without going into the open question raised by the possible rebound effect, also known as Jevons effect, of a downstream “solution” to emissions, it can be relevant to connect that these solvent payers are mostly public bodies. The cost of such remediation actions is therefore to be borne by public assets. Noteworthy, the private profits made by the oil sector over the last 50 years is estimated at 3 billion dollars a day over 50 years,¹¹² with no foreseeable substantial and specific redistribution of such private wealth. It is also in this context, that the interest in carbon capture and re-use policies to safeguard fossil production and trading-related profits can be analyzed, especially in the case that fossil assets were to become stranded assets due to fuel extraction bans.¹¹³

In summary, some elements of economics (like the sub-Nash equilibrium linked to the risk of cooperation failure and the fragility of schemes requiring environmental co-benefit profits), suggest that chemical research aimed at industrialization of CO₂-mitigating solutions as a means to tackle climate change

Table 3 Representative example of cooperative failure in a simplified two-country coalition (two-player game) for public goods (or bads) like country-wide greenhouse gas emission reductions policies. The sub-optimal Nash equilibrium is in bold.⁷ In each cell of the table, “X,Y” should be read X = economic gain for country A, and Y = economic gain for country B, X + Y = total gain for the system. The maximum total gain for the system is equal to 10 (5 + 5), when countries A and B both reduce their emissions (cooperation). The minimum total gain for the system, equal to 6 (3 + 3), is when both countries do not engage in country-wide greenhouse gas emission reductions policies. The intermediary situation is when only one country, either A or B, engages in gas emission reductions policies. This would lead to collective gains of 8 (6 + 2 or 2 + 6). In this case, the country reducing its emissions would bear alone the whole cost of the collective improvement (gain of only 2), while the other country – the free rider – would reap most of the benefits (gain of 6). Therefore, both countries would tend not to engage, and thus lead to cooperative failure and remain in the sub-Nash equilibrium of status quo, with total gain of 6 (3 + 3)

Relative gains	Country B reduces	Country B pollutes
Country A reduces	5, 5	2, 6
Country A pollutes	6, 2	3, 3



might face the same market-driven economic pressures as research that has no such CO₂-mitigating ambitions, such as the requirement that they be cheaper, possibly after public subsidy, than fossil-based solutions in order to displace them.

4.2. Methane and hydrogen: are conflicts over control and usage taken into consideration?

4.2.1 Methane and armed conflicts. The potential for conflicts around the use and control of methane sources, like those for fossil fuels, is well-established in political science. While the correlation between abundant oil and conflict areas is not bijective, it remains strong, and armed conflict can be considered to closely mirror land usage conflict. The chemical community has started to integrate the relevance of armed conflict among its points of attention. For example, the European Chemical Society has labeled carbon among its conflict elements (Fig. 5). Wars are fought over the control of carbon-source fossil fields, and revenues collected from fossil fuel production are used to fight wars.^{114,115} This correlation is not expected to disappear when the role of methane increases with respect to other fossil sources, as proposed in some scenarios. Nevertheless, increased use of bio-methane could help address these concerns, since biomethane generated from agricultural practices should be less sensitive to geographical land usage conflicts. At the same time, all the scenarios produced so far consider biomethane as a minor contributor to the energy transition, thus it will not completely address the conflicts of usage.

The technical, social and political issues around hydrogen were already questioned by R. S. Cherry in 2004 in a paper entitled "A hydrogen utopia?".¹¹⁶ Cherry stressed that most of the issues related to the development of hydrogen as an energy carrier were centered on three main topics, *i.e.*, safety, storage and cost, while externalities (side-effects) were very rarely considered. For example, he mentioned energy equity, where remote and less populated areas may encounter difficulties in accessing a competitive hydrogen infrastructure. Indeed, most projects involving a hydrogen society focus on two major bottlenecks: economy (price of hydrogen) and technology (production efficiency). This approach masks other aspects and sources of potential conflicts that nevertheless need to be addressed. Here, we will take two examples: land use and water impact.

4.2.2 Hydrogen and land use conflicts. Hydrogen production through electricity generated by photovoltaics (PV) will have an impact on the space needed to deploy solar panels. The surface area required for green hydrogen is significantly larger than that necessary for gray hydrogen. Ewan and Allen¹¹⁷ showed that compared to PV-powered production, the production of hydrogen from high-density energy sources (*i.e.*, natural gas) requires an area about 40 times smaller per MW of hydrogen produced. If one considers that 4% of the land area in the United Kingdom can be devoted to PV, with a captured energy efficiency of 15%, only half of the average power requirement of the country could be covered (300 GW). However, recent data are more optimistic. Taking into account

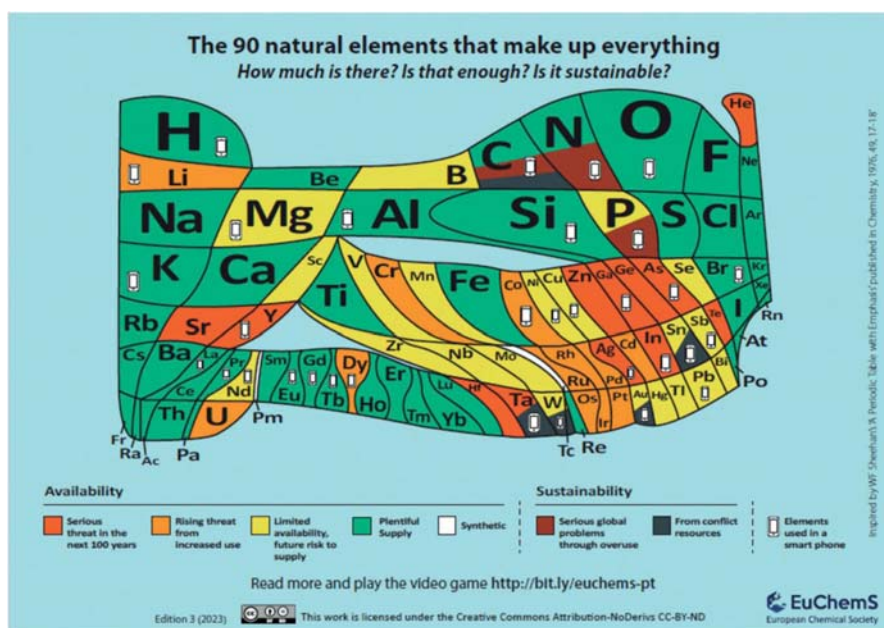


Fig. 5 The 2024 EuChemS periodic table of elements depicts element sustainability and causes of concern for future availability, including increased use and production from conflict resources, and impact on Earth system processes ("Serious global problems through overuse"). CC-BY-ND licence.

a 2050 scenario for the EU28, van Wijk¹¹⁸ planned that the production of 70 Mt of hydrogen in Europe would require 0.2% of total European land area for PV, 0.5% for onshore wind and 1.1% of sea area for offshore wind. An additional 150 Mt of H₂ would be needed from North Africa, Norway, and Ukraine, with PV occupying 0.7% of the land area in North Africa.¹¹⁸ These types of extra-territorial (extra-European) scenarios have obvious geopolitical ramifications linked, for example, to the installation and access to the PV panels, or to hydrogen production and transport infrastructures.

If 70 Mt of hydrogen were produced by PV in Europe alone, the land area required would increase to 22 500 km² (*i.e.*, about 0.5% of the total land covered by EU28, or about 4% of mainland France). Despite the apparent modesty of these figures, it should be kept in mind that, in densely populated areas, or in places where agriculture and forestry are already vying for space, adding large PV harvesting stations might be problematic, and the difficulty should not be underestimated. For this reason, the Sunergy technological roadmap targets higher solar-to-hydrogen conversion efficiencies of 30%. Recent social and political setbacks in the Netherlands related to the objectives for renewable installation at the local level¹¹⁹ illustrate the potential conflicting situations arising from high hydrogen-production goals. Occupation of land may also lead to poor social acceptance, due to inequalities and non-inclusive development processes for renewable energies, leading to unwanted land uses, unfair compensation for expropriation or forced relocations. History shows that these would particularly affect vulnerable and marginalized communities (such as indigenous communities), and examples abound in Morocco, Mexico, and South Africa, where local communities were exposed to a power imbalance with energy developers.¹²⁰ Land use is definitely a place where technology development must interact with the social sciences to ensure independent local assessment of the impact of massive renewable energy projects.

4.2.3 Hydrogen and water usage conflicts. Regarding the impact on water, based on projections of a massive production of

2.3 Gt of hydrogen per year in all sectors,¹²¹ and on a stoichiometric electrolysis reaction, the process can be estimated to consume 20.5 Gt of water (*i.e.*, 20.5 billion m³) per year.¹²² This amounts to 1.5 ppm of all the freshwater available on Earth, and is 50 times less than the volume consumed by agriculture. It should be noted that other scenarios may encompass a different energy mix, and thus project a lower demand for green hydrogen (for instance about 420 Mt by 2050 in the IEA scenario).

The Sunergy analysis²⁶ – focused on Europe – calculated that if the current hydrogen production was to rely entirely on water electrolysis, this would demand 3700 TWh of electricity annually, and the freshwater requirement would amount to 630 Mt per year. This is 0.7% of the annual EU28 freshwater consumption, and remains lower (one third) than the volume of freshwater used by the service industry (2400 Mt per year). Considering that the demand for hydrogen in Europe is about 15% of the global demand, the Sunergy analysis appears to confirm that the use of freshwater is not a major barrier to the development of hydrogen through electrolysis. This figure may be underestimated: additional water may be needed due to the other processes involved in water electrolysis, such as cooling of the electrolyzers, or treatment of the input water to meet the purity standards for electrolyzers, furthermore, this is a global scale analysis, and care must be taken in areas where freshwater is not easily accessible. Desalination could be an option, and in this case Beswick *et al.*¹²² calculated that the energy and cost additions would be minimal. However, desalination adds penalties in terms of (i) CO₂ emissions when the required energy is produced from fossil fuels, and (ii) brines (salt-rich mixtures potentially contaminated with chemicals), which must be disposed of in the oceans, and that may impact the marine ecosystem. Other options, still at the research level, would be to use ambient humidity for hydrogen production.¹²³ In addition, water stress (the ratio between the fresh water withdrawals and the total renewable freshwater resources) will need to be assessed locally as it varies considerably from one country to another (Fig. 6). The IRENA (International RENewable Agency) foresees that more than 70% of

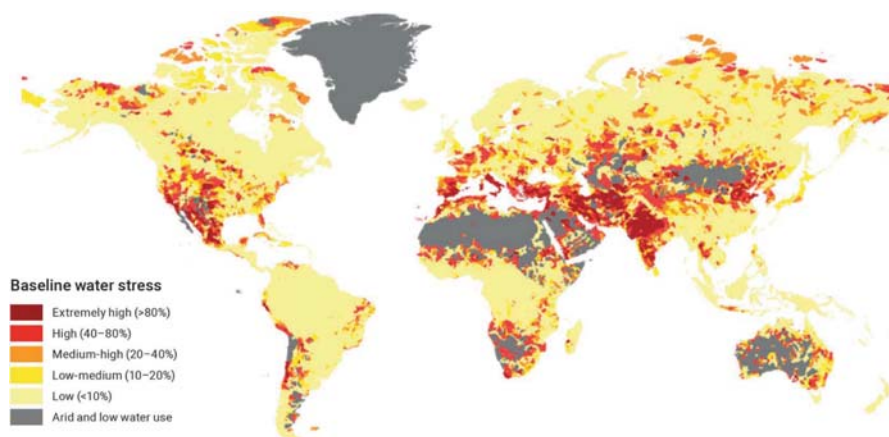


Fig. 6 Annual baseline water stress. Source: WRI (2019). Licence Creative Commons Attribution 4.0 International (CC by 4.0).¹²⁸

planned electrolyzer projects will be in water-stressed regions, with most water provided through desalination.¹²⁴ Again, conflicts of usage over water and other resources will not be easy to resolve if they arise at the local level. In 2022, social struggles over water reservoirs for agriculture¹²⁵ and the cooling of nuclear plants in Southern France¹²⁶ show that local obstacles due to limited water supply that the generalization of large-scale hydrogen production could induce locally should not be underestimated. The NOOR I solar thermal power plant in Ouarzazate (Morocco) is another example where the constraints on water resources were experienced as a negative impact for the local communities.¹²⁷ Attempt to scale H_2 production must therefore be analyzed also in the context of practices' fairness.

In summary, this quick overview of possible increasing conflicts linked to land and water usage upon deployment of scenarios relying heavily on hydrogen or methane-based solutions reveals non-zero risks of creating or reinforcing existing geopolitical tensions, as well as triggering local social unrest.

4.3. Ammonia: should a molecule which is today a major environmental burden be scaled up and become an important energy vector in the future?

Ammonia is advanced in the scenarios analyzed as a green hydrogen carrier, or even a fuel in itself, mostly for the maritime sector (see Section 3.5). Replacing the current use of diesel for shipping by ammonia would consume approximately an additional 586 million tons of ammonia per year, *i.e.*, four times the current annual production.⁹⁹ For comparison, the planetary boundary for reactive nitrogen species is estimated at around 62 million tons per year at most.¹² Wolfram *et al.* recently pointed out that overstepping this boundary to power maritime shipping will necessarily cause major disruption in the global nitrogen cycle.⁹⁹ Moreover, they estimated that if just 0.4% of ammonia fuel were converted and released into the atmosphere as N_2O , it would completely offset the GHG emission benefits resulting from switching from diesel fuel. They point out that it is likely that leakage in extended NH_3 supply lines will result in additional N_2O emissions through natural denitrification, which will likely prove difficult to monitor and mitigate.

Beyond the projected usage, currently ammonia is mainly converted to urea and nitrates, for use as fertilizers. The scenarios reviewed identify two main approaches: blue and green ammonia (see Fig. 4). These approaches consider ammonia production through the Haber–Bosch process as an item to be improved, mostly at the level of upstream CO_2 emissions (see eqn (1) in Fig. 4), rather than as a major disruptor in ecological cycles. As a result, these approaches fail to address the severe ecological issues linked to disproportionate ammonia dispersion in the environment.^{12,129}

Because of the N_2O emissions linked to poor Nitrogen Use Efficiency (NUE), even just from a climate change mitigation perspective, “green and blue” approaches are not a suitable answer when the full impact is considered. While the IPCC report points toward ways of improving NUE through nutrient recycling, or changes in agricultural practices (agroforestry,

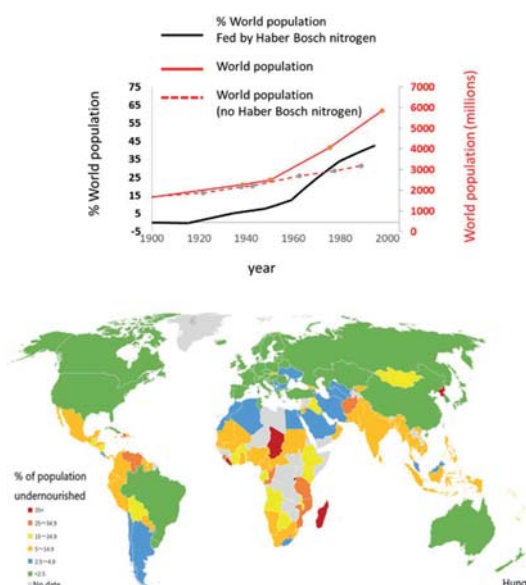


Fig. 7 Top: Evolution of world population over time (historical data) and projected world population without the development of the Haber–Bosch process, adapted from J. W. Erisman, *et al.*⁶² Right: the Food Hunger Map provided by the Food and Agricultural Organization of the United Nations.¹³⁰ Global data make a clear causality link between the use of fertilizers and a growing population, but inequalities in access to food remain nonetheless. If ammonia really does feed “half of the world”, which half would that be?

cover crops, hydroponics), it also points out that climate change is having a negative effect on the protein content of crops, leading to a compensatory increase in fertilizer use.

The argument that “ammonia feeds half of the world”⁶² is regularly used to help justify the magnitude of our current reliance on it, but the argument loses some of its power and becomes tainted with condescension in the context of global North–South food inequality (Fig. 7). The next question could be phrased: if ammonia really does feed “half of the world”, which half would that be? This serves to exemplify the recurring deception that global world-average statistics can induce with respect to disparities, geographical or other. Meaningful disparities can become invisible under such global averages.

By questioning the chemical strategy linking ammonia to fertilizers, it is interesting to note that the reduction of elemental nitrogen (N^0 in N_2) to NH_3 (N^{III-}) consumes costly dihydrogen to ultimately oxidize it to N^{V+} in nitrates through the NO_x -emissive Ostwald process. It was the most efficient way to secure reactive nitrogen in Europe when the continent could no longer easily access South-American guano at the dawn of the 20th century.¹³¹ At the time, CO_2 emissions and the downstream environmental impact of nitrogen use were almost completely ignored. But in the current framework of Anthropocene leading to the crossing of planetary boundaries related to most of the Earth system processes, this choice calls for a wider multidisciplinary assessment.



In summary, some elements taken from the scenarios for the possible role for ammonia in the energy transition combined with the current transgression in terms of reactive nitrogen release raise serious questions: Do these projections account for perturbation of the nitrogen cycle at a global scale? How could a ten-fold increase in ammonia production not have major environmental consequences, when even today – before any such increase – the environment appears severely compromised by the current production and usage?

4.4. Plastics: are we really prepared to take the consequences in our own back yards?

By contrast to CO₂, which is diluted and invisible, plastic waste is more visible and easily identifiable. It has thus elicited waste-handling strategies. Even though plastic waste trade involves a complicated network, the general flow can be identified. Worldwide waste has been transferred from Europe and North America toward Asia since the late 1980s, and China's ban in 2017 shifted the destination toward Southeast Asian countries.¹³² This practice was considered as a win-win policy where the exporter gets rid of their waste, while the importer gains access to valuable material to enrich their economy,¹³³ resulting in an overall saving of energy and resources.¹³⁴ This type of commercial exchange, where one group's waste is sent across the world can be considered a NIMBY ("not in my backyard") attitude according to social science. One could say that, besides the plastic waste itself, the object of the commercial transaction is to shift formal responsibility for plastic pollution. The plastic waste trade, among other things, moves the burden of responsibility from the actual users and producers of waste (exporters) to the final collector.

In 2019, The European Green Deal acknowledged the issue by suggesting "that the EU should stop exporting its waste outside of the EU". The report stated that this would be tackled by revisiting "the rules on waste shipments and illegal exports", which by 2020 still accounted for more than 10% of all plastic waste produced (3.789 Mt out of 37.068 Mt).¹³⁵ Since 2021, the shipment of unsorted and hazardous waste from the EU to non-OECD countries has been banned, and only clean, non-hazardous waste can be exported for the specific purpose of recycling.¹³⁶ However, is it really sustainable, and fair, to export (even part of) our plastic waste to other parts of the planet? Regarding sustainability, the consequences of the Anthropocene will ultimately affect the global North, notwithstanding the original destination of the waste. Moreover, regarding fairness, from the importers' point of view, plastic waste trade can be considered an unwanted remnant of colonial ideology, contributing to the exploitation of populations in the global South.¹³⁷

A partial solution to this situation, the third R of the "Reduce, Reuse and Recycle" strategy is to create new waste treatment facilities within our borders, on a scale compatible with the size of the problem to be treated. In other words, one more technology-intensive industrial infrastructure must be added to European material needs (steel, cement, metals, *etc.*) to handle its transition to better waste-handling.

The production of bio-sourced conventional bioplastics will not solve the recycling question, as these plastics are still in

large part non-biodegradable and not always easy to recycle. On the other hand, a fraction of bioplastics are also biodegradable. This difference must be highlighted to avoid confusion caused by the prefix "bio". However, biodegradability remains a general concept. Biodegradable materials are defined as those that break down into natural elements or small molecules under the influence of microbial activity in a relatively short timeframe and in naturally occurring conditions.¹³⁸ Although it is mostly accepted that the ultimate products of such degradation processes are water, CO₂, methane and biomass,^{139,140} biodegradable biopolymers are quite often only broken down into oligomers, called metabolites, which then enter the catabolism of nature.¹⁴¹ Assuming that the eventual biodegradation of plastics in the amounts currently produced would not cause imbalance in the ecosystem is a risky bet. The open questions on the end-of-life effects of bio-sourced plastics on the environment remain.

4.5. What does the scalability requirement say about cultural representations?

The need to scale-up emerging technologies is central to the vast majority of "Net-Zero-Emissions" roadmaps. The benefits of this intensification are clearly presented in terms of reduced GHG emissions and through the traditional levers of the economy of scale to power the energy transition and the electrification of the chemical industry, with the related costs and hurdles generally being also partly discussed.

Solar and wind energy, while ubiquitous, are naturally intermittent, low-density sources of energy. Consequently, collecting and storing them will take up much more space and require far more units than current power plants.^{142,143} Moreover, direct electrification has been prioritized due to the excellent energy yield it offers (especially for transportation with electric vehicles). At the same time, transport and storage of electricity will require considerable construction of novel infrastructure, which explains in part the projected increases in mineral resource consumption.¹⁴⁴ Even replacing fossil fuels with "green fuels", such as hydrogen, relies on significant critical metal availability (see ESI, Section SI-5†). This rampant increase in resource consumption is not new. In fact, it has been a defining aspect of the Anthropocene, and it remains a dynamic on which the energy transition is being constructed. Indeed, the IEA forecasts a six-fold increase in mineral demand by 2040 to meet the target of NZE by 2050, mostly driven by steel, rare earths, graphite, copper, aluminum, zinc, cobalt, nickel, silicon, and lithium.¹⁴⁴ The extraction of these resources is mainly performed in open-pit mines with a high land footprint and causing extensive ecosystem disruption.^{145–147} Moreover, extracting these non-renewable resources will itself consume significant energy, and generate substantial pollution at the site of extraction. Is it reasonable to keep labeling some scenarios as "sustainable solutions", notwithstanding these (generally less addressed) aspects (with respect to carbon footprint, for example)?

Associated with this increased demand for mineral resources is the fact that in our current globalized world, the targeted elements from the mineral resources are often not used where



they are produced. North America and Europe exhibit by far the highest domestic material consumption per capita, but Europe in particular generates the lowest amount of ore per capita, with the exception of West Asia.¹⁴⁸ For instance, the vast majority of the world's cobalt comes from the Democratic Republic of Congo, while nickel is mainly produced in Indonesia, Iran, and the Philippines, and the biggest producer of copper is Chile.^{144,149} Much like with plastic waste management, the outsourcing of metal supply directly transfers pollution to places where environmental and health fallouts are less controlled and regulated, particularly in the context of the increasing development of artisanal mining operations.^{150–152} In addition, the scale of disruption expected for the energy transition is enormous, as fossil resource mining operations are expected to shut down, while exploitation of other resources is expected to surge rapidly.^{153,154} Due to the urgency imposed by the accelerating climate crisis, such a drastic and fast-paced shift is bound to lead to numerous “casualties” on the social and human front.^{155,156} How are the interdependencies between countries and their dramatically different circumstances taken into account? Is it a mistake to continue to adopt a neutral and universal viewpoint when describing the problems and their possible solutions? Is considering the Earth in terms of “resources” part of the problem?

Overall, it appears to us that the proposed pathways toward a low-carbon economy are essentially built on most of the same mechanisms and dominant beliefs that led to the very advent of the Anthropocene: consuming ever-increasing amounts of energy, ultimately requiring most likely increasing natural resources that are incompatible with Earth system processes, while at the same time failing to set the social implications of the desired transition as a guiding principle. It is notable that, historically, the interests of indigenous peoples have suffered as a result of large-scale resource extraction or energy production projects. There seems to be high probability of conflicts that will emerge from the intensification of resource extraction and the building of large-scale installations. Some of the places concerned are already the most threatened by the ongoing climate crisis, and socio-political problems have already started, such as forced migrations or unconsidered health problems, for example caused by mining. Is the projected energy transition really going to be “clean”? Does this transition deal with different cultural representations?

4.6. Does the notion of energy transition really make sense? And if so, how?

The common narrative associated with the history of energy transitions is a succession of dominant energy sources and regimes, particularly since the advent of the Industrial Revolution at the end of the 18th century. Western society moved from an organic energy regime, based on photosynthesis and brute (animal) force, to a fossil energy regime, the consolidation of which occurred in the 19th century. Starting with coal, then petroleum and natural gas, societies underwent successive energy changes, especially following the development of electricity in the 20th century. According to this narrative, the

energy transition in the 21st century would constitute a new, albeit ambitious, phase in history, with the replacement of dominant CO₂-emissive energy sources by renewables and other non-emissive sources.

However, this narrative is hardly correct: our modern energy scenario has not so much evolved through transitions and shifts, as through addition and accumulation.¹⁵⁷ The massive development of coal extraction in the 19th century did not lead to the disappearance of so-called organic sources of energy, especially animal strength. During the 19th century, the number of horses in France increased by 50% and water and wind mills continued to meet the need of a large part of the European population.^{158,159} In the mid-20th century, the rapid increase of oil supply did not lead to an equivalent decline in coal extraction; nor did the later development of nuclear power. Today, according to the IEA, the world's coal, oil, and natural gas supply is at more than 490 000 000 TJ, more than ever before in modern history.¹⁶⁰

Furthermore, these energy layers have not been added as mere juxtapositions. Energy sources have, throughout history, been combined with each other, and with material resources. An example is provided by the massive use of wood in the coal age, to consolidate mine shafts, build railway tracks, as cable supports for the emerging telegraph, *etc.* Thus, coal only developed thanks to the parallel use of wood and steel. This is what has been called energy and material “symbioses”.¹⁶¹

Through this historical lens, the challenges for the 21st-century energy transition increase immeasurably: the complete replacement of CO₂-emissive energies by non-CO₂-emissive energies would be unprecedented. It will not be simple to achieve as it will require significant reconfiguration of current energy and material symbioses – see the need for rare earths or lithium for batteries intended for electric, low-carbon mobility.¹⁴⁴

In chemical terms, it is therefore hardly possible to tackle today's challenges by reasoning in silos, molecule by molecule, without considering from the outset that molecules combine, not only in the literal, microscopic sense – through catalysis, for example – but also in the figurative, macroscopic sense, in material and socio-technical configurations that must be kept in mind. To produce NH₃ with low GHG emissions, we need to think about green hydrogen and about all the materials needed to store and transport it. We also need to think about all the energy and material combinations on which this NH₃ and hydrogen could be grafted, to be sure that they will not support other GHG-emissive technologies or symbioses – a major issue that is not really addressed in the scenarios mentioned above. This will require chemists to constantly broaden how they view their own field of specialization.

History also teaches us that energy is never only a matter of source or technology. Indeed, energy systems have always required infrastructure (*e.g.*, distribution networks such as pipelines),¹⁶² business models (*e.g.*, large vs. small companies, rent distribution, marginal pricing strategies for electricity),^{163,164} institutional rules (*e.g.*, anti-trust laws, energy policies),¹⁶⁵ and even cultural representations and practices (*e.g.*, pressing a button to get light in no way resembles



switching on a paraffin lamp and having to ensure the availability of fuel).¹⁶⁶ If the notion of transition might be meaningful from a historical perspective, it is not just in relation to energy sources or technologies *per se*, but when energy systems as a whole are considered.

For researchers in chemistry, this has two further implications. First, it means that when working on a molecule or a specific reaction, chemists do not work only on specific materials or related technologies; they also indirectly tap into broader components of the energy or material system, including infrastructure, business models, and policies, but also cultural representations, and habits.¹⁶⁷ For instance, turning CO₂ into a raw material would certainly change what is now a waste product into a valuable material, but it would also mean changing the representations associated with CO₂. Why should we strive to reduce emissions if CO₂ is now a “good” thing? This might have detrimental effects if as a result emissions remain too high – no longer being avoided, with the public thinking that a high atmospheric CO₂ concentration is no longer an issue – compared to the absorption and transformation capacities of new technologies.⁷⁵ This threat can be exemplified by the recent German request to postpone the termination of commercialization of internal combustion engine vehicles, set by the EU for 2035, on the basis, among other considerations, that by that time we will be able to produce CO₂-neutral e-fuels.¹⁶⁸ It is therefore legitimate for chemists to wonder about the systemic effects of the chemical processes they work out and to act so that no misleading or detrimental cultural representations emerge or is strengthened thanks to their discoveries.

The second implication is that in energy systems the difficulties with changing long-lasting technological trajectories and habits – or path dependencies – have not only material (or chemical) and economic (related to profitability) explanations, but also institutional and cultural ones. This might seem obvious, but it may not be so obvious when faced with social demand for (technical and profitable) solutions to the ecological crisis from fundamental and applied sciences, as if the technological lever was the cornerstone of future changes. It is worth remembering that levers other than technology exist (*e.g.*, energy demand modulation, new spatial planning, reduced packaging, better sharing of existing resources) to ensure the transition to a non-CO₂-emissive energy system.

4.7. Discussion

4.7.1 On the scientific method. New research avenues expected to lead to operational technologies for the energy transitions are projected as a necessary part of the solution, with a massive scale-up that should be deployed fast. In Section 3, we reviewed the consensus that the low-maturity of some of these technologies raises doubts about whether scale-up is technically feasible. This section of the paper (Section 4), focused on interdisciplinary elements, shows that such technical uncertainty is compounded by risks linked to environmental, geopolitical, and social effects, even when novel technologies were to be technically available at scale.

As a first example of the just mentioned risks, focused on potential environmental impacts, several Earth system processes, which are connected to the interdependencies outlined (*e.g.* freshwater Earth system process for hydrogen and water conflicts, and Land Use Earth system process for hydrogen and land use conflicts, Novel Entities Earth for the section on plastics) are generally either ignored or overlooked by the scenarios analyzed. Returning within some of the identified planetary boundaries is not explicitly stated as a goal of the scenarios, and little evidence is provided to project that the transgression of these boundaries could eventually be reversed. While the main focus of the scenarios we have chosen is, by construction, one particular Earth system process (*i.e.*, dominance of climate change-tailored actions through the recurrent notion of the carbon footprint), other interconnected consequences of a move away from fossil fuels are seldom adequately treated (*e.g.*, land, water and resource management connected to the energy transition; effect on biodiversity; consequences of the introduction of novel entities). On the contrary, in some cases, the energy transition scenarios analyzed carry a serious risk of further exacerbating the overstepping of a planetary boundary, even when the situation is already dire (*e.g.*, ammonia).

As a second example of the possible risks, focused on the potential geopolitical and social impacts of the proposed scenarios, (some) people are overlooked by scenarios. Many of the proposed strategies are blind to North-South inequalities, and the scenarios may contribute to maintaining or even exacerbating conflicts linked to extractivism, productivism, commodification of resources, and waste management (*e.g.*, through extra-European mining activities connected with metal resources required to establish fossil fuel-decoupled European mobility).

Concurrently, this interdisciplinary analysis of scenarios, examined through the prism of five molecular substances at the energy-chemistry nexus, also highlights one invariant between the present time and the projected transition(s): the hierarchy of values.

Even though the triple-bottom line of sustainability – the “three Ps”, People, Planet, and Profit, *i.e.*, economically viable, socially just, and ecologically sound – is mentioned throughout some scenarios and prospective sustainability exercises, these are generally established and projected in a hierarchical order. Profitability appears as a necessary condition, with scalability and commodification being the main – if not the only – reasonable strategy, while at the same time *de facto* omitting important aspects of the Planet and People bottom lines.^{155,169} This will potentially have problematic consequences in terms of environmental and social justice.

Notwithstanding possible intrinsic limits to the efficiency of some industry-targeted research, as discussed in the context of proposed energy-transition-related solutions (*e.g.*, sub-optimal Nash equilibria), the strategies analyzed overwhelmingly retain private profit as a necessary principal driver. This driver has a structural tendency to increase production and/or exclude less profitable beneficiaries, thus echoing and substantiating the two aspects of concern highlighted above: supply the world



with commodities beyond its planetary limits and/or prosper by excluding or exploiting some groups of people or resources. Consequently, the trajectory associated with the development and scaling-up of several novel technologies could potentially mimic some aspects of the dynamics that led to the Anthropocene in the first place. For this review, we considered scenarios requiring the creation of and need for new entities, with an expectation of a dramatically-expanding market: non-fossil fuels and technologies, and commodities, infrastructure, *etc.*, associated with their production. We are poised to see a considerable acceleration of new variables, potentially representing additional energy sources rather than complete substitutions for current fuels. The question relates less to the common objective (to decrease fossil fuel consumption) and the possible means to achieve it (alternative energy sources, increased efficiency, *etc.*) than to the overall arc traced by these scenarios, and the method(s) that will reveal it. This question is further complexified by the fact that through interdisciplinary dialog, we are able to catch a glimpse of the non-scientific – some philosophers have used the term “imaginary”¹⁷⁰ in contexts akin to the one under study here – dimensions underlaying our scientific developments. This interdisciplinary dialog has helped show that, in order to build up and justify our scientific choices, we rely on “cultural axioms”, that we mostly do not question nor explicitly mention.

We propose that including inter/transdisciplinary thinking as part of a broader and more systemic vision of the energy transition, relying not only on productivity and CO₂ emission numbers, could produce more balanced and equitable roadmaps (see ESI, Section SI-1.3† for our distinction between interdisciplinarity and transdisciplinarity). For instance, established and measurable global descriptors, such as planetary boundaries, could be used to assess and teach^{171,172} the impact of any proposed approach, along with systems thinking. In addition, notions of social and environmental justice, that go beyond the use of measurable descriptors, could be included when considering societal organization, resource use, and waste disposal. In ecological economics for instance, *i.e.* a research arena gathering both economists and environmental scientists, some initiatives do exist to cross indicators and recommendations for a more sustainable future, with varying degree of heuristics power. Kate Raworth's doughnut economics, combining social thresholds and ecological ceilings, is one example.¹⁷³ Richard Norgaard's coevolutionary economics, examining the interrelation between socio- and ecosystems, is another one.¹⁷⁴

Developing transdisciplinary tools to explore and analyze the complex ramifications of the global shift in economic, social, and technological models represented by the energy transition appears to us not only beneficial, but necessary, to break the hegemonic view currently put forward and to generate novel paradigms for the chemistry-energy nexus. We note that alternatives have been and continue to be proposed.¹⁷⁵ The relevance of non-hegemonic frameworks may need to be assessed to widen the narrow and potentially dangerous path currently set out by the dominant scenarios analyzed. We mentioned Profit, Planet and People: examples of existing scientific and minoritarian

frameworks in non-mainstream economics (ecological economics, degrowth/post-growth, political ecology) and in critiques of dominant power structures, including economic ones, are all relevant in this quest to deconstruct the current implicit hierarchy of values that could very problematically guide the future of research at the chemistry-energy nexus.

In summary, the take-home message is two-fold: the path offered by the scenarios is narrow and is associated with numerous pitfalls. This suggests that alternatives based on a broader, transdisciplinary method of analysis with closer attention to historically overshadowed – or politically suppressed – theories can be revisited by chemists as a source of inspiration.

4.7.2 On the timeframe. Even among scenario proponents (with no attention to Planetary boundaries or the North-South divide), doubts on their own feasibility exist given the scale and timeframe. Scenario after scenario, the timeframe is shrinking. The solutions proposed in scenarios published some time ago are not being picked up, but updated scenarios essentially propose more of the same over a shorter period (despite the previous failure to adopt). Goals are re-evaluated every five years. “Progress needs to be faster” and yet little has been achieved so far in light of the magnitude and speed of the global changes unfolding.

In 1972, twelve scenarios were presented by Meadows' team, in the “limit to growth” report,¹⁷⁶ regarding the trends for five key interconnected indicators (resources, population, food per capita, pollution, industrial output per capita) between 1900 and 2100. Modeling their interdependencies and carve system-based scenarios were termed “wicked problems” by the Club of Rome. In 2021, almost 50 years later, current analyses¹⁵⁶ after a 30 years update¹⁷⁸ suggest that among all the scenarios considered, the one that is statistically the furthest from empirical data is the “Stabilize the World” scenario (see Fig. 8). While this scenario contributed to the UN “sustainable development” definition that still permeates some current discourse, other scenarios like “Business As Usual” and “Comprehensive Technology” are on the contrary the most compatible with current data (see ESI, Fig. SI-4†). Pointedly, the “comprehensive technology” scenario assumes “exceptionally high technological development and adoption rates”. This, compounded with the feasibility doubts mentioned by technology-driven proponents mentioned above, show that there is an active possibility for a path to the most unstable future which entails brutal collapse of population and resources (see “business as usual” models, Fig. SI-4†).

To return to the topic of this paper, there is still a chance that the common elements of the five “energy transition” scenarios discussed above (Section 3.7) could be enacted, if the incessant, increasing, and here-to-fore only very partially addressed calls for substantial changes were finally met. However, even if these calls were met, some of the flaws consubstantial with the scenarios mentioned above would become a reality (*e.g.*, recurrent disregard of the global South and disregard of Earth system processes (other than CO₂-related problems)).

Therefore, the urgency is evident: we must make sure that we have the appropriate tools to avoid the aforementioned failure to



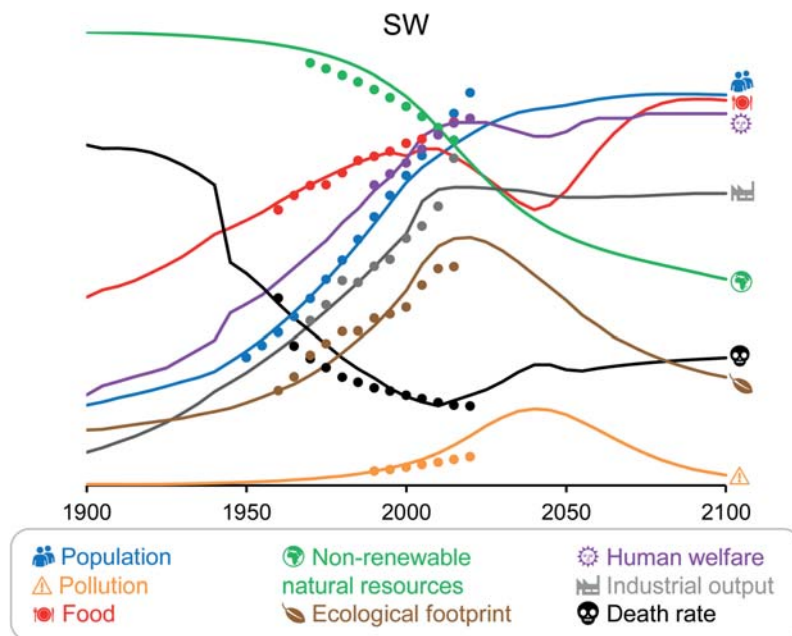


Fig. 8 SW (stabilize the world) scenario for the projected evolution of population (blue line), pollution (orange line), food per capita (red line), non-renewable resources (green line), ecological footprint (brown line), human welfare (pink line), industrial output (gray line), and death rate (black line), and comparison with corresponding empirical data (dots), adapted from Herrington¹⁷⁷ and Meadows.¹⁷⁸ SW is referred as the sustainable model: indicators are stabilized on the long-term thanks to meaningful policy changes. Data for three other scenarios (Business As Usual and Comprehensive Technology) are available in ESI, Section SI-6 and Fig. SI-4.†

change, but we must also make sure that we have the appropriate tools to avoid the risks associated with implementation of some aspects of the dominant scenarios discussed above.

5. General conclusion and perspectives

5.1. Broader scenarios needed

We are living in the Anthropocene, and as such the quality of human life on Earth is jeopardized by certain choices, and modeled and institutionalized under some ideas of how we should inhabit Earth. These choices and ideas permeate the research horizons and the specific research subjects we as scientists must treat.

One of the pervasive messages surrounding the energy transition, included in the chemistry-oriented responses analyzed through the pivotal molecules dealt with in this paper, is that the energy transition is designed to avoid future crises that remain to be faced. However, this minimizes the fact that the planet is already in crisis. We further showed that this crisis was potentially caused by some aspects that are still present in some of the responses that are currently proposed as solutions to implement the energy transition. We also showed that this crisis presents multiple aspects that are not addressed by the response specifically tailored to the energy transition challenge. We therefore

propose as first conclusion to this paper that there is a potential incongruity between the problem stated and several of the scientific research avenues proposed in the scenarios analyzed here.

The second conclusion is based on the disciplinary fragmentation we face in our academic practice. This is a complicating factor when trying to address such types of incongruity. In contrast, transdisciplinarity appears to help circumvent deadlocks emerging from proposing disciplinary approaches to systemic problems. Indeed, one lead from this paper is that a radically interdisciplinary dialog – between the natural and social sciences – must be explored. Progress in natural science has the power to facilitate a change in society, just as much as the pressures exerted by a changing society or politics can lead to intensified efforts in some specific areas of research in natural science. Echoing a classification proposed by German philosopher Dilthey,¹⁷⁹ chemistry is a science that focuses on mastering how transformations occur, while social sciences and humanities describe and interpret why transformations occur. This is not to say that social sciences can explain why the transformation of matter and energy occurs in physical or chemical terms, but that, since the transformation of technologies and production processes also has social motivations and implications, social scientists provide critical information about the connection between, on one side, these motivations and implications and, on the other side, the technological and material change itself: What are the social motivations and implication that contribute to the chemists being asked to search for CO₂-based

materials? What sort of (social and economic) hypotheses are implicitly embarked in their research? *etc.* As a consequence, social scientists should be involved in chemistry projects, not as side contributors but more granularly throughout the projects. In a sense, the project that led to this paper explored precisely this suggestion. Intertwining aspects of the chemical sciences, relevant to the transformation of matter at the energy-chemistry nexus, through the prism of five molecular substances, with aspects of social sciences and philosophy, connected to transformations of societies at the same nexus, seems to offer a relevant perspective on the transition scenarios during the Anthropocene crisis.

The third conclusion to this work relates to the utility of turning to wider scientific approaches that have been historically/politically suppressed (non-orthodox economics, decolonial and post-colonial studies, gender studies, see Section 4) and of investigating their capacity to inspire chemistries beyond the currently hegemonic one which is, at least partly, problematic. For example, academic chemists' agenda is for now mostly framed, often implicitly, by economic and political ideas such as, for instance, priority given to research likely to lead to economic growth and profitability and toward the quest for groundbreaking technological progress. By looking at other economic, social, and political framings, inspired for instance by ecological economics¹⁷³ and post-growth theories,^{180,181} or decolonial studies,^{182,183} chemists could become inspired in investigating other, less conventional research avenues. For example, community energy projects that could exemplarily contribute to mitigation strategies while inspiring the rise of other energy communities elsewhere,¹⁸⁴ as well as low-tech and nature-inspired approach developed in the global South using a non-hegemonic framing,¹⁸⁵ could inspire global North initiatives to develop low-tech as a way to rethink technology for sobriety, conviviality, and sustainability, options in academia,¹⁸⁶ there included in chemistry research.

5.2. How do research topics align with researchers' values?

Beyond interdisciplinarity and transdisciplinarity interactions with other disciplines, as well as devoting attention to suppressed portions of disciplines, the questioning can be further extended to the forms of knowledge themselves. The production of knowledge that by academic construction rewards and sustains a narrow path (with problematic invariants) is also part of the equation. What values collectively lead us to define research excellence, or, on the contrary, irrelevance? What values are encouraged, allowed or suppressed by the scenarios shaping our research projects? Do these reflect our personal values, and ensure Earth will remain habitable while emphasizing the need for social justice?

In the context of the Anthropocene, this leads to an immediate overarching question: What is our responsibility with respect to the research horizons and the specific subjects we treat as scientists, when we suspect such incongruity? Some may think this has nothing to do with our job as scientists and that we should leave the problem to international organizations, or governments – that we can act only as individuals with individual responsibilities. On the contrary, following in the footsteps of

eminent thinkers (Box 1), we believe that there is a social dimension of responsibility. Quoting the ethical group advising the CNRS, the largest French research body, “the specific purpose [of research], which is to produce knowledge in the service of society, confers on research[ers] the particular responsibility of also questioning the use that can be made of their contributions [...] and the way that this use can help respond positively to the problems encountered by society or, on the contrary, perpetuate or even aggravate them.” We also believe, although we each have our own specialization, that we bear an ethical responsibility for the consequences of our acts, which often lead to consequences well beyond our disciplines. Do our research and the knowledge it produces respond to, perpetuate, or aggravate the problems raised?

“I believe that scientists have absolute responsibility for thinking about the use of their creations, even the abuses by others” – Roald Hoffmann, 1981 Chemistry Nobel Prize winner

Box 1

To explore our own invitation to mobilize concepts produced in the global South as a source of inspiration, the problem might be less related to what we know and what we can do, but more to what we do not know and what we are willingly ignoring.^{187–189} We suggest that overcoming disciplinary isolation, paying attention to critical scientific theories and reaching out to knowledge-producing activities beyond academic circles should be explored to help deflect the ominous course of the Anthropocene through our research activities. Even if we are scientists, the Anthropocene is neither just a matter of academic discussion nor a question of agreement or disagreement. Our posture cannot be that of academic practitioners undertaking compartmentalized disciplinary research based on scenarios that only partially reflect our values.

Author contributions

More information on the authors' contributions can be found in section “SI-1.2 Our Authorship policy” of the ESI.†

Conflicts of interest

We have no conflict of interests to declare. In spirit of transparency, we wish to mention here that VA contributed to the Sunergy technological roadmap discussed in Section 3.



Acknowledgements

The content above is under the sole responsibility of us, the authors, and does not imply endorsement by the authors' affiliations' institutions nor the people or bodies mentioned here below. However, since we all met during the CatEnerChem Winter School which sparked this collective perspective work, we wish to acknowledge the institutions and structures that sponsored that event (see ESI, Fig. SI-2†). All the organizers, speakers and participants at that event are also gratefully acknowledged for nourishing the early stages of this work. The list of can be found at <http://catenerchem.cpe.fr>. We also wish to thank all the people that read intermediate versions and gave us constructive feedback. The reasons why we all wish to be all considered as first co-authors and that a collective email is used as corresponding address, are given in ESI, Section SI-1.2.†

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Cite this: *Mater. Adv.*, 2024,
5, 183Unusual adsorption-induced phase transitions in a
pillared-layered copper ethylenediphosphonate
with ultrasmall channels†Margherita Cavallo, ^a Matteo Signorile, ^a Roberto Köferstein, ^b
Valentina Crocellà ^{*,a} and Marco Taddei ^{*,c,d}

In this work, we thoroughly assess the CO₂ adsorption behaviour of a recently reported, pillared-layered Cu^{II} ethylenediphosphonate of formula Cu₂(H₂O)_{1.7}(O₃P–C₂H₄–PO₃)·1.5H₂O (Cu–EtP), that features narrow channel-like pores (diameter < 5 Å). Once the metal coordinated H₂O molecules are removed, Cu–EtP features a very high density of open metal sites (0.0188 sites Å^{–3}) and can adsorb a significant amount of CO₂ at saturation (2.9 mmol g^{–1}, 6.9 mmol cm^{–3}). Most interesting, it displays a step-shaped CO₂ isotherm, whereby a preliminary adsorption event takes place, followed by a step occurring at higher pressure, during which adsorption kinetics become very slow. Hysteresis in desorption suggests that structural rearrangements could be responsible for the unusual isotherm shape. Cu–EtP does not adsorb N₂, probably due to its very narrow pores, thus it displays virtually infinite CO₂/N₂ selectivity. The isosteric heat of adsorption extracted using the Clausius–Clapeyron equation is in the range of 35–40 kJ mol^{–1}, suggesting a strong physisorptive character. This is further confirmed by CO₂ adsorption microcalorimetry. *In situ* synchrotron powder X-ray diffraction analysis, carried out during evacuation and CO₂ adsorption, proves that the MOF undergoes phase transitions during both stages, with shrinking of the interlayer spacing upon removal of water and partial reopening of the structure once CO₂ is adsorbed. The phase transitions are slow, in agreement with the slow adsorption kinetics observed. *In situ* infrared spectroscopy suggests that CO₂ interacts with the open metal sites generated after removal of strongly adsorbed water and that CO₂ cannot displace H₂O if this is not fully removed from the surface. NO was also used as a probe molecule to further demonstrate the existence of open metal sites, finding that it is not able to diffuse within the framework when pure, but that it can displace coordinated water. Optical spectroscopy suggests that changes in the coordination sphere of Cu take place during evacuation and CO₂ adsorption. Finally, periodic density functional theory calculations were carried out to unravel the structural evolution of Cu–EtP and the energetics of interaction with H₂O and CO₂, finding that the change in coordination environment of Cu is mainly responsible for the observed phase transitions.

Received 2nd July 2023,
Accepted 27th November 2023

DOI: 10.1039/d3ma00356f

rsc.li/materials-advances

Introduction

Structural flexibility is a distinctive feature of metal-organic frameworks (MOFs), which makes them stand out in the realm of porous materials.^{1–3} Flexibility in MOFs can be induced by various external stimuli, such as guest insertion, temperature, pressure, electrical fields, *etc.* Adsorption-driven flexibility in MOFs is widely documented in the literature and occurs in a wide range of forms: framework expansion,⁴ swelling,^{5–7} framework contraction,^{8–10} breathing,^{11,12} subnetwork displacement,^{13–15} and linker rotation.^{16,17} Flexible MOFs usually display step-shaped isotherms, associated with the adsorption of large amounts of gas in a narrow range of pressures, once a threshold pressure is reached that triggers a

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well-defined structural response. Such peculiar behaviour is interesting both from a fundamental standpoint, as some forms of adsorption-driven flexibility, *e.g.*, breathing (“open” to “close” to “open” phase transition as the partial pressure of gas increases)^{11,12} or framework contraction (“open” to “close” phase transition leading to negative gas adsorption),^{8–10} are unique to MOFs, and from a practical standpoint, because it can lead to improved gas separation/storage performance.^{18,19}

Phosphonate-based MOFs are a small subclass of MOFs, notable for their superior stability.^{20–24} Pillared-layered structures, consisting of two-dimensional inorganic building units (IBUs) composed of metal ions linked by phosphonate groups and connected *via* organic linkers in the third dimension, are ubiquitous in metal phosphonate chemistry.^{25–27} These structures are usually non-porous, because of the high density of organic moieties in the interlayer space that leaves little or no room for small molecules to diffuse and adsorb. This structural arrangement is considerably different from other carboxylate-based MOFs, also commonly termed “pillared-layered”, which are typically based on zero-dimensional paddlewheel type secondary building units of general formula $M_2(\text{COO})_4$ (where M is a divalent metal, most often Cu, Zn or Ni), connected in two dimensions by dicarboxylic linkers, *e.g.*, terephthalic acid, to form layers with square lattice topology that are pillared in the third dimension by aza-heterocyclic linkers, *e.g.*, 1,4-diazabicyclo[2.2.2]octane (DABCO).^{28,29} These frameworks usually display high porosity and, in some instances, flexible behaviour.^{30–32}

Nonetheless, a few examples of porous pillared-layered metal phosphonates have appeared in the literature.^{26,33,34} One of the most notable is a Zr^{IV} -based compound containing both a sterically demanding diphenyldiphosphonate linker and a phosphite ligand, which displays ordered microporosity.³⁵ “Unconventional” MOFs based on disordered pillared-layered metal phosphonates with broad pore size distribution in the mesoporous regime have also been reported.²¹ The “accordion effect” in response to solvent adsorption observed in pillared-layered Zr^{IV} -phosphonates, obtained by partial topotactic exchange of the dihydrogen phosphate groups of $\gamma\text{-Zr}^{\text{IV}}$ phosphate with diphosphonic acids with either aliphatic or polyethylenoxide chains, is a prototypical example of flexible behaviour in organic–inorganic hybrid materials, being described already in 1998.^{36,37}

The family of metal phosphonates does feature a few interesting examples of flexible open frameworks, such as Al^{III} , La^{III} , Ce^{III} , Nd^{III} - and Zr^{IV} -based derivatives of the linker N,N' -bis-(phosphonomethyl)-piperazine,^{38–41} a Zr^{IV} -based derivative of the linker N,N,N',N' -tetrakis-(phosphonomethyl)-1,4-diaminocyclohexane,^{42,43} a La^{III} -based derivative of the linker N,N' -bis-(phosphonomethyl)-bipiperidine,⁴⁴ and isorecticular mixed linker Cu^{II} -based derivatives of the linker N,N,N',N' -tetrakis-(phosphonomethyl)-1,6-diaminohexane with either 4,4'-bipyridine or 1,2-bis(pyridyl)ethane as ancillary ligands.⁴⁵ Notably, all these materials display three-dimensional crystal structures based on one-dimensional IBUs and linkers with

aliphatic nature, whose combination allows enough degrees of freedom to enable flexible behaviour.

We report here on the recently discovered pillared-layered Cu^{II} ethylenediphosphonate of formula $\text{Cu}_2(\text{H}_2\text{O})_{1.7}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{PO}_3)\cdot 1.5\text{H}_2\text{O}$ (hereafter Cu-EtP),⁴⁶ which features both porosity to H_2O and CO_2 , and a rather unusual structural behaviour induced by adsorption and desorption of these species, as evidenced by gas sorption analysis, adsorption microcalorimetry, *in situ* synchrotron powder X-ray diffraction (PXRD), *in situ* infrared (IR) spectroscopy, optical spectroscopy and density functional theory (DFT) calculations.

Results and discussion

Crystal structure of Cu-EtP

The crystal structure of Cu-EtP (Cambridge Structural Database refcode UXUPEK)⁴⁶ is constituted of layers built from the connection of Cu^{II} ions and phosphonate groups, pillared by the aliphatic chain of the linker (Fig. 1a and Fig. S1, ESI†). The interlayer distance (as indicated by the 200 reflection) is 7.42 Å. Cu is coordinated by four phosphonate oxygens and two water molecules in distorted octahedral geometry (Fig. 1b). Each phosphonate group connects four Cu atoms *via* two crystallographically equivalent monodentate oxygens O1 and one bidentate oxygen O2 (Cu–O1 = 1.932 Å, Cu–O2 = 2.024 Å). The coordinated water molecule OW1 is bridging between two Cu atoms (Cu–OW1 = 2.453 Å). OW1 has an occupancy of 0.85. Additional water molecules (OW2 with occupancy of 0.41, OW3 with occupancy of 0.34) are physisorbed within the narrow channels running along the *c* axis. Thus, as-synthesised Cu-EtP can be formulated as $\text{Cu}_2(\text{H}_2\text{O})_{1.7}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{PO}_3)\cdot 1.5\text{H}_2\text{O}$.

The removal of all the coordinated water molecules should, in principle, generate two open metal sites (OMs) per Cu atom, affording a square planar geometry (Fig. S2–S4, ESI†). Indeed, after removal of the coordinated water molecules the colour changes from turquoise to blue (as reported in Fig. S5, ESI†), suggesting that changes are taking place in the Cu coordination sphere. The distance, measured from the atomic centres, between two H atoms belonging to neighbouring linkers along the *b* axis is 5.044 Å. If the van der Waals radii of the two H atoms (1.1 Å)⁴⁷ are subtracted, the distance decreases to 2.844 Å, in the sub-ultramicroscopic regime.^{48,49} Assuming that the unit cell was to keep the same volume (432.0 Å³), this ideal, fully dehydrated MOF of formula $\text{Cu}_2(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{PO}_3)$ would have a formula weight of 313.1 g mol^{−1} and a density of 2.41 g mL^{−1}. This corresponds to a density of 0.0094 Cu atoms Å^{−3}, that is, 0.0188 OMs Å^{−3}. Such a density of OMs is much higher than most MOFs known in the literature, such as MOF-74 (0.0045 OMs Å^{−3}),⁵⁰ HKUST-1 (0.0026 OMs Å^{−3}),⁵¹ MAF-35 (0.0104 OMs Å^{−3})⁵² and F4_MIL-140A(Ce) (0.0034 OMs Å^{−3})¹⁷ (Table S1, ESI†).

Gas sorption properties

The evacuation of as-synthesised Cu-EtP was initially assessed by thermogravimetric analysis (TGA). In the original report,⁴⁶



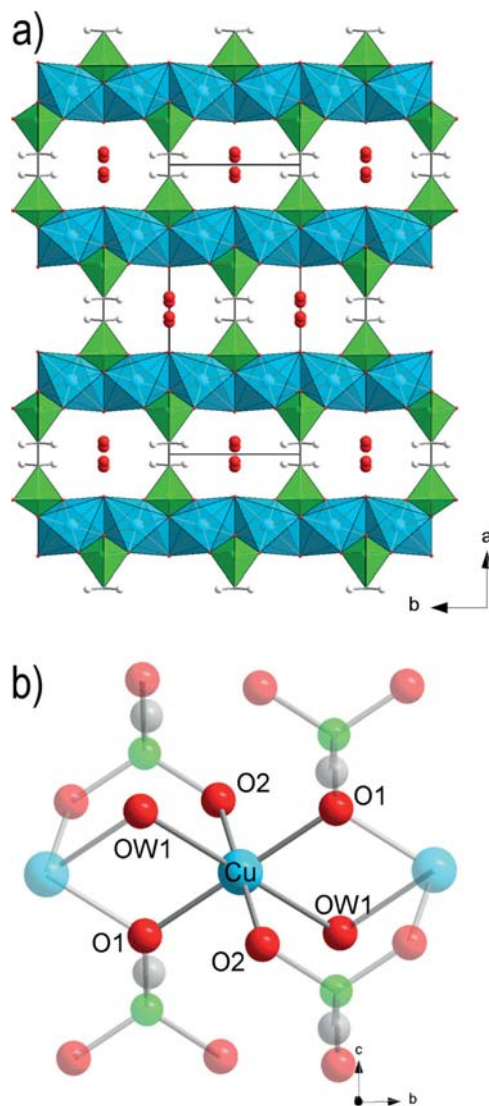


Fig. 1 Polyhedral representation of the crystal structure of as synthesised Cu-EtP, viewed along the *c* axis (a) and detail of the local connectivity around the Cu^{II} atoms (b, atoms not directly connected to the central Cu are shaded to highlight the coordination sphere of the central atom). Colour code: Cu, cyan; P, green; C, grey; O, red; H, white.

the TG curve (recorded in air at a rate of 10 K min⁻¹) displayed two distinct weight losses ending at 313 K and 413 K, associated with the release of physisorbed and coordinated water, respectively (Fig. S6, ESI†). The total weight loss amounted to 14.8%, in good agreement with the expected 15.5%. Here, we kept Cu-EtP at 413 K under an Ar stream (100 mL min⁻¹), observing a gradual weight loss taking place over eight hours, after which the curve had plateaued at a residual mass of about 86.3% (Fig. S7, ESI†). At this point, the temperature was decreased

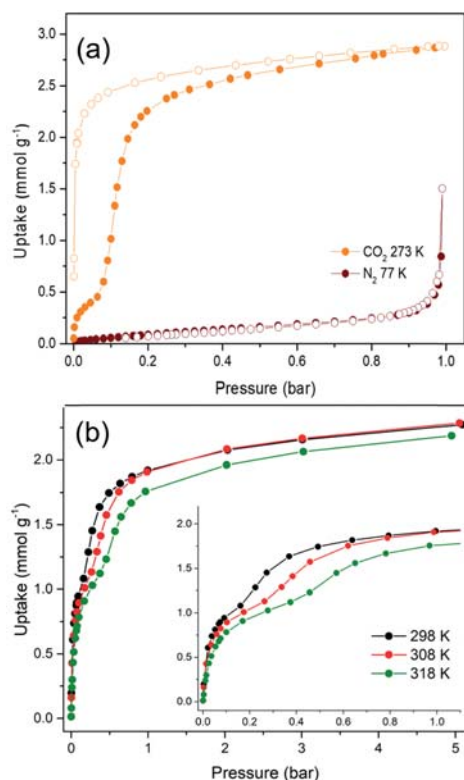


Fig. 2 Low pressure N₂ (77 K, wine) and CO₂ (273 K, orange) adsorption/desorption isotherms (a) and high pressure CO₂ adsorption isotherms collected at 298 K (black), 308 K (red) and 318 K (green) (b). The isotherms were collected using 60 s of equilibration time.

to 313 K and, as soon as it was equilibrated, the gas stream was switched to a 90:10 CO₂/Ar mixture (100 mL min⁻¹). The solid immediately started gaining weight, clearly indicating adsorption of CO₂, but equilibrium was not achieved over three hours of exposure to the CO₂-rich mixture. The mass gain after three hours was 4.6%, corresponding to about 1.0 mmol g⁻¹. This experiment provided two important pieces of information: the first is that Cu-EtP must be held at 413 K for six hours under an Ar stream to fully remove the coordinated water, the second is that the evacuated solid can adsorb an appreciable amount of CO₂, even though with apparently slow kinetics.

The textural properties of Cu-EtP, upon an overnight activation at 393 K under dynamic vacuum, were first investigated by performing adsorption/desorption isotherms with N₂ at 77 K and CO₂ at 273 K (Fig. 2a and b). The isotherm collected with N₂ at 77 K can be classified as a type III (following IUPAC classification),⁵³ suggesting the non-porous nature of Cu-EtP or, alternatively, an extremely low affinity towards this molecular probe. Additionally, the use of N₂ at 77 K as probe for ultra- or sub-ultra-microporous materials has different drawbacks, due to the uncertainty in the evaluation of its cross-sectional



area, the micropore filling shifted at very low relative pressures ($P/P_0 \sim 10^{-7}$) and the diffusion limitations imposed by the cryogenic temperature.⁵⁴ In contrast, the material adsorbs CO₂ at 273 K, displaying a peculiar step-shaped adsorption isotherm with a hysteresis loop in desorption and a considerable maximum CO₂ uptake of 2.9 mmol g⁻¹ (6.9 mmol cm⁻³, if a density of 2.41 g mL⁻¹ is assumed) at 1 bar, corresponding to about 67 cm³ (STP) g⁻¹. This value is equivalent to 12.8 wt% of CO₂ adsorbed, which translates to about 0.9 molecules of CO₂ per formula unit, as opposed to the 3.2 molecules of water (1.7 coordinated to Cu plus 1.5 physisorbed within the channels) per formula unit present in the as synthesised Cu-EtP. The considerable adsorption of CO₂ at 273 K suggests that its smaller kinetic diameter (3.3 Å), together with a higher adsorption temperature with respect to 77 K employed for N₂ isotherm, help the diffusion of this molecule inside the sub-ultramicroporous structure of Cu-EtP. However, the peculiar hysteretic step-shaped isotherm implies that Cu-EtP might undergo a phase transition upon adsorption of CO₂, which is only reversible in desorption at low pressure. This behaviour is usually associated with an adsorption-induced transition from a “narrow pore” to a “large pore” phase.^{11,12,30} By using CO₂ at 273 K, the highest achievable relative pressure is ~ 0.03 , therefore it is able to probe the textural properties of materials with a pore size lower than 10 Å.⁵⁵ By applying the Brunauer-Emmett-Teller (BET) equation to the desorption branch of the CO₂ adsorption isotherm, we extracted a value of specific surface area of 295 m² g⁻¹ for the new phase that appears to persist over a large range of pressures (Fig. S8, S9 and Tables S2, S3, ESI†). It is worth noting that, due to the structural rearrangement induced by CO₂ adsorption, the value of the surface area extracted from the desorption branch of the isotherm by means of the BET equation is related to the material no more in the fully evacuated form, therefore it should be considered as a mere estimation of the CO₂ accessible surface in Cu-EtP. Indeed, the application of the BET model to the adsorption isotherm is prevented by its peculiar step-shaped behaviour. The peculiar shape of the adsorption isotherm is also preventing the study of pore size distribution and pore volume by means of conventional non local DFT method. A valid alternative to estimate the micropore volume is the application of *t*-plot to the desorption branch of the isotherm which results in a micropore volume of 0.093 cm³ g⁻¹. The CO₂ adsorption of Cu-EtP was further investigated by collecting adsorption/desorption isotherms up to 5 bar pressure at three temperatures, namely, 298, 308 and 318 K. Fig. 2b shows a comparison of the adsorption branches, whereas the full isotherms and respective fittings are available in the ESI† (Fig. S10–S15 and Tables S4, S5). The adsorption isotherms display a steep increase at pressures below 0.2 bar, when the loading is in the range of 1 mmol g⁻¹. After this first adsorption event, a step appears, leading to the adsorption of additional CO₂, followed by saturation at about 2 mmol g⁻¹ at pressures exceeding 1 bar. The step shifts to higher pressures as the temperature increases, as observed for other adsorbents displaying analogous behaviour.^{4,14,17,56}

An interesting insight comes from inspection of the kinetic curves recorded during collection of the isotherms in Fig. 2b, which display a significant slowdown of the adsorption rate at pressures associated with the step (Fig. S16–S18, ESI†). This behaviour suggests that there could be either a slow structural rearrangement associated with the adsorption of CO₂ or a kinetics effect due to the small size of the channels of Cu-EtP, which is comparable to the kinetic diameter of CO₂ (3.3 Å), or a combination of the two. Since the kinetics may have an impact on the adsorption of CO₂ in the sample, another CO₂ adsorption isotherm was collected at 273 K with the low-pressure apparatus, using twice the equilibration time compared to the one employed for the isotherms reported above (Fig. S19, ESI†). By comparing the two isotherms collected using 60 and 120 s equilibration time, it is possible to observe a change in the shape of the adsorption branch, which displays a step shifted towards lower pressures at a shorter equilibration time (Fig. S19, ESI†). These observations suggest that the shape of the adsorption isotherm depends on how equilibrium conditions (*i.e.*, equilibration time and pressure tolerance) are defined and how sensitive the instrument is in terms of pressure resolution. The root of such variability is most likely the sluggish kinetics observed during CO₂ adsorption. It is worth noting that the equilibration time does not affect the desorption branch of the isotherms. For this reason, the desorption isotherms can be reasonably employed to estimate the CO₂ accessible surface. Indeed, by applying the BET equation to the desorption branch of the CO₂ isotherm measured with an equilibration time of 120 s, a value of 278 m² g⁻¹ was computed. This result is in line with the value obtained at 60 s of equilibration time (Fig. S20 and Tables S6, S7, ESI†). Additionally, the micropore volume, estimated by applying the *t*-plot method to the desorption isotherm, is 0.094 cm³ g⁻¹, fully in agreement with what obtained from the 60 s isotherm.

N₂ adsorption was also assessed by collecting an isotherm at 298 K up to 5 bar pressure (Fig. S21, S22, ESI†). The isotherm displays an almost linear shape and the uptake of N₂ at 5 bar reaches only 0.2 mmol g⁻¹. The ideal adsorbed solution theory (IAST) selectivity was calculated from this isotherm and the CO₂ isotherm collected at the same temperature, assuming a 15 : 85 CO₂/N₂ mixture, representative of post-combustion capture from a coal-fired power plant (Fig. S23, ESI†). The IAST selectivity increases with increasing total pressure, displaying values that vary between 2300 and 11 000 in the 0.1–2 bar pressure range. Such ultrahigh values indicate that Cu-EtP might be able to separate CO₂ from N₂ *via* a molecular sieving mechanism, taking advantage of the larger kinetic diameter of N₂ (3.6 Å), which considerably restricts its diffusion in the sub-ultramicropores of Cu-EtP.

The isosteric heat of CO₂ adsorption (Q_{st}) was extracted from the three high-pressure isotherms using the Clausius-Clapeyron equation (Fig. S24, ESI†). The isotherms were fitted using both the dual site Langmuir and the dual site Langmuir-Freundlich models, obtaining a better result with the latter, even though the shape of the isotherms was not fully reproduced by the model (Fig. S13–S15 and Tables S4, S5, ESI†).



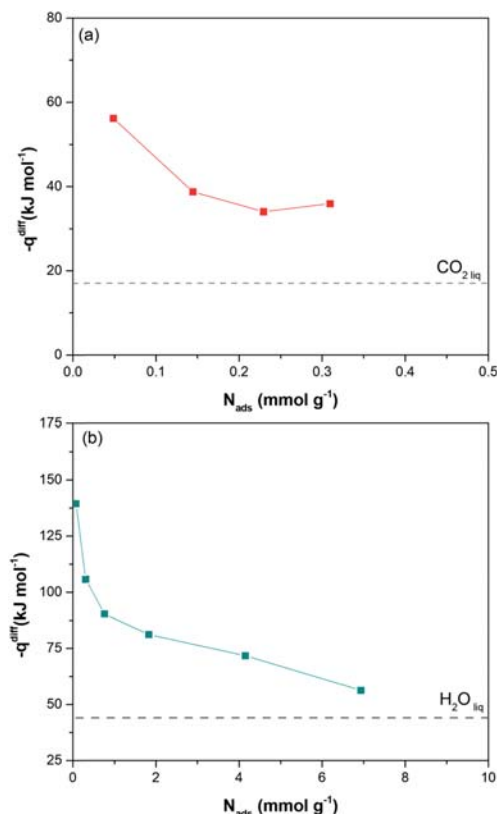


Fig. 3 Differential molar adsorption heat curves related to the adsorption of CO₂ at 308 K (a) and H₂O at 303 K (b). The dotted horizontal line represents the standard molar heat of liquefaction of CO₂ and H₂O (17 kJ mol⁻¹ and 44 kJ mol⁻¹, respectively).

Given the difficulty in fitting the curves, the Q_{st} values at low loading and near saturation suffer from a certain degree of error, but the plot suggests that there are two events associated with a Q_{st} in the range of 40 kJ mol⁻¹, before the step in the isotherm, and a Q_{st} in the range of 30 kJ mol⁻¹, in correspondence of the step. Additionally, since the shape of the adsorption isotherm step is affected by the equilibration time (see Fig. S19, ESI[†]), also the Q_{st} values could slightly change by modifying this parameter and, therefore, they should be considered as estimated isosteric heats of CO₂ adsorption. Anyhow, these values are consistent with a strong physisorptive character, which might involve the interaction of CO₂ with the abundant OMSs present in the evacuated MOF.

Direct evidence of the heat of adsorption is provided by adsorption microcalorimetry. The differential molar adsorption heat of CO₂ at 308 K and H₂O at 303 K was measured on dehydrated Cu-EtP samples (Fig. 3 and Fig. S25, ESI[†]). The CO₂ differential molar adsorption heat curve (Fig. 3a) shows an initial differential heat of 56 kJ mol⁻¹ and then a rapid decrease to 38 kJ mol⁻¹ at 0.15 mmol g⁻¹. This value remains almost

constant up to 0.3 mmol g⁻¹, in agreement with the isosteric heat of adsorption derived from Clausius–Clapeyron equation. Notably, the adsorption isotherm obtained with the volumetric line coupled with the microcalorimeter does not perfectly correspond with the low-pressure volumetric CO₂ isotherm performed at 308 K (Fig. S26, ESI[†]). This behaviour is consistent with what previously observed for the volumetric isotherms and provides further proof of the dependence of the shape of the isotherm to the definition of the equilibrium conditions. Indeed, in adsorption microcalorimetry, equilibrium is not defined as a pressure variation over a set time, but by the achievement of thermal equilibrium. This can lead to small deviations in the final shape of the adsorption isotherm. Additionally, it is worth mentioning that the CO₂ differential molar adsorption heat curve is limited to 0.3 mmol g⁻¹, corresponding to 0.1 bar of absolute pressure (Fig. S24a, ESI[†]). Unfortunately, higher CO₂ pressures coincide with a reduction of the overall adsorbed amount (the slope of the adsorption isotherm decreases reaching a sort of plateau before the step at 0.6 bar) and with the slowdown of the adsorption rate according to the kinetic curves (Fig. S17, ESI[†]). Both these issues prevent a correct measurement of the adsorption heat at higher coverage.

In agreement with the very steep H₂O adsorption isotherm at low pressure (Fig. S25b, ESI[†]), the differential molar adsorption heat of H₂O exhibits a very high initial value (about 140 kJ mol⁻¹ at 0.08 mmol g⁻¹). The differential heat rapidly decreases to 90 kJ mol⁻¹ at 0.77 mmol g⁻¹ and then it slowly lowers until 70 kJ mol⁻¹ at a coverage of 4 mmol g⁻¹. After that, the differential heat curve again changes slope, gradually approaching the heat of liquefaction of H₂O (44 kJ mol⁻¹). The high differential heats at low H₂O coverage (higher than 90 kJ mol⁻¹), suggest the presence of strong defective interaction sites in Cu-EtP sample. The second family of sites, associated with a weaker interaction (between around 85–75 kJ mol⁻¹) at higher H₂O coverages (1–4 mmol g⁻¹), could be compatible with the adsorption of coordinated water molecules on the OMSs of the MOF.

In situ powder X-ray diffraction

To gain a deeper understanding of the structural origin of the step in the CO₂ adsorption isotherm of Cu-EtP, we performed an *in situ* PXRD study. First, we followed the evacuation process of as synthesised Cu-EtP. The sample was held in a capillary and heated with a hot air blower under vacuum (pressure in the range of 10⁻⁵–10⁻⁶ bar). The sample was equilibrated for 10 min at 303, 353, 373, 393 and 413 K, observing no significant changes in the PXRD pattern (Fig. S27, S28, ESI[†]). Heating to 433 K induces rearrangements in the pattern, visible already after 10 min. The sample was held at 433 K for 300 min, collecting one pattern every 10 min, showing that the structural evolution continued for at least 120 min (Fig. S29 and S30, ESI[†]). Fig. 4 shows a comparison of the PXRD patterns of the as synthesised and evacuated Cu-EtP. The first observation to be made is that the evacuated Cu-EtP is characterised by a basal peak located at higher 2θ angles than the as synthesised



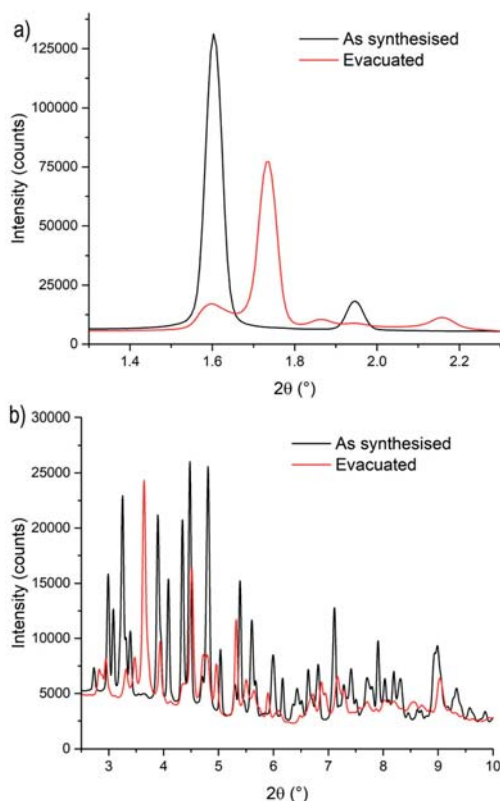


Fig. 4 Comparison of the low angle (a) and high angle (b) regions of the PXRD patterns of as synthesised (black line) and evacuated (red line) Cu-EtP. The evacuated pattern was collected upon cooling to 308 K, observing no changes from the one at 433 K.

Cu-EtP. This suggests that the structure is rearranging to a slightly more compact conformation upon removal of water. In the as synthesised MOF, the interlayer distance (as deduced from the position of the 200 reflection, located at $1.60^\circ 2\theta$) is 7.42 Å, while in the evacuated MOF it is reduced to 6.86 Å (as deduced from the position of the most intense Bragg reflection located at $1.73^\circ 2\theta$), corresponding to a 7.5% contraction. The second observation is that the phase transition appears not to be complete, as evidenced by the residual peak at $1.60^\circ 2\theta$ and by the IR spectra discussed herein. Unfortunately, due to the simultaneous presence of two crystalline phases and to the loss of long-range order upon evacuation, all our attempts to index the unit cell for the new phase failed, preventing us from gaining further structural information.

Next, we introduced increasing pressures of CO_2 in the capillary at the temperature of 308 K. No changes were observed at pressure as high as 0.490 bar, while new reflections appeared when the pressure was 1.064 bar and kept growing in intensity over 70 min at the expense of the characteristic reflections of the evacuated form (Fig. S31 and S32, ESI†). Apparently, the

residual as synthesised phase was not involved in the process, as demonstrated by the constant intensity of the reflection at $1.60^\circ 2\theta$. Further increasing the pressure to 1.271 bar did not cause any other change in the pattern. Notably, the pressure of 0.490 bar is located at the end of the step in the isotherm collected at the same temperature (Fig. S33, ESI†), where one would expect a possible phase transition to be well underway, yet no changes are observed in the PXRD pattern. This could be due to the slow kinetics of phase transition, already anticipated by the adsorption kinetics previously discussed. To gain further insight into this aspect, the sample was evacuated again and subsequently exposed to a fixed CO_2 pressure of 1.410 bar at 308 K for 65 min (Fig. S34 and S35, ESI†). The reflection at $1.65^\circ 2\theta$, associated with a new crystalline phase, appeared as soon as CO_2 was introduced in the capillary and kept increasing in intensity during the whole experiment, confirming the slow kinetics of phase transition. The CO_2 loaded Cu-EtP displays a PXRD pattern (Fig. 5 and Fig. S36, S37, ESI†) that retains features of the evacuated Cu-EtP, plus a new crystalline phase characterised by an interlayer distance of 7.19 Å (as deduced from the position of the Bragg reflection located at $1.65^\circ 2\theta$).

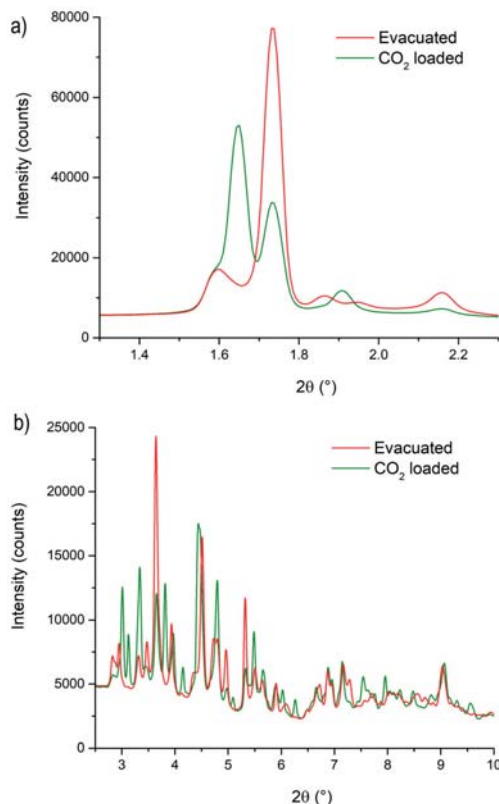


Fig. 5 Comparison of the low angle (a) and high angle (b) regions of the PXRD patterns of evacuated (red line) and CO_2 loaded (green line) Cu-EtP.



The coexistence of three crystalline phases in this sample made any further structural analysis impossible.

In situ infrared spectroscopy

We used *in situ* IR spectroscopy to further investigate both the structure and the role of Cu sites in the adsorption of small molecules. As in the PXRD experiment, the evacuation of Cu-EtP was evaluated first (Fig. 6a). The sample was outgassed under low vacuum conditions ($\sim 7 \times 10^{-3}$ mbar) and then heated from 313 K to 393 K at a 1.5 K min^{-1} rate. The as synthesised Cu-EtP sample (see the black dot spectrum in Fig. 6a and Fig. S38, ESI†) is characterised, in the 3600–1450 cm^{-1} spectral region, by the broad intense bands of the OH stretching vibrations (3600–3000 cm^{-1}) and of the HOH bending vibrations (1680–1530 cm^{-1}) and by two sharper bands at ~ 2940 – 2820 cm^{-1} associated to CH stretching modes.⁵⁷ In the lower frequency region (1450–550 cm^{-1}), the spectrum

displays vibrational modes ascribed to the Cu-EtP framework, among which: (i) a sharp component at 1413 cm^{-1} characteristic of the bending vibrations of the methylene $-\text{CH}_2$ groups bonded to P atoms, (ii) an out of scale intense band in the 1200–800 cm^{-1} frequency range, associated to both C–C and P–O stretchings of the phosphonate groups and (iii) a wide number of signals between 800 and 550 cm^{-1} due to the overlapping of several framework vibrations.^{57,58} The outgassing of the sample at beam temperature causes the desorption of physisorbed water, as proved by the erosion of the molecular water signals (OH stretching and HOH bending). A slight downward shift of the 1413 cm^{-1} band to 1410 cm^{-1} is observed accordingly. Upon heating, a new band at 1424 cm^{-1} grows at the expense of the 1410 cm^{-1} component, which progressively decreases in intensity, as also testified by the isosbestic point located at 1419 cm^{-1} . However, even after a prolonged heating at 393 K (around 12 h) the 1410 cm^{-1} band does not totally disappear and the two signals stay unchanged upon cooling down the sample in vacuum (Fig. S39, ESI†). The spectral modifications occurring in the 1440–1405 cm^{-1} spectral range, related to the deformations of the CH_2 groups bonded to P atoms, suggest a partial rearrangement in the Cu-EtP structure during the removal of molecularly adsorbed H_2O . It is worth noting that those spectral modifications are fully in agreement with PXRD data (Fig. 4) that prove the formation of a new dehydrated phase which coexists with the original hydrated one. In the whole mid-IR spectral region (Fig. S38, ESI†), the spectrum of the totally evacuated Cu-EtP sample displays the erosion of the broad band of interacting OH species at ~ 3600 – 3200 cm^{-1} and the simultaneous growth of a sharp signal at $\sim 3660 \text{ cm}^{-1}$, probably associated with the formation of isolated P–OH groups.^{39,59} It may be noted that, during evacuation, the HOH bending region (see inset of Fig. 6a) is deeply modified, progressively revealing a more complex band evolution: a new component appears at 1680 cm^{-1} close to the main 1654 cm^{-1} band that decreases in intensity upon heating, while another signal at lower wavenumber (1580 cm^{-1}) gradually appears, persisting also at higher temperature. The different stability of these bands suggests that the former ones, which rapidly decrease with the temperature, should be associated to the physisorbed water, while the latter one, which can be detected even at temperature higher than 378 K, is probably ascribable to the water strongly coordinated to Cu^{II} sites.⁶⁰ Eventually, the bands in the low spectral region (800–550 cm^{-1}), assigned to the superposition of many framework vibrations, are strongly perturbed during the material evacuation (as displayed in Fig. S40, where the ATR-IR spectra are reported to better highlight the spectral modifications observed in the low frequency region, ESI†), in accordance with the proposed structural rearrangement.

After studying the spectral evolution upon dehydration, Cu-EtP, previously evacuated at 393 K for 12 h under vacuum, was exposed to increasing pressures of H_2O (from 0.35×10^{-4} to 1.5×10^{-4} bar) (Fig. 6b and Fig. S41, S42, ESI†). The changes observed during the hydration of the material reflect what

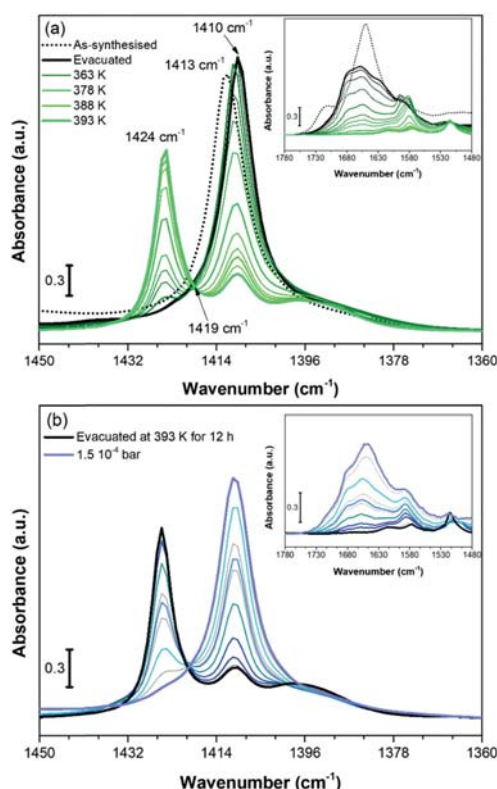


Fig. 6 IR spectra of Cu-EtP collected in the 313–393 K temperature range (a) and dosing 0.35 – 1.5×10^{-4} bar of H_2O (b), reported in the 1450–1360 cm^{-1} spectral region. Dashed black curves represents the as synthesised Cu-EtP, black curves the evacuated sample at RT (a) and 393 K (b), green bold curves represent Cu-EtP spectra at increasing temperatures and blue bold curves the incremental pressure doses of H_2O employed during the IR experiment and specified in Fig. S41 (ESI†). The insets report the corresponding 1780–1480 cm^{-1} spectral region.



previously noted upon H₂O desorption. In particular, the 1424 cm⁻¹ band present in the evacuated material progressively decreases upon increasing the H₂O pressures, while the band at 1410 cm⁻¹ is totally restored. In the same way, in the HOH bending region, the water is first adsorbed on the most energetic Cu^{II} sites, originating the 1580 cm⁻¹ (coordinated water) band and only at higher H₂O coverage, the 1680–1654 cm⁻¹ bands associated to physisorbed water appear. The band evolution suggests a total rehydration of the material, since the final spectrum of Fig. 6b perfectly matches with the IR spectrum of the as synthesised material. It is worth noting that the total rehydration of the sample occurs at very low relative pressure of water (between 0.3–2.2 × 10⁻³), suggesting that Cu-EtP has a strong affinity for water, in agreement with the calorimetric isotherm (Fig. S25, ESI†). The spectral evolution observed during Cu-EtP dehydration/hydration proves the occurrence of a reversible structural rearrangement upon H₂O adsorption/desorption.

We also investigated the vibrational behaviour of a fully dehydrated Cu-EtP sample when exposed at beam temperature (*i.e.* around 313 K) to an increasing CO₂ pressure (in the range between 0.005 and 0.55 bar). The time between the different CO₂ incremental doses was gradually increased when approaching the pressures corresponding to the second isotherm step (0.2–0.8 bar), due to the slow kinetics observed for this adsorption event (Fig. S43 and S44, ESI†). The incremental CO₂ doses are responsible for significant changes in both the CO₂ asymmetric stretching region between 2400 and 2220 cm⁻¹ (Fig. 7a) and in the 1450–1360 cm⁻¹ spectral range (Fig. 7b).

As reported in Fig. 7a, upon CO₂ dosing, the ν_3 OCO asymmetric stretching vibrations in the 2400–2220 cm⁻¹ are quickly going out of scale due to the large extinction coefficient of this spectral mode. Already after the first incremental doses of CO₂, an intense band at 2329 cm⁻¹ with a low frequency shoulder at 2318 cm⁻¹ appears, exhibiting a rapid increase of intensity. At lower wavenumber, a much weaker signal at 2264 cm⁻¹ forms at low CO₂ coverage exhibiting a slight upward shift to 2268 cm⁻¹ by increasing the coverage. The component at 2329 cm⁻¹ could be assigned to CO₂ interaction with Cu^{II} sites present in the Cu-EtP sample after H₂O removal. However, the 2329 cm⁻¹ signal is significantly downward shifted compared to the asymmetric signals of CO₂ in gas phase (2349 cm⁻¹) while, usually, the linear interactions of CO₂ over acid sites results in an upward shift of the ν_3 band, whose extent should be correlated with the acid strength of the site.⁶¹ However, a similar behaviour has been previously observed by Bordiga *et al.* on HKUST-1, in which a band at 2333 cm⁻¹ was assigned to the interaction of CO₂ with the full Cu₂(CO₂)₄ unit.⁶² Similarly, the 2329 cm⁻¹ band could be due to a more complex CO₂ interaction with Cu-EtP sample involving not only the bare adsorption on Cu^{II} cations. Even if this attribution cannot be carried out with absolute certainty, a clue in favour of this assignment comes from the analysis of the desorption CO₂ spectra (Fig. S44b, ESI†). In the 2400–2220 cm⁻¹ spectral region, the CO₂ asymmetric vibrations quickly decrease in intensity, except for the 2329 cm⁻¹ band

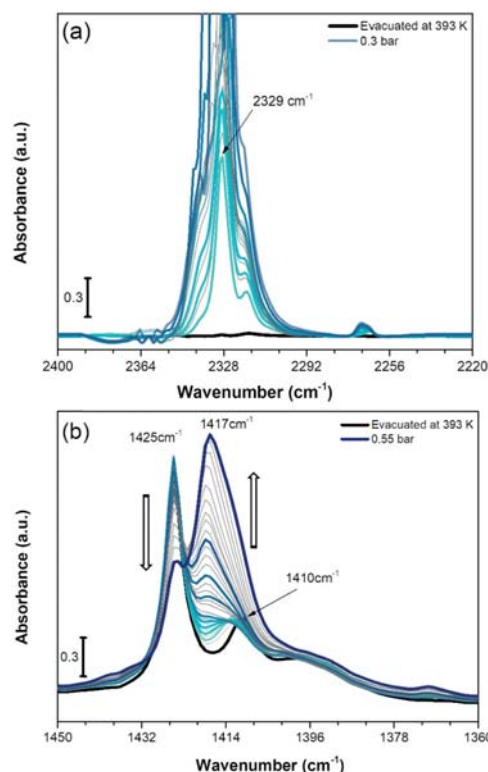


Fig. 7 IR spectra of CO₂ adsorption on Cu-EtP evacuated at 393 K reported in the 2400–2200 cm⁻¹ (a) and 1450–1360 cm⁻¹ (b) spectral ranges. The incremental pressure doses of CO₂ employed during the IR experiment are reported with thicker coloured curves and specified in Fig. S43 (ESI†). The 2400–2200 cm⁻¹ spectral region is corrected by subtracting the rotovibrational profile of gaseous CO₂, the original spectrum is reported in Fig. S44a (ESI†).

that persists even after prolonged outgassing under dynamic vacuum. The high stability of this band further suggests the presence of a strong interaction between CO₂ and the OMSs of Cu-EtP. The same interaction involving ¹³CO₂ is responsible for the appearance of the weak 2264 cm⁻¹ band, while the 2268 cm⁻¹ is probably due to ¹³CO₂ in the gas phase, which has been subtracted in the spectra for the most abundant ¹²CO₂ isotopic form.

In the P-CH₂ vibrations spectral range (1450–1360 cm⁻¹), the fully evacuated sample shows both the 1425 cm⁻¹ band (indicative of the dehydrated phase) together with a partial persistence of the 1410 cm⁻¹ (deriving from the residual hydrated phase of Cu-EtP), as previously described in Fig. 6a. By increasing the CO₂ pressure, a new vibrational mode of P-CH₂ moieties appears at ~1417 cm⁻¹, suggesting the formation of a new phase, in accordance with the PXRD data. Interestingly, at low CO₂ coverage (until 0.2 bar) the bands at 1425 and 1410 cm⁻¹ are not perturbed, while the new band at 1417 is gradually growing. Upon increasing the CO₂ pressure



(0.2–0.4 bar), the bands at 1425 cm^{-1} and 1410 cm^{-1} slightly decrease, while the 1417 cm^{-1} band increases. Finally, at higher CO_2 pressures (0.4–0.5 bar), the 1425 cm^{-1} band suddenly decreases while the 1417 cm^{-1} band rapidly increases, generating an isosbestic point at 1422 cm^{-1} . However, the 1417 cm^{-1} band exhibits a shoulder at lower wavenumbers. By performing the computer-assisted deconvolution of the $1450\text{--}1360\text{ cm}^{-1}$ bands (Fig. S45, ESI[†]), the increase of the 1410 cm^{-1} band becomes evident at higher CO_2 coverages. It is worth noting that the increase of the 1410 cm^{-1} band and the simultaneous decrease of the 1425 cm^{-1} signal was previously observed during the hydration of the material. To keep up with the slow kinetics of the CO_2 adsorption, after contact with the highest CO_2 doses, the sample was left for a long time in the cell under static conditions, leading to some (uncontrollable) H_2O contamination, as also proved by the increase of both the OH stretching and HOH bending bands (Fig. S46, ESI[†]). In a CO_2 saturated atmosphere, the co-presence of a slight fraction of H_2O seems to facilitate the entrance (and consecutive adsorption) of CO_2 and the transition of Cu-EtP to a new, partially opened structure.

Finally, increasing CO_2 pressures were dosed directly on a sample outgassed at 298 K , where only physisorbed (and not coordinated) water was removed, to observe the CO_2 interaction on Cu-EtP in the open phase (Fig. S47, ESI[†]). In this case, the CO_2 asymmetric stretching region ($2400\text{--}2220\text{ cm}^{-1}$) shows only the signals typical of CO_2 in the gas phase, while the $1750\text{--}1450\text{ cm}^{-1}$ and the $1450\text{--}1360\text{ cm}^{-1}$ spectral regions totally coincide with those of as synthesised sample, suggesting that Cu^{II} OMSs, saturated by coordinated H_2O , are totally inaccessible to CO_2 .

Nitrogen oxide (NO) was chosen as molecular probe to further investigate the accessibility of Cu^{II} OMSs, not only for the affinity displayed toward Cu^{II} sites by this molecule, but also for its small kinetic diameter ($3.17\text{ \AA}$).⁶³ Indeed, the sub-ultramicroscopic nature of Cu-EtP avoids the entrance of the mostly used basic molecular probes, such as CO , whose kinetic diameter is $3.76\text{ \AA}$.⁶³ 0.12 bar of NO was dosed on a sample evacuated at 393 K overnight. Initially, NO does not interact with Cu-EtP and only its rovibrational profile was observed in the IR spectrum. Only after 12 h , a band at 1887 cm^{-1} , ascribable to the interaction of NO with Cu^{II} sites, appears together with the 1875 cm^{-1} signal of NO in the gas-phase (Fig. 8). However, as previously observed for the CO_2 interaction, the prolonged contact time is responsible for some H_2O contamination (see the appearance of HOH bending modes at 1654 cm^{-1} in the inset of Fig. 8). The presence of a small fraction of H_2O favours the transition to the partially opened structure and the consecutive NO adsorption at Cu^{II} OMSs, as testified, in the $1450\text{--}1350\text{ cm}^{-1}$ region, by the simultaneous decrease of the 1425 cm^{-1} band in favour of the 1410 cm^{-1} one (see Fig. S48, ESI[†]). Also for NO, an experiment was performed on a sample outgassed at 298 K , in order to observe the possible NO interaction on Cu-EtP in the open phase (Fig. S49, ESI[†]). In this case, the signal at 1887 cm^{-1} (generated by the interaction of NO with Cu^{II} sites) appears after just 2 h . No major changes

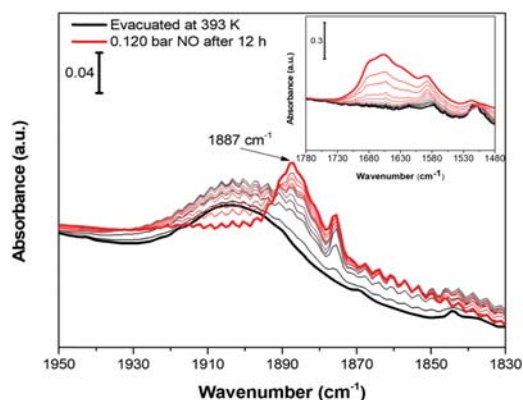


Fig. 8 IR spectra of Cu-EtP evacuated at 393 K after adsorption of 0.122 bar of NO at beam temperature and following outgassing. Black curve represents the sample evacuated at 393 K for 12 h , red curve represents 0.120 bar of NO dosed on Cu-EtP measured after 12 h and thinner coloured curves the intermediate pressures reached during outgassing. The inset reports the corresponding $1780\text{--}1480\text{ cm}^{-1}$ spectral region.

can be detected in the P-CH_2 vibrational region, except for some intensity variation of the 1410 cm^{-1} signal. This behaviour is in accordance with the existence of an already opened structure, which does not display any significant change upon adsorption of NO. It is worth noting that, unlike CO_2 , NO seems unable to create a new crystalline phase upon adsorption but is still able to interact with Cu^{II} sites even in the presence of a partially hydrated structure, replacing part of the H_2O molecules (see the inset of Fig. S49a (ESI[†]) showing an intensity decrease of the HOH bending modes after NO dosing). However, also CO_2 may display some interactions with partially hydrated Cu-EtP after a prolonged contact time but, unfortunately, as previously pointed out, a slight H_2O contamination occurs upon an overnight exposure to CO_2 under static conditions, preventing a complete understanding of the CO_2 adsorption process.

Optical spectroscopy

In situ PXRD and IR spectroscopy clearly demonstrated that Cu-EtP experiences a structural rearrangement upon evacuation and, subsequently, CO_2 adsorption. Nevertheless, none of these techniques provided a direct information on the rearrangement of the local coordination sphere around the Cu^{II} cations. Electronic spectroscopies represent the election tool for this type of investigation, as the electronic transition associated to the metal centre directly correlate with the energies of involved orbitals that, in turn, depend on the ligand field around the metal itself. Accordingly, we collected diffuse reflectance optical spectra for Cu-EtP in its as synthesised form, after evacuation at 393 K and upon contacting the evacuated material with CO_2 , specifically focussing on the analysis of the spectral region typical of d–d transitions, as shown in Fig. 9.

In the as synthesised material, a doublet of bands with maxima at *ca.* $13\,500$ and $10\,000\text{ cm}^{-1}$ are observed, in



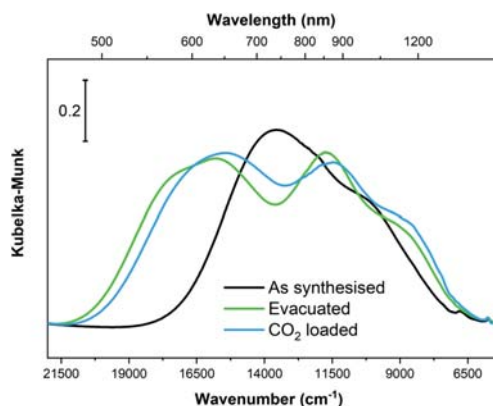


Fig. 9 Diffuse reflectance optical spectra of Cu-EtP collected on the as synthesised material, upon evacuation at 393 K and after contacting the evacuated material with CO₂ (ca. 0.5 bar).

agreement with previous report.⁴⁶ According to crystal field theory, and as already detailed in ref. 46 in the as-synthesised sample, three distinct d-d transitions are expected given the distorted octahedral geometry of ligands around Cu^{II} (four almost equivalent O atoms from phosphonate groups on the equatorial xy plane + two O atoms from apical water molecules at longer distance along the z axis). Upon evacuation at 393 K, the d-d transitions of Cu-EtP significantly change, with a blue-shift of the absorption maxima to ca. 15 500 and 11 500 cm⁻¹. A third component is instead red-shifted to ca. 8500 cm⁻¹. Such shifts are compatible with a change in the coordination sphere of Cu^{II} causing a variation in the gap between the non-degenerate d orbitals of the cation, most probably toward a square planar coordination geometry (see Fig. S50, ESI†). By loading CO₂ (at a pressure compatible with the second step in the adsorption isotherm) on the evacuated sample, a small red-shift of the absorption features is observed, though in overall the shape of the d-d transitions remains very similar to those of evacuated Cu-EtP, suggesting the CO₂ only weakly interacts with the Cu^{II} site by likely giving a new distorted octahedral coordination sphere. It is worth mentioning that PXRD showed that the formation of the CO₂ loaded phase at the expense of the evacuated one is only partial, further supporting the fact that associated optical spectra look similar to each other.

Computational simulations

The foregoing experimental evidence collectively point towards structural rearrangements occurring in Cu-EtP in response to

evacuation and adsorption of CO₂, respectively. Given the impossibility to gather insight into the atomic structure of the different crystalline phases of Cu-EtP using PXRD, we resorted to periodic DFT calculations to gain insight into said structural rearrangements. First, a triclinic subcell (space group *P1*) was identified for the as synthesised MOF, whose volume is half that of the original monoclinic unit cell (space group *C2/m*). This choice allows to work with 16 independent atoms in the unit cell to describe the framework, plus those needed to describe H₂O and CO₂, when the as synthesised and the CO₂ loaded forms are respectively considered. Three models were built for the as synthesised, evacuated and CO₂ loaded forms of Cu-EtP (Fig. S51–S56 and Table S8, ESI†). In these models, the inorganic layers lie on the (110) plane. The DFT optimised structures suggest that the main structural rearrangements occurring during evacuation and CO₂ adsorption involve the inorganic part of the framework, as outlined in Table 1 and Fig. 10.

In the as synthesised material, the local Cu coordination is distorted octahedral, with pairs of inequivalent Cu–O distances in the equatorial plane and axial ligands (*i.e.*, H₂O) positioned at a significantly longer distance. Upon desolvation, the coordination environment around Cu rearranges to a square planar geometry with a reduced inequivalence in the equatorial Cu–O distances. The introduction of CO₂ leads to a situation that is midway between those discussed above, with an apparently octahedral coordination characterised by an even higher distortion of the ligand field, as suggested by the very long Cu–O axial distances. All the PO–Cu bond lengths shrink when water is removed from the coordination sphere of Cu and increase again once CO₂ is adsorbed. The change of the coordination geometry of Cu also confirms the modification in the optical properties of Cu-EtP upon desolvation and consequent CO₂ loading.

The coordination rearrangements lead to changes in the interlayer spacing in line with those experimentally observed by PXRD: the Cu–Cu distance along the [110] direction varies from 7.621 Å to 7.404 Å to 7.436 Å in the as synthesised, evacuated and CO₂ loaded Cu-EtP, respectively. While these values appear to be systematically overestimated, compared to those experimentally observed, they suggest that DFT provides a reliable description of the structural evolution. The organic part of the framework appears to be relatively unaffected during evacuation, with the P–P distance inside the linker changing from 4.443 Å (as synthesised) to 4.449 Å (evacuated), while CO₂ adsorption causes an increase to 4.539 Å.

The interaction energy per H₂O/CO₂ molecule adsorbed was computed considering the adsorption of two molecules per

Table 1 DFT computed Cu–O distances (both equatorial, from PO, and axial, from adsorbates), adsorption energy, enthalpy and Gibbs free energy per H₂O/CO₂ molecule adsorption over the evacuated Cu-EtP structure. Distances expressed in Å, energies in kJ mol⁻¹

Model	Adsorbate	<i>d</i> (Cu–O _{eq})	<i>d</i> (Cu–O _{ax})	Δ <i>E</i>	Δ <i>H</i>	Δ <i>G</i>
As synthesised	H ₂ O	1.928/2.026 (1.932/2.024) ^a	2.439 (2.453) ^a	–89.6	–83.8	–40.8
Evacuated	—	1.924/1.968	—	—	—	—
CO ₂ loaded	CO ₂	1.911/2.035	2.610	–45.9	–42.7	4.1

^a In brackets, experimental values from crystallographic data reported in ref. 46.



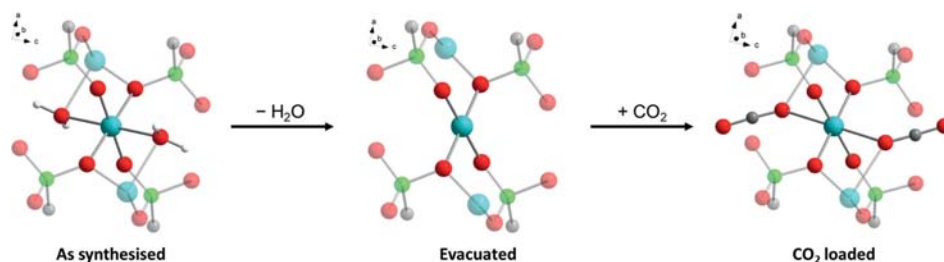


Fig. 10 Ball-and-stick representation of the local connectivity around the Cu^{II} atoms in the as synthesised, evacuated and CO₂ loaded DFT models. Colour code: Cu, cyan; P, green; C, grey; O, red; H, white.

formula unit from gas phase onto the evacuated structure. In the same way, adsorption enthalpy and Gibbs free energy were calculated (at 298 K and 1.013 bar). The results are summarised in Table 1. H₂O binds with a high interaction energy, compatible with a strong physisorption as inferred by microcalorimetry. In detail, the computed adsorption enthalpy of $-83.8 \text{ kJ mol}^{-1}$ nicely reproduces the heat experimentally evolved at intermediate coverages. This suggests that H₂O adsorption over OMSs takes place at intermediate coverages, whereas the higher adsorption heat evolved at low coverages may be reasonably associated with coordination of water on defective sites. The adsorption of water is significantly favoured, as demonstrated by the largely negative Gibbs free energy associated to the process, in line with the strong competitive adsorption H₂O exhibits toward other adsorbates. A similar good agreement with experimental heat values for CO₂ adsorption is observed as well. Interestingly, CO₂ adsorption is a slightly endergonic process, featuring a positive (though small in magnitude) Gibbs free energy. This feature could explain the only partial conversion of the evacuated phase of Cu-EtP into the CO₂ loaded one, as inferred by PXRD.

DFT simulation also allowed investigating in closer details the peculiar evolution of spectroscopic features observed during *in situ* IR experiments. The simulated spectra in the region typical of CH₂ bending modes are shown in Fig. S57 (ESI†). In absolute terms, the computed frequencies for the three considered structures are overestimated with respect to the experimental results, with an upshift of approximately 40 cm^{-1} for the as synthesised model. Nonetheless, the dataset can be effectively considered in a relative way, *i.e.*, accounting for the shift of the $\delta(\text{CH}_2)$ mode as a consequence of the presence/absence of the different adsorbates. Through this method, the computed shift of the CH₂ bending mode upon interaction with H₂O and CO₂ compared to the evacuated model experiences a shift of -15 cm^{-1} and -5 cm^{-1} , respectively. These values are in good agreement with the experimental shift of -14 cm^{-1} and -8 cm^{-1} , as derived at the maximum coverage experimentally considered, further confirming the supposed structure of the adsorbed molecules within Cu-EtP.

Additionally, to validate the unconventional experimental quantification of the BET area and micropore volume using the desorption isotherm, we performed an estimation of the

surface area for the evacuated model. This verification was carried out using the Zeo++ software.⁶⁴ In this simulation, we systematically adjusted the probe diameter, gradually reducing it from the kinetic diameter of N₂ ($3.60 \text{ \AA}$) to the maximum value that yielded a non-zero surface area in the simulation (see Table S9, ESI†). It is important to note that a reduced probe radius (compared to the experimental one), as required to observe a non-zero surface area within the theoretical framework employed by the Zeo++ software, has been previously documented in the literature.⁶⁵ By employing this approach, we identified an optimal probe diameter of $2.8 \text{ \AA}$, which resulted in a simulated surface area of $262 \text{ m}^2 \text{ g}^{-1}$. This simulated value closely matches the experimental surface area we obtained, proving the validity of our non-conventional BET area quantification. To further validate our findings, we repeated the same procedure for the as synthesised model. However, in this case, the results consistently indicated a negligible surface area, regardless of the selected probe diameter. Additionally, we carried out a simulation of the pore size distribution (Fig. S58, ESI†), which revealed a single family of pores with a diameter of $3.5 \text{ \AA}$ and a total accessible pore volume of $0.099 \text{ cm}^3 \text{ g}^{-1}$. It is worth noting that the pore volume is fully consistent with the value extrapolated from the *t*-plot. This simulated pore size distribution provides further confirmation of the ultramicroporous nature of Cu-EtP and highlights the need for specific characterisation strategies to comprehensively evaluate its textural properties.

Conclusions

By combining gas sorption analysis, adsorption microcalorimetry, *in situ* PXRD, *in situ* IR, optical spectroscopy and DFT calculations, we have investigated in depth the CO₂ adsorption properties of Cu-EtP and the associated structural transitions. The phase transitions occurring in Cu-EtP in response to adsorption/desorption of H₂O and CO₂ are rather unexpected, since its structure is based on rigid, two-dimensional IBUs, and the connectivity along the third dimension is ensured by a very short aliphatic chain with a limited number of degrees of freedom. We find that the rearrangement of the coordination sphere of Cu, which switches between distorted octahedral and



square planar, is mainly responsible for the observed behaviour. The structural response of Cu-EtP to the adsorption/desorption of water and CO₂, involving partially complete phase transitions, is distinct from common stimuli responsive MOFs, such as MIL-53, ELM-11 and ZIF-7, where clear cut transitions take place, driven by cooperative phenomena that imply a flexible behaviour of the framework but no changes in the coordination geometry of the metal. Thanks to the strong interaction with CO₂ and its ultrasmall channels, Cu-EtP can separate CO₂ from N₂ by molecular sieving, which makes it a potentially interesting solid sorbent for post-combustion carbon capture. However, given the slow CO₂ adsorption kinetics associated with the phase transition, the hysteretic CO₂ desorption isotherm, and the high affinity for H₂O, further investigation is needed to fully assess its real separation potential. Analogues of Cu-EtP based on organic linkers with longer aliphatic chains have been reported in the literature,^{66,67} but their adsorption properties were never assessed to the level of depth reached here, and it is reasonable to expect that these compounds might as well display peculiar structural behaviour, by virtue of the potentially higher flexibility of the organic part of the framework.

Experimental procedures

Materials

1,2-Ethylenediphosphonic acid (97%) was purchased from Alfa Aesar, Cu(NO₃)₂·3H₂O (ACS grade) was purchased from Riedel-Haën and urea (puriss.) from VEB Laborchemie Apolda. All reagents were used as received, with no further purification.

Synthesis of Cu-EtP

Cu-EtP was synthesised by slightly modifying a literature procedure: 1 g urea was added to 5 mL of a 0.1 M aqueous solution of 1,2-ethylenediphosphonic acid in a round bottom flask, which was kept at 80 °C in a drying oven. After 17 h, 5 mL of a 0.2 M Cu(NO₃)₂-solution was added, whereupon a light blue precipitate appeared. The whole solution was further kept at 80 °C for 4 h. The formed turquoise fine crystalline precipitate was washed with distilled water several times.

Thermogravimetric analysis

Thermogravimetric analysis was performed either using a Netzsch STA 449 instrument heating at 10 K min⁻¹ up to 1273 K under an air flow, or with a TA Instruments SDT-Q600 instrument heating at 10 K min⁻¹ up to 413 K under an Ar flow for 8 h, followed by cooling to 313 K and switching to a 90 : 10 CO₂/Ar flow for 3 h.

Gas adsorption volumetry

N₂ and CO₂ isothermal physisorption measurements were performed on a Micromeritics 3Flex at 77 K and 273 K (using 60 and 120 s as equilibration time) respectively (Fig. 2a). For CO₂ adsorption the temperature was kept constant thanks to a home-made patented glass coating cell in which a coolant or

heating fluid, connected to a thermostatic bath (JULABO F25), is recirculating.⁶⁸ Prior to the measurement, the sample was heated overnight at 393 K under vacuum. Specific surface areas were determined, by using the Brunauer–Emmett–Teller (BET) equation, from the desorption branch of the CO₂ isotherm measured at 273 K using both 60 and 120 seconds of equilibration time and 5% tolerance (Tables S2, S3 and Fig. S8, ESI†). The micropore volume was extrapolated from the *t*-plot curve derived from the desorption branch of CO₂ isotherms at 273 K using 60 and 120 s of equilibration time, considering the statistical thickness range 6 < *t* < 17 Å.

High pressure adsorption–desorption isotherms were measured with a Quantachrome iSorb High Pressure Gas Analyser. CO₂ isotherms were collected up to 5 bar at 298, 308 and 318 K using 60 s equilibration time and 0.5 mbar tolerance. N₂ isotherm was collected up to 5 bar at 298 K. About 450 mg of sample was used for the adsorption studies. The sample was degassed at 413 K under dynamic vacuum for 6 h prior to analysis and at 413 K for 1 h in between subsequent measurements.

The adsorption branches of the high pressure CO₂ isotherms were fitted using either the dual site Langmuir equation:

$$q = \frac{q_1 K_1 P}{1 + K_1 P} + \frac{q_2 K_2 P}{1 + K_2 P}$$

Or the following version of the dual site Langmuir–Freundlich equation:

$$q = \frac{q_1 (K_1 P)^{n_1}}{1 + (K_1 P)^{n_1}} + \frac{q_2 (K_2 P)^{n_2}}{1 + (K_2 P)^{n_2}}$$

where *q* is the gas loading at pressure *P*, *q*₁ and *q*₂ are the saturation loadings for each site, *K*₁ and *K*₂ are the affinity constants for each site, *n*₁ and *n*₂ are the indices of heterogeneity for each site. We note that the physical meaning of the models might not be representative of the actual CO₂ adsorption phenomenon occurring in Cu-EtP, but they provide a reasonable fit of the experimental data nonetheless (see Fig. S13–S15 and Tables S4, S5, ESI†). Using the isotherms fitted with the dual site Langmuir–Freundlich model, the isosteric heat of adsorption was extracted using the linear version of the Clausius–Clapeyron equation in the loading range 0.1–2.0 mmol g⁻¹.

The high pressure N₂ adsorption isotherm was fitted using the single site Langmuir equation:

$$q = \frac{q_{\text{sat}} K P}{1 + K P}$$

where *q* is the gas loading at pressure *P*, *q*_{sat} is the saturation loading, and *K* is the affinity constant.

The IAST CO₂/N₂ selectivity for a 15 : 85 mixture in the total pressure range 0.1–2 bar was calculated using the software IAST++.⁶⁹



Adsorption microcalorimetry

The differential molar heat of adsorption was evaluated on Cu-EtP by means of a heat flow microcalorimeter (Calvet C80 by Setaram) connected to a high-vacuum ($\approx 10^{-4}$ mbar) glass line equipped with a Varian Ceramicell 0–100 mbar gauge and a Leybold Ceramicell 0–1000 mbar gauge. Prior to the measurement, the sample was activated in vacuum at 120 °C for 12 h and subsequently placed overnight in the calorimeter under isothermal conditions for the equilibration. The measurement in CO₂ was performed at 308 K (35 °C), intermediate temperature previously selected for one of the high-pressure isotherms (Fig. 3a and Fig. S24a, ESI†). For H₂O the selected temperature was 303 K (30 °C) (Fig. 3b and Fig. S24b, ESI†). The measurement was performed for both CO₂ and H₂O following a well-established step-by-step procedure described elsewhere.⁷⁰ By means of adsorption microcalorimetry it is possible to determine, for small increments of the adsorptive pressure, both the integral heats evolved ($-Q_{\text{int}}$) and the adsorbed amounts (N_{ads}). The heats of adsorption obtained for each small dose of gas ($-q_{\text{diff}}$) are reported as a function of coverage, in order to obtain the (differential) enthalpy changes. The differential heat plot was obtained by taking the middle point of the partial molar heat ($\Delta Q_{\text{int}}/\Delta N_{\text{ads}}$, kJ mol⁻¹) vs. N_{ads} histogram relative to the individual incremental dose. A volumetric isotherm of CO₂ at 303 K was also collected by means of a Micromeritics ASAP 2020 instrument, in order to compare the isotherm obtained with the microcalorimetric apparatus (Fig. S25, ESI†).

In situ PXRD

The *in situ* PXRD study here described took place at Beamline P02.1 (PETRA III, DESY, Hamburg).⁷¹ PXRD patterns were collected using 60.0 keV (0.207124 Å) radiation. The sample was held in a 0.5 mm internal diameter glass capillary, which was mounted on a custom-built spinner device that allows for rotating a gas-filled capillary mounted on a commercial Huber goniometer head by 360° forth and back. The temperature of the sample was controlled between 298 and 413 °C with an Oxford Hot-Air Blower. The beamline was equipped with a PerkinElmer XRD1621 CN3 – EHS detector (200 × 200 μm² pixel size, 2048 × 2048 pixel area). The detector was positioned at 1000 mm from the sample stage. Each PXRD pattern was collected in the 0.0071–16.3041° 2θ range, with a 0.0067° 2θ step size and a total acquisition time of 30 s. The resulting 2D images were azimuthally integrated to 1D diffraction patterns using the software Fit2D.⁷²

In situ IR spectroscopy

IR spectra were performed on a Bruker Invenio equipped with a MCT (mercury cadmium telluride) cryo-detector. All the spectra were recorded in a spectral range of 4500–250 cm⁻¹ with a resolution of 2 cm⁻¹ and an average of 32 scans. Before the analysis self-supported pellets were prepared starting from the Cu-EtP powder.

Firstly, the evolution of IR spectra at increasing temperatures was studied. The sample pellet, inserted in a AABISPEC

cell, was heated from 313 K to 393 K with 1.5 K min⁻¹ temperature ramp, under mild vacuum conditions ($\sim 7 \times 10^{-3}$ mbar). IR spectra were automatically recorded every 60 seconds and plotted after a baseline correction (Fig. 6a in the main text and Fig. S37, ESI†). After reaching 393 K, the sample was left under isothermal conditions for 1 h, without detecting significant changes (spectra not reported in the manuscript for the sake of brevity). Finally, the sample was cooled down to 313 K and compared to the sample heated at 393 K (Fig. S38, ESI†).

A further comparison of the spectral evolution of Cu-EtP under activation condition was carried out by performing ATR-IR spectra of the as-synthesised sample, of the sample evacuated for 12 h at RT and of the sample evacuated for 12 h at 393 K (Fig. S39, ESI†). The spectra were collected using a Bruker Alpha II spectrophotometer located inside the glovebox. The spectra were recorded under controlled atmosphere with a DTGS detector by accumulating 32 scans (64 for the background spectrum), with a resolution of 2 cm⁻¹.

The study of the interaction of Cu-EtP with H₂O was carried out sending incremental doses of H₂O (0.35–1.5 10⁻⁴ bar) on the activated sample (see Fig. 6b for the 1450–1360 cm⁻¹ spectral region, Fig. S41 (ESI†) for the full spectral region and Fig. S40 (ESI†) for the schematic representation of the incremental pressures of H₂O dosed in time during the IR experiment).

Next, the vibrational behaviour of Cu-EtP previously evacuated at 393 K overnight was investigated upon exposure to increasing CO₂ pressures in the range between 0.005 and 0.550 bar, at beam temperature (*i.e.*, around 313 K). The time between consecutive CO₂ doses was gradually increased by approaching the isotherm step, due to the slow kinetics of the CO₂ adsorption process (Fig. S42, ESI†). The same experiment was repeated on Cu-EtP not fully activated (*i.e.*, evacuated at RT for just 1 h) to follow the CO₂ adsorption process in presence of (coordinated) water (Fig. S46, ESI†).

Lastly, NO interaction with the sample were studied by dosing a proper amount of gas (~ 0.12 bar) into the cell at beam temperature. Also in this case, the experiment was performed on both fully activated sample (overnight evacuated at 393 K) and evacuated one (evacuated at RT for 1 h) (Fig. 8 in the main text and Fig. S48, ESI†). The spectra reported for both the experiments were collected in outgassing through subsequent expansions, until complete degas was achieved.

Optical spectroscopy

Optical spectra were recorded in reflectance mode on a Varian Cary 5000 spectrophotometer, equipped with an integration sphere. Polytetrafluoroethylene powder was measured as the 100% reflectance reference before measuring Cu-EtP. The sample, loaded in a sealable Suprasil quartz cuvette, was evacuated and subsequently loaded with >0.5 bar of CO₂ following the same thermo-chemical protocol as for IR. In between the different experimental steps, all sample manipulations were performed in a N₂-filled glovebox, in order to avoid its re-exposure to moist air.



Periodic DFT simulations

Periodic DFT simulations were performed with the CRYSTAL17 code.^{73,74} The B3LYP functional^{75,76} was adopted in conjunction with the POB-TZVP-rev2 basis set.⁷⁷ Since Cu^{II} is an open-shell ion (d⁹ electron configuration), the unrestricted Kohn–Sham formalism was adopted: an antiferromagnetic spin state was imposed in agreement with experimental evidence.⁴⁶ Dispersive interactions were empirically included in the Hamiltonian according to the Becke–Johnson dumped version of the Grimme's D3 scheme.^{78,79} Calculations were performed on a reduced triclinic unit cell having half the volume of the original C-centred monoclinic cell and containing a single unit formula of the compound, without imposing any symmetry constraint during geometry optimization. Initially, a model derived by removing water molecules featuring the OW2 and OW3 atoms from the experimental one was optimized, aiming at reproducing the as synthesised structure. The evacuated structure was modeled by relaxing a structure where the water molecule represented by the OW1 atoms were further removed. Finally, a CO₂ loaded structure was modelled by introducing two CO₂ molecules per unit cell, with one of their oxygen atoms placed at the same coordinates as for OW1. Adsorption interaction energies were computed and corrected for the basis set superposition method through the counterpoise method.⁸⁰ For each of the models above, harmonic frequencies were computed, confirming all the relaxed structures are minima (no imaginary frequencies). Furthermore, IR intensities and thermodynamic functions (enthalpy and Gibbs free energy) were computed.

Author contributions

R. K. carried out the synthesis. M. C., V. C. and M. T. carried out the gas sorption experiments and data analysis. M. C. and V. C. carried out the IR and adsorption microcalorimetry experiments and data analysis. M. S. performed the optical spectroscopy experiments and the DFT calculations and data analysis. M. T. carried out the PXRD experiments and data analysis. M. C., M. S., V. C. and M. T. drafted the manuscript. V. C. and M. T. coordinated the work. M. T. conceived the study.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The *in situ* PXRD experiments were carried out at P02.1/PETRAIII at DESY, a member of the Helmholtz Association (HGF) (Proposal I-20190224 EC). The research leading to this result has been supported by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON2020. The authors acknowledge the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no 663830 (M. T.). The authors

acknowledge the University of Pisa for funding through the Progetti di Ricerca di Ateneo scheme (PRA2020_39) (M. T.). The authors (M. C., M. S., V. C.) acknowledge support from the Project CH4.0 under the MUR program “Dipartimenti di Eccellenza 2023–2027” (CUP: D13C22003520001). M. S. acknowledges the C3S consortium for granting computational resources on the OCCAM cluster, funded by the Compagnia di San Paolo. The authors acknowledge Dr Alexander Schökel and Dr Sergej Wenz (Beamline P02.1 at PETRAIII, DESY) for technical assistance during the beamtime. The authors acknowledge Prof. Ferdinando Costantino (University of Perugia) and Dr Athanasios Koutsianos (TU Dortmund) for support during the beamtime. The authors acknowledge Dr Stephen J. I. Shearan and Dr Matthew J. McPherson (Swansea University) for help with gas sorption analysis during the early stages of the work.

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Selective Carbon Dioxide versus Nitrous Oxide Adsorption in Cerium(IV) Bithiazole and Bipyridyl Metal-Organic Frameworks

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The two Ce^{IV} MOFs [Ce₆O₄(OH)₄(TzTz)₆] (Ce-TzTz) and [Ce₆O₄(OH)₄(TzTz)₄(PyPy)₂] (Ce-TzTz-PyPy; H₂TzTz = [2,2'-bithiazole]-5,5'-dicarboxylic acid, H₂PyPy = 2,2'-bipyridine-5,5'-dicarboxylic acid) are prepared starting from a pre-formed [Ce₆] glycinate-capped cluster. N₂ isotherms collected at 77 K revealed BET specific surface areas of 1136 and 238 m² g⁻¹, respectively. Their CO₂ and N₂O adsorption capacity is assessed at T = 273 and 298 K and p = 1 bar. Ce-TzTz shows the highest gas uptake (7.9 and 9.7 wt% at 298 K and 11.5 and 12.5 wt% at 273 K for CO₂ and N₂O, respectively). More interestingly, this homo-linker MOF possesses a higher capacity, thermodynamic affinity [(Q_{st})_{CO2} = 18.2 kJ mol⁻¹ vs (Q_{st})_{N2O} = 25.4 kJ mol⁻¹] and selectivity (IAST S_{N2O/CO2} = 1.6 at T = 273 K) toward N₂O than the mixed-linker sample. At variance, Ce-TzTz-PyPy shows a slightly higher capacity, thermodynamic affinity [(Q_{st})_{CO2} = 29.5 kJ mol⁻¹ vs (Q_{st})_{N2O} = 26.4 kJ mol⁻¹] and selectivity (IAST S_{CO2/N2O} = 1.4 at T = 298 K) toward CO₂. DFT optimizations carried out on the [N₂O@Ce-TzTz] and [CO₂@Ce-TzTz-PyPy] systems revealed that the primary adsorption sites are the cerium ions of the [Ce₆] metallic node for N₂O and the thiazole N-atoms on the TzTz linker for CO₂, respectively.

greenhouse gases. In 2021, in the United States the anthropogenic activities contributed with CO₂ and N₂O emissions reaching 79% and 6%, respectively, of all greenhouse gases emissions.^[1] The steady increase of CO₂ in the atmosphere, with the value of 424 ppm measured in May 2023, has recently raised a deep global concern. The same holds for N₂O, with an average global concentration in the atmosphere of 337 ppb in August 2023 that is still increasing.^[1] In spite of the fact that its abundance in the atmosphere is several orders of magnitude lower than that of CO₂, the effect of N₂O is even worse: the impact of N₂O on atmosphere warming is almost 300 times that of CO₂. N₂O is the third most prevalent anthropogenic greenhouse gas (after CO₂ and methane (CH₄)) due to its significant global warming potential and extensive atmospheric lifetime (>100 years). In this respect, all the main World industrial countries gathered together at COP-28^[1] in Dubai (UAE) in November 2023 with the common wish to

limit global warming to well below 2 °C with respect to pre-industrial levels and to work hard to keep the 1.5 °C target alive. While waiting for renovated anthropogenic processes with lower impact on climate to be effective, CO₂ and N₂O

1. Introduction

Together with methane and fluorinated gases, carbon dioxide (CO₂) and nitrous oxide (N₂O) are among the so-called

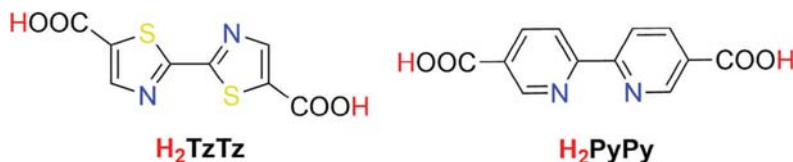
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DOI: 10.1002/adfm.202403017



Scheme 1. The ditopic linkers used in this study for the construction of Ce^{IV} MOFs: [2,2'-bithiazole]–5,5'-dicarboxylic acid (H_2TzTz) and 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2PyPy).

sequestration from the atmosphere seems the most feasible solution. CO_2 and N_2O are linear molecules sharing the same molecular weight (44 a.m.u.) but having different electronic properties. CO_2 is quadrupolar, while N_2O possesses a small dipole moment. Metal-organic frameworks (MOFs) are promising materials for the capture of both gases. MOFs are crystalline materials whose 3D polymeric open structures result from the self-assembly of metal ions or metal clusters (the inorganic nodes) and organic linkers.^[2] The vast libraries of nodes and linkers and their versatility in self-assembling enable the tailor-made design and synthesis of MOFs with high specific surface area and ad hoc functional properties, ranging from adsorption^[3] to separation,^[4] heterogeneous catalysis,^[3,4] luminescence^[5] and energy storage.^[6] As per 2020, more than 100 000 crystal structures of MOFs have been deposited in the Crystal Structure Database,^[7] and their number is constantly increasing. Cerium is a relatively abundant and low-cost metal. Cerium MOFs show two unique properties: i) the redox activity of the $[\text{Ce}_6]$ nodes due to the $\text{Ce}^{\text{III/IV}}$ couple;^[8] ii) the photocatalytic activity triggered by ligand-to-metal charge transfer (LMCT) phenomena.^[9] Since the pioneering work of Lammert et al. on the synthesis and characterization of Ce-UiO-66-BDC-X (H_2BDC = terephthalic acid; $\text{X} = \text{H}$, F , Cl , CH_3 , NO_2), Ce-UiO-66-Fum (H_2Fum = fumaric acid) and UiO-67(Ce) MOFs,^[10] Ce^{IV} has been exploited to prepare cerium-containing MOFs sharing the same structural motif of the Zr^{IV} analogues. Despite these promising features, cerium MOFs syntheses and applications are still limited. Up to 2021, *ca.* forty publications on cerium MOFs have appeared in the literature.^[11] Among them, examples of application of cerium MOFs in gas adsorption/separation can be found, in particular dealing with carbon dioxide.^[12] While MOFs have been thoroughly designed to selectively bind CO_2 , N_2O adsorption and activation has only been studied in a small number of largely unrelated MOFs. To our knowledge, no examples of cerium MOFs exploited for N_2O adsorption have been reported to date. Combining our interest in finding new MOF materials for selective $\text{CO}_2/\text{N}_2\text{O}$ adsorption^[13] and in Ce -MOF synthesis and characterization,^[12a,c,f,14] in this work we have prepared two Ce^{IV} MOF containing the heterocyclic linkers [2,2'-bithiazole]–5,5'-dicarboxylic acid (H_2TzTz) and 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2PyPy , Scheme 1). The MOFs Ce-TzTz and Ce-TzTz-PyPy have been thoroughly characterized in the solid state and eventually tested as CO_2 and N_2O adsorbents at $p = 1$ atm and $T = 298/273$ K. Intriguingly, the pure bithiazole-based MOF Ce-TzTz shows a preference for N_2O while the mixed-linker bithiazole/bipyridyl MOF Ce-TzTz-PyPy is more selective toward CO_2 .

2. Experimental Section

2.1. Materials and Methods

The commercially available 2,2'-bipyridine-5,5'-dicarboxylic acid H_2PyPy was used as received from Sigma Aldrich without further purification. The glycinate-capped cluster $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{NH}_3\text{CH}_2\text{COO})_8(\text{NO}_3)_4(\text{H}_2\text{O})_6\text{Cl}_8 \times 8\text{H}_2\text{O}]^{15}$ and the heterocyclic ligand [2,2'-bithiazole]–5,5'-dicarboxylic acid H_2TzTz ^[16] were prepared following literature procedures. Linkers quantification in the mixed-linker MOF (MIXMOF) Ce-TzTz-PyPy $^1\text{H-NMR}$ analysis was performed at ambient temperature on a BRUKER AVANCE 400 MHz spectrometer, adopting the following conditions: acquisition time 20 min, relaxation delay $\tau = 16$ s, 216 scans. Chemical shifts (δ) are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and calibrated against the residual protiated solvent resonance. The solid (≈ 10 mg) was digested in 0.7 mL of a $\text{D}_2\text{SO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$ mixture heated at 343 K for 12 h. UV-vis spectra were collected on thick self-supported pellets with a VARIAN CARY 5000 UV-vis-NIR spectrophotometer equipped with a reflectance sphere and working in diffuse reflectance mode in the 200–2500 nm region, with resolution of 1 nm. The elemental analyses were performed using a Thermo FlashEA 1112 Series CHNS-O elemental analyzer with an accepted tolerance of $\pm 2\%$ on carbon (C), hydrogen (H), nitrogen (N) and sulfur (S). ICP analyses were performed with an ICP OES Agilent 5800 instrument, by dissolving 50 mg of sample in 3 mL of an aqueous solution 37% m/m HCl and 6 mL of an aqueous solution 65% m/m HNO_3 , followed by dilution to a total volume of 50 mL. Cerium was quantified considering its absorption at 418.659 nm. Thermogravimetric (TG-DTG) and differential scanning calorimetry (DSC) analyses were performed simultaneously on powdered batches (≈ 10 mg) under a flow of N_2 over the temperature range 303–1173 K and with a heating rate of 10 K min^{-1} , employing a Netzsch STA 409 PC Luxx instrument. X-ray fluorescence (XRF) qualitative elemental analyses were performed in air on powdered batches (≈ 10 mg) of the two MOFs with a Panalytical MINIPAL 2 instrument equipped with a Cr X-ray source. Electron microscopy images were acquired using a Tescan GAIA 3 FIB/SEM, at the CeME electron microscopy facility (CNR-ICCOM, Florence). For the sample preparation, a spatula tip of the powder was dropped on a stub covered by adhesive SEM tape. Excess (unadhered) sample was then removed by applying a gentle flux of Ar on the surface of the stub. The as-prepared sample was analyzed

without further conductive coating, using an e-beam energy of 10 keV. GAIA 3 is equipped with the EDS-X-ray microanalysis system (EDAX, AMETEK, USA) and with the TEAM EDS Basic Software Suite TEAM™.

2.2. Synthesis of $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6] \cdot 7(\text{DMF})$ (Ce_TzTz_DMF)

Following the synthetic protocol described by the group of Stock for the preparation of other Ce^{IV} MOFs starting from pre-formed $[\text{Ce}_6]$ clusters,^[11b,15,17] H_2TzTz [MW = 256.3 a.m.u.; 0.100 g, 0.390 mmol] was dissolved in *N,N*-dimethylformamide (DMF, 12 mL) and the resulting yellow solution was brought to 373 K under magnetic stirring. The glycinato-capped cluster $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{NH}_3\text{CH}_2\text{COO})_8(\text{NO}_3)_4(\text{H}_2\text{O})_6\text{Cl}_8 \times 8\text{H}_2\text{O}]$ [MW = 2349.1 a.m.u.; 0.123 g, 0.065 mmol] was suspended in distilled water (1.8 mL), and the suspension was slowly added to the linker hot DMF solution. Immediate formation of a yellow solid precipitate of Ce_TzTz_DMF was observed. Stirring at 373 K was maintained for 15 min to complete the reaction. After that time, the reaction mixture was cooled to room temperature and the solid was recovered after centrifugation (3000 rpm, 3 min), washed with ethanol (3×10 mL) and petroleum ether (3×10 mL) and finally dried under a nitrogen stream at room temperature. Yield: 0.141 g (72%, based on the minimal formula $\{[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6] \cdot 7(\text{DMF})\}$). The phase purity was checked every time through PXRD. Elem. Anal. for $\text{C}_{53}\text{H}_{73}\text{N}_{15}\text{O}_{39}\text{S}_8\text{Ce}_6$ (FW = 2641.44 a.m.u.): calc. C, 24.10; H, 2.79; N, 7.95; S, 9.71; Ce, 31.83%. Found: C, 24.41; H, 2.82; N, 8.12; S, 9.94; Ce, 31.40% (ICP). IR bands (KBr, cm^{-1} , Figure S1, Supporting Information): 3400 (s) $[\nu(\text{O-H})]$, 3093 (w) $[\nu(\text{C-H})]$, 2962 (w) $[\nu(\text{C-H})_{\text{DMF}}]$, 1651 (s) $[\nu(\text{C}=\text{O})_{\text{DMF}}]$, 1568 (s) $[\nu(\text{COO})]$, 1507 (m) $[\nu(\text{C}=\text{C})]$, 1385 (vs) $[\nu(\text{C-N})_{\text{DMF}}]$, 1282 (w), 1144 (w), 1111 (m), 932 (m), 770 (m) $[\gamma(\text{C-H})_{\text{DMF}}]$, 574 (m) $[\nu(\text{C-S})]$, 416 (w).

2.3. Synthesis of $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_4(\text{PyPy})_2] \cdot 4(\text{DMF})$ (Ce_TzTz_PyPy_DMF)

The preparation of the MIXMOF can be accomplished following two different procedures that lead to the same final product. Both methodologies are reported here for the sake of completeness. (A) *Solvent-assisted linker exchange from Ce_TzTz_DMF*: a sample of Ce_TzTz [MW = 2498.2 a.m.u.; 0.070 g, 0.03 mmol] was suspended in a DMF solution (10 mL) of H_2PyPy [MW = 244.2 a.m.u.; 0.020 g, 0.09 mmol, 3 equiv.] and the mixture was kept at 363 K for 15 h under gentle magnetic stirring. After that time, it was cooled to room temperature and the yellow Ce_TzTz_PyPy_DMF solid recovered through centrifugation (3000 rpm, 3 min) was washed with ethanol (3×10 mL) and petroleum ether (3×10 mL) and finally dried under a nitrogen stream at room temperature. Yield: 0.045 g (54%, based on the minimal formula $\{[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_4(\text{PyPy})_2] \cdot 4(\text{DMF})\}$). (B) *Direct synthesis*: H_2TzTz [MW = 256.3 a.m.u.; 0.075 g, 0.293 mmol] and H_2PyPy [MW = 244.2 a.m.u.; 0.036 g, 0.147 mmol] in a (4:2) stoichiometric ratio with respect to the Ce^{IV} reagent were dissolved together in DMF (20 mL) and the resulting yellow solution was brought to 373 K under magnetic stirring. The glycinato-capped

cluster $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{NH}_3\text{CH}_2\text{COO})_8(\text{NO}_3)_4(\text{H}_2\text{O})_6\text{Cl}_8 \times 8\text{H}_2\text{O}]$ [MW = 2349.1 a.m.u.; 0.172 g, 0.073 mmol] was suspended in distilled water (2 mL), and the suspension was slowly added to the linkers hot DMF solution. Immediate formation of a yellow solid precipitate of Ce_TzTz_PyPy_DMF was observed. Stirring at 373 K was maintained for 15 min to complete the reaction. After that time, the reaction mixture was cooled to room temperature and the solid recovered after centrifugation (3000 rpm, 3 min) was washed with ethanol (3×10 mL) and petroleum ether (3×10 mL) and finally dried under a nitrogen stream at room temperature. Yield: 0.180 g (89%, based on the minimal formula $\{[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_4(\text{PyPy})_2] \cdot 4(\text{DMF})\}$). In both cases, the linkers relative ratio within the MIXMOF was determined through signal integration of the ^1H NMR spectrum of the solution obtained after digesting the sample in a $\text{D}_2\text{SO}_4/\text{D}_2\text{O}/\text{DMSO-}d_6$ mixture and heating at 343 K for 12 h (see Figure S2, Supporting Information). The phase purity was checked every time through PXRD. Elem. Anal. for $\text{C}_{60}\text{H}_{56}\text{N}_{14}\text{O}_{36}\text{S}_6\text{Ce}_6$ (FW = 2582.24 a.m.u.): calc. C, 27.91; H, 2.19; N, 7.59; S, 7.45; Ce, 32.56%. Found: C, 27.31; H, 2.23; N, 7.65; S, 7.38; Ce, 32.15% (ICP). IR bands (KBr, cm^{-1} , Figure S1, Supporting Information): 3413 (s) $[\nu(\text{O-H})]$, 3099 (w) $[\nu(\text{C-H})_{\text{TzTz}}]$, 2959 (m) $[\nu(\text{C-H})_{\text{DMF}}]$, 2927 (w) $[\nu(\text{C-H})_{\text{PyPy}}]$, 2871 (w) $[\nu(\text{C-H})_{\text{PyPy}}]$, 1695 (m, sh) $[\nu(\text{C}=\text{O})_{\text{DMF}}]$, 1640 (m, sh) $[\nu(\text{COO})_{\text{PyPy}}]$, 1592 (s, br) $[\nu(\text{COO})_{\text{TzTz}}]$, 1577 (s) $[\nu(\text{C}=\text{C})_{\text{TzTz/PyPy}}]$, 1394 (vs) $[\nu(\text{C-N})_{\text{DMF}}]$, 1282 (m), 1247 (m), 1120 (m), 1025 (m), 933 (m), 780 (s) $[\gamma(\text{C-H})_{\text{DMF}}]$, 650 (w) $[\nu(\text{C-S})]$, 574 (m).

2.4. Crystal Structure Characterization

PXRD data measurements were performed employing a Bruker AXS D8 Advance vertical-scan θ/θ diffractometer, equipped with a sealed X-ray tube ($\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$), a filter of nickel in the diffracted beam, a Bruker Lynxeye linear position-sensitive detector, and the following optical components: primary and secondary beam Soller slits (2.5°), fixed divergence slit (0.5°), anticatter slit (8 mm). The generator was set at 40 kV and 40 mA. Powdered samples ($\approx 50 \text{ mg}$) of Ce_TzTz and Ce_TzTz_PyPy were deposited into the 0.2 mm deep cavity of a silicon free-background sample holder (Assing Srl, Monterotondo, Italy). The samples purity and crystallinity were checked with a preliminary PXRD measurement in the 2θ range $3.0\text{--}35.0^\circ$, with steps of 0.02° and a time per step of 1 s. PXRD acquisitions for the assessment of the crystal structure were carried out in the 2θ range $4.0\text{--}105.0^\circ$, with steps of 0.02° and an approximate scan time of about 12 h. A visual comparison between the PXRD pattern of $\text{Ce\_TzTz/Ce\_TzTz\_PyPy}$ and that of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6]$ ^[16] suggested that the three MOFs are isostructural. A whole powder pattern profile refinement with the so-called Le Bail approach^[18] performed with TOPAS-R V3^[19] and employing the space group and unit cell parameters of UiO-67(Ce)^[10] confirmed the suggestion. The crystallographically independent portion of PyPy^{2-} , TzTz^{2-} and DMF were modelled as rigid bodies using the z-matrix formalism, assigning to the bond distances and angles^[20] idealized values based on a search in the Cambridge Structural Database (v. 2023) for crystal structures collected at ambient conditions and containing the three molecules. The molar ratio between the PyPy^{2-} and

the TzTz^{2-} ligands in $\text{Ce}_6\text{TzTzPyPy}$ was set at the value retrieved from the ^1H NMR signal integration of the digested sample (see the main text and the Supporting Information). In the initial steps of the structure assessment, both the metal cluster atoms (Ce and O) and the centre of mass of the rigid bodies describing the spacers were located according to the crystal structure of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6]$. For the sake of simplicity, no hydrogen atoms were bound to the oxygen atoms of the cluster (half of a hydrogen atom bound to each of the two independent oxygen atoms of the cluster would be the most meaningful alternative choice). In the case of $\text{Ce}_6\text{TzTzPyPy}$, an idealized distribution of the two linkers in both independent positions were assumed. The linkers orientation was then allowed to refine. Positional disorder was assumed for the N atoms versus the C-H groups in PyPy^{2-} (hence, an equal probability of having a *cis* or a *trans* PyPy^{2-} was assumed): N and C-H were set to occupy each of the four possible positions with a site occupancy factor of 0.5. The residual smeared electron density in the pores of Ce_6TzTz and $\text{Ce}_6\text{TzTzPyPy}$ was described by means of two and one independent DMF molecules, respectively, which were located with the Simulated Annealing approach^[21] implemented in *TOPAS-R V3* and whose site occupation factor was refined. In the case of Ce_6TzTz , one water molecule, modelled as the bare oxygen atom, was also employed. A Chebyshev-type polynomial function was used to model the background. A refined isotropic thermal factor [$B_{\text{iso}}(\text{M})$] was attributed to the Ce^{IV} ion; the isotropic thermal factor of the other atoms of the cluster and of the ligands was calculated as $B_{\text{iso}}(\text{L}) = B_{\text{iso}}(\text{M}) + 2.0 \text{ \AA}^2$; the isotropic thermal factor of the atoms describing the chlorinated solvent was calculated as $B_{\text{iso}}(\text{S}) = B_{\text{iso}}(\text{M}) + 3.0 \text{ \AA}^2$. The instrumental contribution to the peak profile was modelled through the Fundamental Parameters Approach.^[22] The sample contribution to the peak anisotropic broadening was described by means of Lorentzian spherical harmonics. During the final stages of the crystal structure refinement, instrumental and structural parameters were collectively refined by means of the so-called Rietveld refinement.^[23] The final Rietveld refinement plots are shown in Figure S3 (Supporting Information).

Crystal data for $\text{Ce}_6\text{TzTzDMF}$, $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_6] \cdot 4.2\text{DMF} \cdot 6\text{H}_2\text{O}$, $\text{C}_{60.6}\text{H}_{57.4}\text{Ce}_6\text{N}_{16.2}\text{O}_{42.2}\text{S}_{12}$, FW = 2913.38 u.m.a., cubic, $Pn\bar{3}$, $a = 26.003(2) \text{ \AA}$, $V = 17\,583(4) \text{ \AA}^3$, $Z = 24$, $Z' = 4$, $\rho = 1.10 \text{ g cm}^{-3}$, $F(000) = 5648$, $R_{\text{Bragg}} = 0.5\%$, $R_p = 1.7\%$ and $R_{\text{wp}} = 2.2\%$, for 5031 data and 83 parameters in the $4.4\text{--}105.0^\circ$ (2θ) range.

Crystal data for $\text{Ce}_6\text{TzTzPyPyDMF}$, $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{TzTz})_4(\text{PyPy})_2] \cdot 5.4\text{DMF}$, $\text{C}_{72.2}\text{H}_{61.8}\text{Ce}_6\text{N}_{17.4}\text{O}_{37.4}\text{S}_8$, FW = 2868.91 u.m.a., cubic, $Pn\bar{3}$, $a = 26.049(2) \text{ \AA}$, $V = 17\,675(4) \text{ \AA}^3$, $Z = 24$, $Z' = 4$, $\rho = 1.08 \text{ g cm}^{-3}$, $F(000) = 5568$, $R_{\text{Bragg}} = 0.3\%$, $R_p = 1.7\%$ and $R_{\text{wp}} = 2.2\%$, for 5031 data and 74 parameters in the $4.0\text{--}105.0^\circ$ (2θ) range.

2.5. Variable-Temperature Powder X-Ray Diffraction

The thermal behaviour of Ce_6TzTz and $\text{Ce}_6\text{TzTzPyPy}$ was investigated in situ through variable-temperature powder X-ray diffraction (VT-PXRD) using a custom-made sample heater (Officina Elettrotecnica di Tenno, Ponte Arche, Italy). A powdered sample ($\approx 20 \text{ mg}$) of the two materials was heated in air with

Table 1. VT-PXRD data acquisition parameters used for Ce_6TzTz and $\text{Ce}_6\text{TzTzPyPy}$.

MOF	T range [K]	2θ range [$^\circ$]
Ce_6TzTz	298–678	4.5–25.0
$\text{Ce}_6\text{TzTzPyPy}$	298–698	4.5–25.0

steps of 20 K acquiring a PXRD pattern at each step in isothermal conditions, adopting the experimental conditions collected in Table 1. Treatment of the data of Ce_6TzTz acquired before an appreciable crystallinity loss was performed by means of a parametric whole powder pattern refinement with the Le Bail method, available in *TOPAS-R V3*, to depict the behaviour of the unit cell parameters as a function of the temperature. The VT-PXRD data of $\text{Ce}_6\text{TzTzPyPy}$ were not treated due to the limited sample crystallinity.

2.6. N_2 , CO_2 and N_2O Adsorption

All the samples were activated at 403 K under high vacuum (10^{-6} Torr) for 12 h before any measurement. The Brunauer–Emmett–Teller (BET) specific surface area and pore volume were estimated by volumetric adsorption with an ASAP 2020 Micromeritics instrument, using N_2 as adsorbate at 77 K. A typical measurement used 40 mg of sample. For the BET specific surface area calculation, the 0.01–0.1 p/p_0 pressure range was used to fit the data. Within this range, all the Rouquerol consistency criteria^[24] are satisfied. The materials (micro)porosity was determined from the N_2 adsorption isotherms using a DFT method and assuming a cylindrical pore shape (typical of metal oxides). CO_2 and N_2O adsorption isotherms were measured at 273 and 298 K up to the maximum pressure of 1.2 bar. The isosteric heat of adsorption (Q_{st}) was calculated working on these isotherms by applying a variant of the Clausius–Clapeyron equation (Equation 1):^[25]

$$\ln \left(\frac{p_1}{p_2} \right) = Q_{\text{st}} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \quad (1)$$

where p_n ($n = 1$ or 2) denotes the pressure value for the n^{th} isotherm; T_n ($n = 1$ or 2) denotes the temperature value for the n^{th} isotherm; R is the gas constant expressed in the appropriate units ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). The IAST A/B adsorption selectivity (A , $B = \text{CO}_2$, N_2O) of binary mixtures at a total pressure of 1 bar^[26] and at $T = 298$ and 273 K was determined as the ratio of the adsorbed molar fractions of the two gases divided by the ratio of the gas phase initial molar fractions:^[27]

$$S_{A/B} = \frac{\left(\frac{\chi_A}{\chi_B} \right)_{\text{ads}}}{\left(\frac{\chi_A}{\chi_B} \right)_{\text{gas}}} \quad (2)$$

The $(\chi_A)_{\text{ads}}$ and $(\chi_B)_{\text{ads}}$ values were derived from the application of the free software *pyIAST* (<https://github.com/CorySimon/pyIAST>) to the experimental single-component isotherms collected at the chosen temperature. The initial composition (%) selected for the calculation was [50:50] for the

[N₂O:CO₂] pair. The Henry and Langmuir models were employed for the CO₂ and N₂O isotherms fitting, respectively. For a detailed explanation of these models and the related parameters, see the pyIAST webpage and documentation.

2.7. Infrared Spectroscopy

FT-IR spectra were collected on a BRUKER INVENIO spectrophotometer equipped with a MCT (mercury cadmium tellurium) cryo-detector. All the spectra were collected in the 4000–650 cm⁻¹ spectral range with a resolution of 2 cm⁻¹ and an average of 32 scans. Before the analysis, all the samples (in form of self-supported pellets protected by a gold envelope) were inserted in a special home-made quartz cell. The samples were then heated at 403 K overnight under dynamic vacuum to achieve the proper activation (see Figures S15, S16, Supporting Information for the details). In order to probe the nature of the acidic sites present in the two MOFs, acetonitrile in the deuterated form (CD₃CN) was used as molecular probe. Due to the probe-framework interaction strength, the adsorption was performed at RT by dosing on previously activated MOF samples $\approx$ 80 mbar (i.e., approximately the vapour tension) of CD₃CN. The latter is usually preferred to CH₃CN, whose Fermi resonance between the combination mode of $\nu(\text{C}-\text{C}) + \delta(\text{CH}_3)$ and the $\nu(\text{C}\equiv\text{N})$ mode of liquid CH₃CN would be observed as a doublet at 2254 and 2294 cm⁻¹, hampering the spectral analysis.^[28] CD₃CN was then finally outgassed collecting consecutive IR spectra (Figure 6; Figure S17, Supporting Information in the whole spectral range). In order to study the possible interactions of CO₂ and N₂O with the MOFs, incremental quantities of CO₂ and N₂O were dosed to the previously activated samples until reaching 150 and 120 mbar, respectively (see Figure S18, Supporting Information). The materials were then progressively outgassed, acquiring consecutive IR spectra until the restoration of the initial spectra of the activated samples.

2.8. X-ray Absorption Spectroscopy

Ce₂TzTz and Ce₂TzTz_PyPy were characterized through the X-ray Absorption Spectroscopy (XAS) technique at the Ce K-edge, carrying out the data collections at the BM23 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble.^[29] To ensure a uniform particle size within the powdered samples, the latter were first finely grinded and subsequently pressed in a self-supporting pellet. Thereafter, the pellets were securely placed within a dedicated sample holder and analysed under air at room temperature.^[30] Ex situ Ce K-edge XAS measurements were performed in transmission mode, employing a water-cooled double-crystal Si(111) monochromator moving in continuous mode. The experimental XAS spectra were acquired within the energy range of 40 100–42 180 eV,^[31] with an acquisition time of $\approx$ 2 min scan⁻¹. Harmonic rejections were facilitated using a pair of flat Si mirrors positioned at 2.8 mrad angle. Ionization chambers, filled with a He/Kr mixture, were employed for detecting both incident and transmitted photons.^[30] Both the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectral regions were

included in the analysis.^[32] Following this, normalization to the unity edge jump at the Ce K-edge was systematically executed using the ATHENA software from the Demeter suite.^[33] Fourier-transformed (FT-)EXAFS spectra were derived transforming the k^2 -weighted $\chi(k)$ curves within the 2.6–15.0 Å⁻¹ k -range. The experimental EXAFS spectra provided important but qualitative insights into the local configuration and coordination environment proximate to the absorber atom. Then, a critical step for advanced structural elucidations was the EXAFS fitting analysis.^[34] This method relies on fitting the experimental EXAFS data to theoretical models. ARTEMIS from the Demeter suite is a user-friendly graphical interface designed for EXAFS fitting analysis which uses the FEFF program.^[34,35] It enables the computation of photoelectron scattering parameters for individual scattering paths. Consequently, the single and multiple scattering paths (SS and MS respectively) are parametrized using structural parameters, finding values that minimize discrepancies between the model predictions and the experimental spectra.^[36] The EXAFS fitting analysis was performed on the experimental spectra collected at room temperature under air for both Ce₂TzTz and Ce₂TzTz_PyPy by employing a DFT-optimized Ce-cluster model as initial input, aiming for a further validation of their structural properties. The analysis was conducted in R-space within the 1.0–3.9 Å range. In the SS parametrization of both samples, the passive amplitude reduction factor (S_0^2) was set at the ideal value of 1.0, while the energy shift (ΔE) value was refined throughout the analysis. The fitting procedure involved first-shell O atoms, parametrized based on their perspective interatomic distances from the absorber, as well as second-shell Ce atoms. Specifically, the three proximal O atoms (O₁^c) to the Ce absorber were parametrized using the same radial shift parameter (ΔR) and Debye-Waller (DW) factor (σ^2), assuming comparable interatomic distances at Reff = 2.13 Å. Concurrently, the more distant O atoms (O₂^c at Reff = 2.34 Å and O₃^c at Reff = 2.46 Å) were treated with independent radial shift parameters and DW factors but considered with their own Reff. Analogously, this methodology was applied to the two second-shell Ce atoms positioned at Reff = 2.34 Å (Ce₁^c) and Reff = 2.46 Å (Ce₂^c), respectively.

2.9. Computational Details

Density Functional Theory (DFT) calculations were carried out with the cost-effective PBEsol0-3c method^[37] recently developed by some of us and implemented in a development version of the CRYSTAL23^[38] code. In the PBEsol0-3c method, the total energy computed with the PBEsol0 hybrid functional combined with a double- ζ quality Gaussian basis set is augmented with two semi-empirical corrections to remove the Basis Set Superposition Error (BSSE) through the geometrical CounterPoisson (gCP)^[39] approach and to properly describe weak interactions via the D3 scheme^[40] in its Becke-Johnson rational damping variant. In the present work, the solid-state basis set adopted by the PBEsol0-3c composite method was extended to treat cerium. The def2-SVP basis set of cerium was modified according to the strategy described in reference [41]. The PBEsol0-3c hybrid composite method accurately and efficiently describes inorganic systems and micro-mesoporous materials including MOFs, for which structural, vibrational, electronic and adsorption

properties have been predicted with excellent results.^[42] More recently, it has been successfully applied to investigate the encapsulation of molecules in HKUST-1 and ZIF-8 for drug delivery (i.e., 5-fluorouracil),^[43] to solid state (fluorescein) lighting^[44] and to elucidate the mechanical properties of defective ZIF-8.^[45] A (75974) pruned grid was employed for the numerical evaluation of the Exchange-Correlation term, corresponding to the XLGRID keyword as used by the CRYSTAL code. Default convergence criteria for geometry optimization were followed. The tolerances for one- and two-electron integrals calculation were set to 10^{-7} , 10^{-7} for the Coulomb and to 10^{-7} , 10^{-7} , 10^{-25} for the Exchange series, respectively. The shrinking factors for the diagonalization of the Kohn-Sham matrix in the reciprocal space were set to 2 for the Monkhorst-Pack net and to 2 for the Gilat net. A full relaxation of both unit cell parameters and atomic positions was performed and the crystal symmetry was maintained during the optimization process.

3. Results and Discussion

3.1. Synthesis and Preliminary Characterization of the Ce^{IV} (MIX)MOFs

The metal precursor used for the preparation of thiazole-containing Ce^{IV} MOFs sharing the same 3D architecture of the UiO-6# family^[46] is a pre-formed [Ce₆O₈] glycinato-capped cluster. Stock and coworkers first synthesized Ce^{IV} MOFs using this cluster in 2018^[15], adopting a fast precipitation strategy to obtain the materials in less than 15 min and operating at relatively low temperatures (≈ 373 K), prior to metal reduction and formation of deleterious Ce(HCOO)₃, with formate coming from the thermal decomposition of *N,N*-dimethylformamide (the typical solvent of MOFs ordinary solvothermal syntheses). This protocol was proven to be successful also with heterocyclic linkers like [2,2'-bithiazole]-5,5'-dicarboxylic acid (**H₂TzTz**) or 2,2'-bipyridine-5,5'-dicarboxylic acid (**H₂PyPy**, Scheme 1). As a matter of fact, the Ce^{IV} bithiazole MOF [Ce₆O₄(OH)₄(TzTz)₆] (**Ce-TzTz**) precipitates out of the DMF/H₂O mixture of linker and metal precursor almost instantaneously as a yellow powder. Its PXRD pattern (Figure S4, Supporting Information) is comparable to that of the Zr^{IV} analogue [Zr₆O₄(OH)₄(TzTz)₆]^[16] suggesting the analogous (UiO-67-type) crystal structure and *fcu* network topology. The IR spectrum of **Ce-TzTz** (Figure S1, Supporting Information) shows the main vibrational modes of **H₂TzTz**, including the most representative $\nu(\text{COO})$ stretching at 1568 cm^{-1} , red-shifted with respect to that of the free linker (1704 cm^{-1}).^[16] The red shift of the carboxylate $\nu(\text{COO})$ stretching frequency is typical when carboxylic acids are bound to metal ions.^[47] The X-ray fluorescence spectrum of **Ce-TzTz** (Figure S5, Supporting Information) confirms the presence of sulphur and cerium and the absence of chlorine, thus suggesting the absence of missing linker defects counterbalanced by chloride anions, at odds with what observed in heterocycle-based zirconium UiO-67-type (MIX)MOFs.^[48] The mixed-linker Ce^{IV} MOF [Ce₆O₄(OH)₄(TzTz)₄(PyPy)₂] (**Ce-TzTz-PyPy**) was obtained through two different procedures. Solvent-Assisted Linker Exchange (SALE) is a consolidated approach for the preparation of mixed-ligand zirconium MOFs^[49] and it works with their cerium analogues as well.^[50] Indeed, partial replacement of the **H₂TzTz**

linker with the bipyridine analogue **H₂PyPy** occurs in **Ce-TzTz** upon suspension of the latter in a DMF solution containing **H₂PyPy** in three-fold excess and heating the suspension at 363 K overnight under gentle magnetic stirring. A new MIXMOF is obtained with a 4:2 ratio of the two spacers, with a maximum uptake of two **PyPy**²⁻ linkers per formula unit. Increasing the linker excess in the initial solution does not lead to any further linker incorporation. As a more advantageous alternative in terms of yields (see the Experimental section), a direct synthesis from the [Ce₆O₈] glycinato cluster and a solution of the two linkers in a (4:2:1) **H₂TzTz:H₂PyPy:[Ce₆]** stoichiometric ratio in DMF/H₂O is also feasible, under the same experimental conditions used for the preparation of **Ce-TzTz**. In both cases, the presence of a solid solution and not of a mixture of two homo-linker phases is confirmed by the PXRD pattern (Figure S6, Supporting Information): the main Bragg reflections of **Ce-TzTz-PyPy** are unique and fall close to those of its homo-linker counterparts **Ce-TzTz** and **Ce-PyPy** [Ce₆O₄(OH)₄(PyPy)₆]^[51]. Another proof of evidence of the obtaining of a single phase comes from the DSC profile (vide infra), where each thermal event is unique. The IR spectrum of **Ce-TzTz-PyPy** (Figure S1, Supporting Information) shows the typical vibrational modes of both linkers. Again, the presence of sulphur and cerium is confirmed by XRF (Figure S7, Supporting Information). The final MIXMOF composition was assessed through both SEM-EDX semi-quantitative elemental analysis (Figure S8, Supporting Information) and digestion of the solid in an acidic solution [D₂SO₄/D₂O/DMSO-*d*₆] followed by ¹H NMR spectrum signal integration (Figure S2, Supporting Information).

3.2. PXRD Structure Characterization of Ce-TzTz and Ce-TzTz-PyPy

The crystal structures of **Ce-TzTz** and **Ce-TzTz-PyPy** were assessed by powder X-ray diffraction. As anticipated above, **Ce-TzTz** and **Ce-TzTz-PyPy** share the same 3D architecture of UiO-67, UiO-67(Ce), **Ce-PyPy** and the Zr^{IV} UiO-67-type (MIX)MOFs with the heteroaromatic ligands **TpTp**²⁻, **TzTz**²⁻ and **SpSp**²⁻ (**TpTp**²⁻ = 2,2'-bithiophene-5,5'-dicarboxylate,^[52] **SpSp**²⁻ = 2,2'-biselenophene-5,5'-dicarboxylate,^[48] Table S1). [Ce₆O₄(OH)₄]¹²⁺ inorganic nodes (where the Ce^{IV} ions are at the vertices of an octahedron and with square antiprismatic coordination geometry) are connected to twelve neighbouring ones by six bidentate spacers (Figure 1a; Figure S9a, Supporting Information). This occurrence yields a 3D open framework of *fcu* topology featuring octahedral and tetrahedral cavities occupied by solvent molecules in the as-synthesized materials (Figure 1b; Figure S9b, Supporting Information). For a comparative structural analysis also involving single-linker or mixed-linker UiO-67 type MOFs, the reader is referred to the Supporting Information.

3.3. Thermal Behaviour

The thermal behaviour of **Ce-TzTz** and **Ce-TzTz-PyPy** was studied by coupling simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with variable temperature powder X-ray diffraction (VT-PXRD). As assessed by

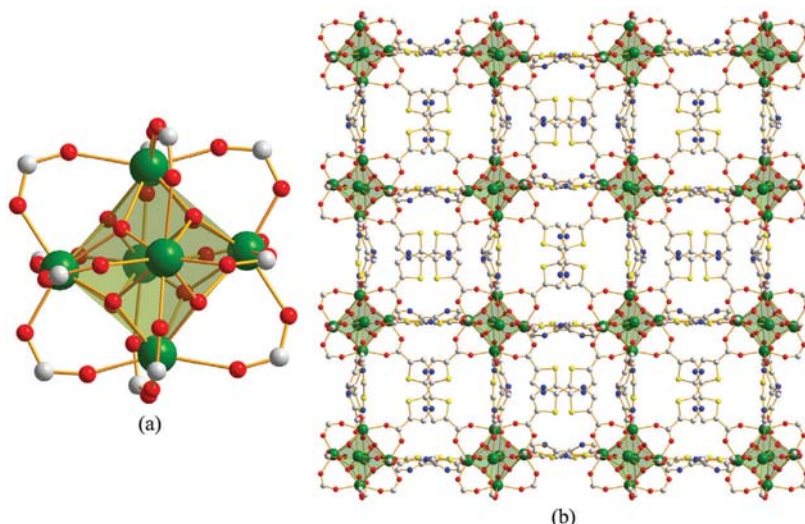


Figure 1. Representation of the crystal structure of **Ce₂TzTz**: a) the node; b) portion of the packing viewed along one of the crystallographic axes. Element colour code: carbon, grey; cerium, green; nitrogen, blue; oxygen, red; sulphur, yellow. The clathrated solvent and the hydrogen atoms have been omitted for clarity. For the analogous representation of **Ce₂TzTz_PyPy** the reader is addressed to Figure S9 (Supporting Information).

TGA (Figure S10a, Supporting Information), in the temperature range 313–493 K **Ce₂TzTz-DMF** undergoes two consecutive mass losses. The first one centred at $T = 365$ K can be assigned to physisorbed water, while the second one centred at $T = 460$ K (17.2 wt%) can be attributed to the loss of clathrated solvent (theoretical mass loss for 7 DMF molecules per formula unit = 17.0 wt%). As a confirmation, in the mass spectrum of the volatiles the peak at $m/z = 73$ a.m.u. ascribed to DMF can be observed in the same temperature range (Figure S10b, Supporting Information). Solvent evaporation is immediately followed by a multi-step decomposition, whose first mass loss is centred at 635 K. VT-PXRD (Figure S10c, Supporting Information) highlighted that the MOF starts losing crystallinity at ≈ 538 K and it is completely amorphous at ≈ 678 K. Data treatment with a parametric whole powder pattern refinement in the temperature range 298–598 K (Figure S10d, Supporting Information) showed that up to ≈ 498 K the a -axis (and the unit cell volume) first shrinks, reasonably because of the solvent loss highlighted by the TGA, then increases due to thermal expansion. The unit cell volume varies, as a maximum, by $|1.2\%|$ (maximum volumetric thermal expansion, $\alpha_v = |76|$ 1/MK); the 3D framework of **Ce₂TzTz** is rather rigid. **Ce₂TzTz_PyPy-DMF** also undergoes consecutive mass losses starting from 313 K (and up to 563 K), with a thermogravimetric profile that is very similar to that of **Ce₂TzTz-DMF** (Figure S11a, Supporting Information). The first loss centred at $T = 359$ K can be assigned to physisorbed water, while the second one centred at $T = 459$ K (9.4 wt. %) can be attributed to the loss of clathrated solvent (theoretical mass loss for 4 DMF molecules per formula unit = 10.6 wt%). As a confirmation, in the mass spectrum of the volatiles the peak at $m/z = 73$ a.m.u. ascribed to DMF can be observed in the same temperature range (Figure S11b, Supporting Information). DMF loss is immediately followed by a multi-step decomposition, whose first

mass loss is centered at 642 K. According to the VT-PXRD experiment (Figure S11c, Supporting Information), **Ce₂TzTz_PyPy** starts losing crystallinity at ≈ 500 K and it is completely amorphous at ≈ 698 K, with a reduced framework stability with respect to the homo-linker analogue **Ce₂TzTz**. Overall, bithiazole- and/or bipyridine-containing Ce^{IV} MOFs are slightly more thermally robust than $\text{UiO-67}(\text{Ce})$. However, all Ce^{IV} species are less thermally stable than their Zr^{IV} analogues (Table S2, Supporting Information), because of the higher oxophilic character of the (hard) Zr^{IV} Lewis acid compared with the (softer) Ce^{IV} ion.

3.4. XAS Analysis

Integrating qualitative XAS analysis and EXAFS fitting provided successful results in discerning the Ce-cluster sites present in both **Ce₂TzTz** and **Ce₂TzTz_PyPy**, thus corroborating the proposed crystal structures. An overview of the obtained results is reported in Figure 2.

As expected, the XANES spectral profiles (Figure 2b) of both MOFs can be attributed to Ce^{IV} , which is consistent with findings in prior studies.^[31,53] Remarkably, the two spectra exhibit perfect overlap, indicating no significant differences in the local Ce^{IV} environment between the two materials. The FT-EXAFS spectra depicted in the inset of Figure 2b reveal two distinct coordination shells. The first coordination shell peak is likely associated with the lighter O atoms constituting the inorganic node. The second peak at ≈ 3.5 Å in the phase-uncorrected spectra characterized by high intensity and distinguishable feature (owing to the presence of heavier scatterers) can be linked to Ce atoms within the node.^[11b,53] Notably, minor variations in intensity between

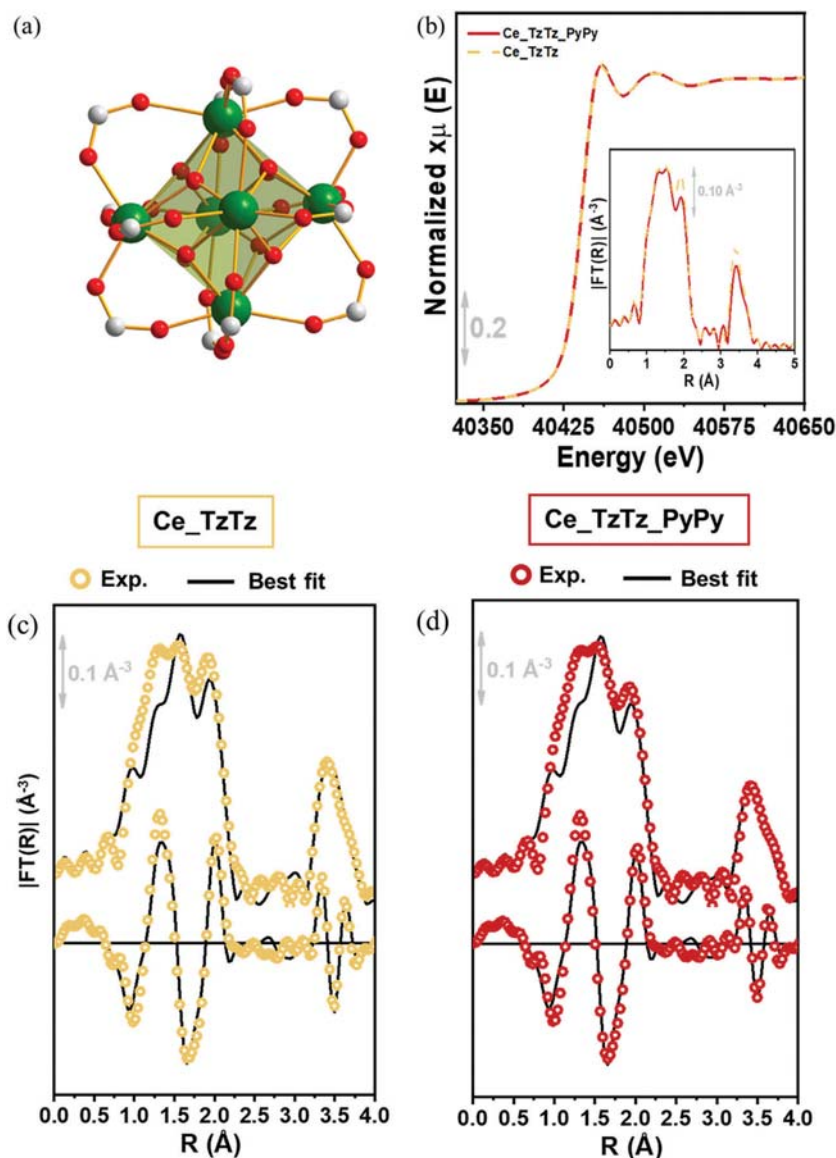


Figure 2. a) Pictorial representation of the DFT-optimized Ce-cluster structure. b) Ce K-edge XANES and k^2 -weighted phase-uncorrected FT-EXAFS (inset) spectra of **Ce_TzTz** and **Ce_TzTz_PyPy** collected at room temperature under air. c) Phase uncorrected modulus (top curves) and imaginary part (bottom curves) of experimental and best fit FT-EXAFS spectra for **Ce_TzTz**. The experimental data are shown as yellow open circles, while the best fits with black solid lines. d) Phase uncorrected modulus of experimental and best fit FT-EXAFS spectra for **Ce_TzTz_PyPy**. The experimental data are shown as red open circles, while the best fits with black solid lines.

the two curves are observable but, as previously mentioned, they do not imply substantial differences in the cerium local structure. From a cerium-centric perspective, we can qualitatively infer that the two materials can be deemed structurally equivalent. With EXAFS fitting analysis we tentatively

searched for differences between the two as-prepared MOFs. Figure 2c,d report the fitting results. In the comprehensive analysis, a good agreement between the experimental spectra and the best-fit curves is evident for both materials, with some minor discrepancies in the first coordination shell. This

Table 2. Left: Pictorial representation of the DFT-optimized Ce-cluster structure, in which the SS contributions are highlighted with coloured circles. Right: results of the fits performed on the k^2 -weighted FT-EXAFS experimental spectrum of **Ce_TzTz** and **Ce_TzTz_PyPy** collected at ambient temperature under air. The parameters set in the analysis are underlined.

EXAFS parameters	Ce_TzTz best-fit	Ce_TzTz_PyPy best-fit
$N_{\text{par}}^{\text{e}}/N_{\text{ind}}^{\text{e}}$	16/30	16/30
R_{factor}	0.07	0.07
S_0^2	<u>1.0</u>	<u>1.0</u>
ΔE (eV)	<u>-4 ± 2</u>	<u>-4 ± 3</u>
$R_{\text{O}_1^{\text{e}}} (\text{\AA})$	2.24 ± 0.02	2.23 ± 0.02
$R_{\text{O}_2^{\text{e}}} (\text{\AA})$	2.39 ± 0.02	2.38 ± 0.02
$R_{\text{O}_3^{\text{e}}} (\text{\AA})$	2.50 ± 0.02	2.50 ± 0.02
$R_{\text{Ce}_1^{\text{e}}} (\text{\AA})$	3.79 ± 0.02	3.79 ± 0.02
$R_{\text{Ce}_2^{\text{e}}} (\text{\AA})$	3.84 ± 0.02	3.84 ± 0.02
$\sigma^2_{\text{O}_1^{\text{e}}} (\text{\AA}^2)$	0.004 ± 0.002	0.004 ± 0.001
$\sigma^2_{\text{O}_2^{\text{e}}+\text{O}_3^{\text{e}}} (\text{\AA}^2)$	0.001 ± 0.001	0.002 ± 0.001
$\sigma^2_{\text{Ce}_1^{\text{e}}+\text{Ce}_2^{\text{e}}} (\text{\AA}^2)$	0.007 ± 0.001	0.008 ± 0.001

occurrence may be attributed to a certain level of structural disorder in the system, underneath the average periodic (non-local) picture provided by X-ray diffraction. For further clarifications, best-fit values for the parameters optimized in the **Ce_TzTz** and **Ce_TzTz_PyPy** EXAFS fits are reported in **Table 2**. As expected, the optimization process yielded a R_{factor} value of $\approx 7\%$ in both cases, underlying a satisfactory but not perfect fit of the experimental spectrum. It is noteworthy that nearly all the optimized interatomic distances of the two compounds are comparable within the fitting error. Conversely, the σ^2 values associated to the Ce-Ce SS contributions are refined to significantly different values. In addition, these values are relatively high, indicating a certain degree of disorder in both systems, as anticipated. Notably, σ^2 is slightly higher for **Ce_TzTz_PyPy** compared to **Ce_TzTz**, an observation that is consistent with the lower crystallinity of the former (Figure S3, Supporting Information).^[54]

3.5. Gas Adsorption Properties

3.5.1. N_2 Adsorption

The MOFs textural properties were evaluated through volumetric N_2 adsorption at 77 K on pre-activated powders (**Figure 3a**). For both MOFs, the isotherm shape is of Type [I+IV], typical of micro-/mesoporous materials, with a very small hysteresis loop along the desorption branch. The BET specific surface area of **Ce_TzTz** is $1136 \text{ m}^2 \text{ g}^{-1}$, comparable to that of UiO-67 but higher than that found for UiO-67(Ce) or for the heterocycle-based UiO-67-type (MIX)MOFs reported in **Table S3** (Supporting Information). The micropore volume (from the t -plot analysis, considering the statistical thickness range $3.5 < t < 13.9 \text{ \AA}$) equals $0.401 \text{ cm}^3 \text{ g}^{-1}$, representing 45% of the total pore volume ($0.885 \text{ cm}^3 \text{ g}^{-1}$ at $p/p_0 = 0.98$). Passing from the homo-linker to the mixed-linker MOF **Ce_TzTz_PyPy**, the

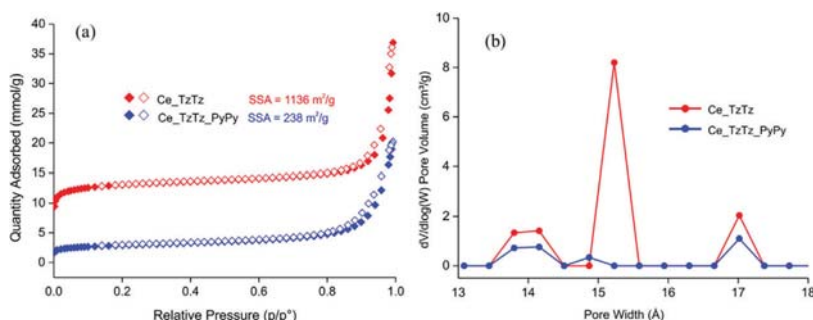


Figure 3. a) N_2 adsorption isotherms measured at $T = 77 \text{ K}$ on the two MOFs discussed in this work. Empty symbols denote desorption branches. b) Micropore size distribution (DFT method, cylindrical pore shape) for the two MOFs.

Table 3. Main CO₂ and N₂O adsorption data for the two MOFs in this study.

Sample	BET area [m ² g ⁻¹]	Q _{st} (CO ₂) [kJ mol ⁻¹]	CO ₂ quantity adsorbed (p = 1 bar) [mmol g ⁻¹]		Q _{st} (N ₂ O) [kJ mol ⁻¹]	N ₂ O quantity adsorbed (p = 1 bar) [mmol g ⁻¹]	
			T = 298 K	T = 273 K		T = 298 K	T = 273 K
Ce_TzTz	1136	18.2	1.8 (7.9 wt%)	2.6 (11.5 wt%)	25.4	2.2 (9.7 wt%)	2.8 (12.5 wt%)
Ce_TzTz_PyPy	238	29.5	1.1 (4.7 wt%)	1.4 (6.0 wt%)	26.4	0.7 (2.9 wt%)	0.8 (3.3 wt%)

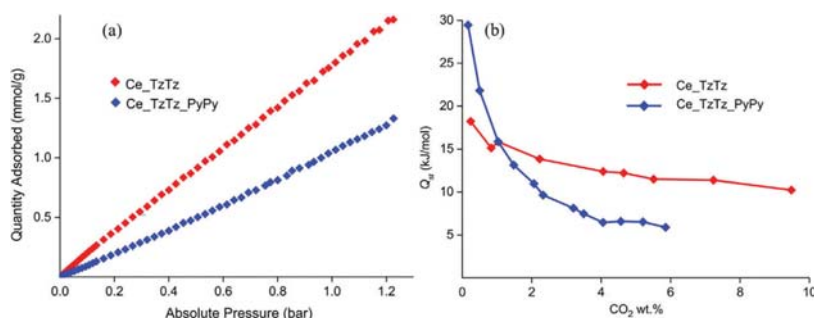


Figure 4. a) CO₂ adsorption isotherms measured at 298 K for the title MOFs. For the isotherms at 273 K the reader is referred to Figure S14a (Supporting Information). b) CO₂ isosteric heat of adsorption as a function of surface coverage for the title MOFs.

specific surface area decreases significantly to 238 m² g⁻¹. The inclusion of the bipyridyl linker in the pristine Ce_TzTz crystal structure implies a crystallinity decrease (Figure S3, Supporting Information)^[54] that may reduce the surface area. In line with this result, a reduction of the total pore volume (0.566 cm³ g⁻¹) and the microporous component (0.050 cm³ g⁻¹, 9%) is also observed with respect to Ce_TzTz. As for the micropore size distribution (Figure 3b; Figure S12, Supporting Information for the goodness of fit graph), both MOFs are featured by micropores falling in the 14 ≤ W ≤ 17 Å size range, similar to those found in UiO-67, UiO-67(Ce) and [Zr₆O₄(OH)₄(TzTz)₆] (Table S1, Supporting Information), highlighting again their structural analogy with these MOFs. Looking at the BJH mesopore size distribution (Figure S13, Supporting Information), Ce_TzTz has

a negligible amount of small mesopores close to the micropore limit (W = 25 Å), in accordance with UiO-67, UiO-67(Ce) and the heterocycle-based (MIX)MOFs quoted above (Table S3, Supporting Information), while Ce_TzTz_PyPy shows larger pores at W = 38 Å.

3.5.2. CO₂ and N₂O Adsorption

In order to assess the thermodynamic affinity and adsorption capacity of the two MOFs toward CO₂ and N₂O, CO₂ and N₂O adsorption isotherms at T = 298 and 273 K were collected on pre-activated samples up to p_{max} = 1.2 bar. The main data are summarized in Table 3. The CO₂ adsorption isotherms at 298

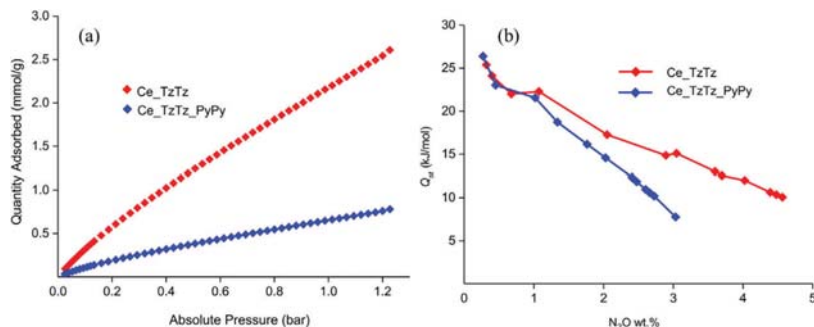


Figure 5. a) N₂O adsorption isotherms measured at 298 K for the title MOFs. For the isotherms at 273 K the reader is referred to Figure S14b (Supporting Information). b) N₂O isosteric heat of adsorption as a function of surface coverage for the title MOFs.

and 273 K are reported in Figure 4a and Figure S14a (Supporting Information), respectively. **Ce_TzTz** shows a good adsorption capacity for carbon dioxide. The total CO₂ uptake at $p_{\text{CO}_2} = 1$ bar and $T = 298$ and 273 K is 7.9 wt% (1.8 mmol g⁻¹) and 11.5 wt% (2.6 mmol g⁻¹), respectively. The absolute gas uptake at ambient temperature is comparable to that found for other thiazole-containing MOFs like NU-1000-PhTz (6.2 wt%),^[13] NU-1000-BzTz (8.7 wt%),^[55] [Zr₆(O)₄(OH)₄(TzTz)₆] (7.5 wt%)^[16] or Cu(5-Tz)₂ (9.0 wt%, 5-Tz⁻ = thiazole-5-carboxylate).^[56] The CO₂ uptake capacity of **Ce_TzTz_PyPy** is lower because of its reduced specific surface area. Comparing the room temperature capacity values, the weight percentage of the stored gas drops from 7.9 wt% in **Ce_TzTz** to 4.7 wt% for **Ce_TzTz_PyPy**, following the same trend observed in the respective surface areas. In terms of CO₂ isosteric heat of adsorption at zero coverage (Q_{st}), **Ce_TzTz** shows a value of 18.2 kJ mol⁻¹, higher than that estimated for UiO-67 (15.9 kJ mol⁻¹)^[57] and identical to that of the zirconium analogue [Zr₆(O)₄(OH)₄(TzTz)₆].^[16] The presence of a basic N atom in the thiazole linkers seems beneficial, because it increases the host thermodynamic affinity for acidic guests like CO₂ (as already observed in other thiazole-containing MOFs).^[13,16,55,56] In accordance with this statement, the interaction CO₂-framework becomes stronger when the *more basic* pyridinic N atom is present in the linkers: Q_{st} for **Ce_TzTz_PyPy** is much higher than that for **Ce_TzTz** (29.5 vs 18.2 kJ mol⁻¹, respectively). Figure 4b illustrates the variation of Q_{st} with increasing CO₂ coverage for both MOFs.

The two MOFs have also been tested as nitrous oxide sponges under the same pressure and temperature conditions used for carbon dioxide (Figure 5a; Figure S14b, Supporting Information). In **Ce_TzTz**, the total N₂O uptake at $p_{\text{N}_2\text{O}} = 1$ bar and $T = 298$ and 273 K is 9.7 wt% (2.2 mmol g⁻¹) and 12.5 wt% (2.8 mmol g⁻¹), respectively, and it is higher than that of CO₂. In comparison with other literature MOFs, the 273 K value is comparable to that shown by the Ni-based MOF [Ni(bptc)_{0.5}(H₂O)] (12.4 wt%; bptc⁴⁻ = biphenyl-3,3',5,5'-tetracarboxylate)^[58] but it is higher than that found in NU-1000-PhTz (9.4 wt%).^[13] The N₂O uptake capacity drops significantly in **Ce_TzTz_PyPy** reasonably be-

Table 4. IAST N₂O/CO₂ adsorption selectivity of binary gas mixtures [50%/50%] at $p_{\text{tot}} = 1$ bar for **Ce_TzTz** and **Ce_TzTz_PyPy**.

MOF	Temperature [K]	$S_{\text{N}_2\text{O}/\text{CO}_2}$
Ce_TzTz	273	1.6
Ce_TzTz	298	1.4
Ce_TzTz_PyPy	273	0.9
Ce_TzTz_PyPy	298	0.7

cause of the lower specific surface area, analogously to what observed for CO₂. At odds with CO₂, there are no significant differences in the N₂O isosteric heat of adsorption at zero coverage between the two MOFs, with the highest value estimated again for **Ce_TzTz_PyPy** (26.4 kJ mol⁻¹). Curiously, while **Ce_TzTz** seems to interact more strongly with N₂O [$(Q_{\text{st}})_{\text{CO}_2} = 18.2$ kJ mol⁻¹ versus $(Q_{\text{st}})_{\text{N}_2\text{O}} = 25.4$ kJ mol⁻¹], **Ce_TzTz_PyPy** shows a slight preference for CO₂ [$(Q_{\text{st}})_{\text{CO}_2} = 29.5$ kJ mol⁻¹ versus $(Q_{\text{st}})_{\text{N}_2\text{O}} = 26.4$ kJ mol⁻¹]. Figure 5b shows the Q_{st} dependence of the two MOFs on the N₂O coverage. As for the IAST CO₂/N₂O selectivity in equimolar binary gas mixtures (Table 4), the trend mirrors the adsorption capacity: **Ce_TzTz** is more selective for N₂O, while **Ce_TzTz_PyPy** shows a slight preference for CO₂. Thus, the introduction of a different heterocyclic linker in the “pure-bithiazole” framework is an unprecedented strategy to switch the MOF thermodynamic preference from N₂O to CO₂. Finally, Table S4 (Supporting Information) collects the (few) literature data available on other MOF materials exploited for the same application, for the sake of comparison with our samples. However, it must be underlined that in the presence of open metal sites in the activated MOF the gas adsorption and mixtures separation capacity are unequivocally higher than those measured on “fully saturated” metal centres (as in **Ce_TzTz** and **Ce_TzTz_PyPy**). To the best of our knowledge, the latter are the first cerium MOFs used for N₂O adsorption and CO₂/N₂O separation.

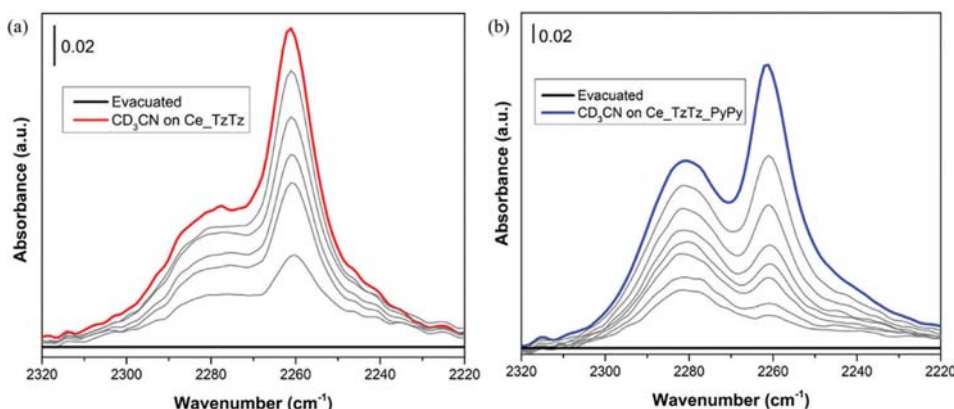


Figure 6. IR spectra of the background-subtracted $\nu(\text{CN})$ stretching zone of CD₃CN dosed on a) **Ce_TzTz**, and b) **Ce_TzTz_PyPy**. Maximum, intermediate, and minimum coverages are reported as coloured, grey and black curves, respectively.

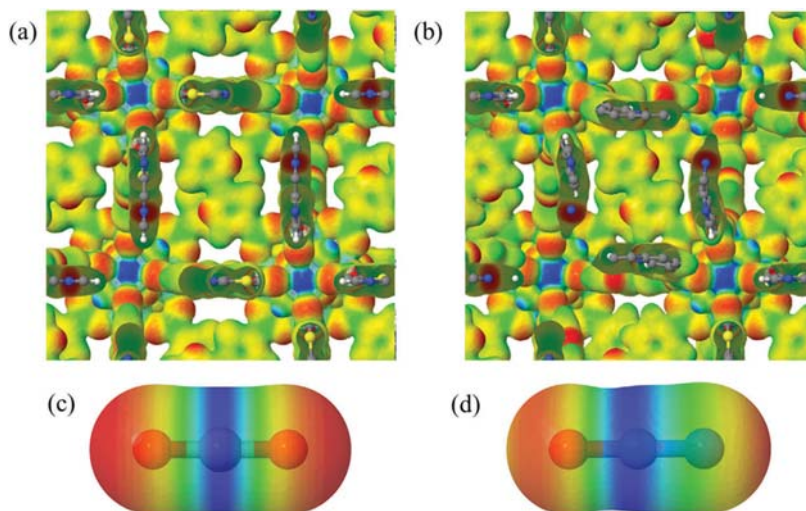


Figure 7. Electrostatic potential mapped on the electron density of **Ce_TzTz** a), **Ce_TzTz_PyPy** b), **CO₂** c) and **N₂O** d). Blue, green, and red colours correspond to positive, neutral, and negative values of the potential. Electrostatic potential range values: MIN, -0.05 au; MAX, $+0.05$ au.

3.6. IR Studies with Probe Molecules: **CD₃CN**, **CO₂** and **N₂O**

CO₂, **N₂O** and **CD₃CN** were used as molecular probes in VT-IR studies as additional MOFs characterization and to investigate the accessibility of their reactive sites leading to potential gas-framework interactions. In case of **CO₂** and **N₂O**, the only detectable signals are the **CO₂** ν_3 asymmetric stretching vibration and the **N₂O** N–N ν_3 stretching vibration (at $\nu = 2349$ and 2225 cm^{-1} , respectively) in the gas phase (Figure S18, Supporting Information). No changes in the carboxylate framework vibrational modes could be detected, since these signals are out of scale in the evacuated MOFs. On the other hand, acetoni-

trile (a strong Lewis base) can interact through its nitrogen atom with acidic sites present in MOFs that might be undetectable to other (less basic) molecular probes as **CO**. Upon adduct formation, σ -donation from the nitrogen lone pair located in a slightly antibonding orbital causes an upward shift in the C–N stretching mode of free **CD₃CN** (2263 cm^{-1}) proportional to the bond strength, helping in the detection of reactive sites of different acidity in the solid phase.^[47] The interaction of **CD₃CN** with **Ce_TzTz** and **Ce_TzTz_PyPy** (Figure 6) shows the formation of two main bands at 2280 and 2261 cm^{-1} . The band at lower wavenumber (that disappears upon outgassing) is related to liquid-like **CD₃CN**, while that falling at 2280 cm^{-1} , much more persistent, can be attributed to the formation of the adduct **D₃C–C $\equiv$ N–Ce^{IV}** (previously reported at 2286 cm^{-1} in **UiO-66(Ce)**).^[14] No other significant changes were observed in the whole spectral region (see Figure S17, Supporting Information). It is worth noticing that the relative intensity of the two bands is different in the two MOFs: the band at 2280 cm^{-1} is lower than the liquid-like signal in **Ce_TzTz**, but it rises in intensity in **Ce_TzTz_PyPy**. This behaviour is in accordance with the specific surface area (SSA) values: **Ce_TzTz** showed the highest SSA value (1136 m^2 g^{-1}), allowing for the physisorption of more **CD₃CN** molecules in the pores. Conversely, **Ce_TzTz_PyPy** ($\text{SSA} = 238$ m^2 g^{-1}) showed a more difficult formation of liquid-like **CD₃CN**.

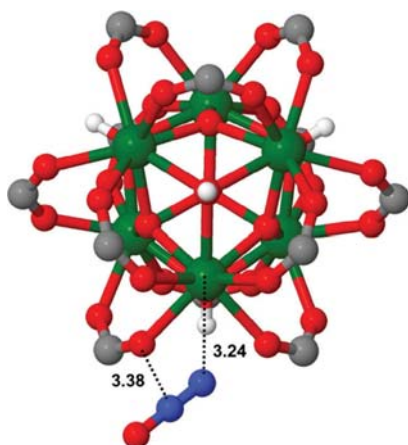


Figure 8. Optimized geometry of the **[N₂O@Ce_TzTz]** system (IBU only, for the sake of clarity). Main gas-framework distances reported (Å).

3.7. DFT Analysis of the Primary **CO₂** and **N₂O** Adsorption Sites

The ideal hydroxylated (defect free) models of **Ce_TzTz** and **Ce_TzTz_PyPy** were built starting from the crystal structures determined from powder X-ray diffraction. To ensure the electroneutrality of the model systems, the μ_3 -oxygen (μ_3 -O) atoms of the Inorganic Building Unit (IBU) were saturated with hydrogen atoms. In principle, in the **Ce_TzTz_PyPy** crystal structure

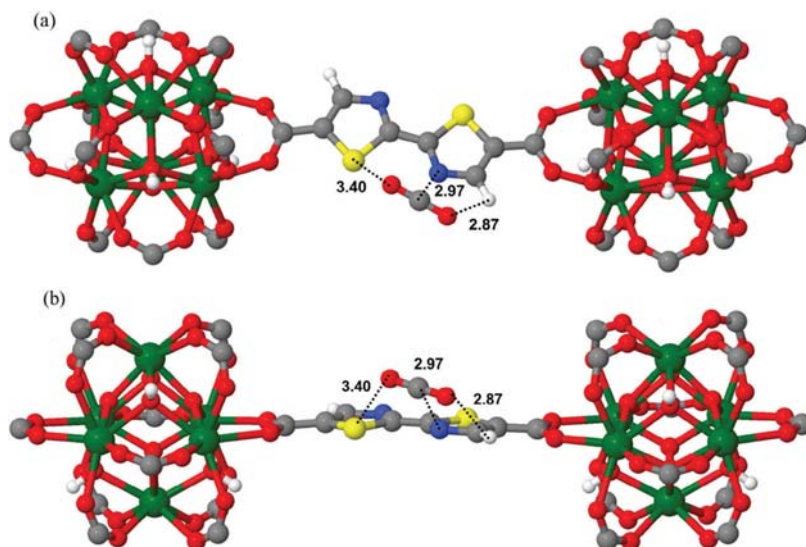


Figure 9. Top a) and side b) view of the optimized geometry of the $[\text{CO}_2@ \text{Ce\_TzTz\_PyPy}]$ system (portion of the crystal structure only, for the sake of clarity). Main gas-framework distances reported (Å).

the PyPy^{2-} linker may adopt two different configurations, with nitrogen atoms in a *cis* or *trans* relative arrangement with respect to the central C–C bond linking the two pyridyl rings; consequently, in a preliminary stage two model structures were built with the linker in *cis* and in a *trans* fashion. It turned out that the *trans* N configuration is more stable than the *cis* by 28 kJ/mol/linker. Therefore, all the reported calculations refer to the *trans* Ce_TzTz_PyPy MIXMOF. Firstly, a full relaxation of both atomic positions and unit cell parameters of the crystal structures of Ce_TzTz and Ce_TzTz_PyPy was carried out. On the optimized structures of the two MOFs, the electrostatic potential maps were computed to pinpoint the possible binding sites for CO_2 and N_2O adsorption. A careful inspection of the electrostatic potential maps as reported in Figure 7 highlights the presence of two specific Lewis acidic sites located on cerium and on the μ_3 -OH groups of the IBU (blue spots) while two other less specific basic sites (red regions) are located on the N atoms of the TzTz^{2-} and PyPy^{2-} linkers and around the carboxylate groups.

Accordingly, CO_2 and N_2O were manually docked within the pores of the two MOFs by maximizing the interaction between the guest molecules and the host framework, based on the complementarity of the electrostatic potential for the four possible adsorption sites. For the adsorption of both CO_2 and N_2O on Ce_TzTz , PBESol0-3c results are reported in Table S5 (Supporting Information). The computed adsorption energies show a slight preference for N_2O , in line with the experimental findings; moreover, the primary adsorption sites of N_2O are located on the Ce atoms of the IBU, where the adsorbate interacts in end-on binding mode through its terminal N atom, and is further stabilized by additional electrostatic interactions with the carboxylate group of the organic linker (Figure 8). In Ce_TzTz_PyPy , our calculations show a slightly higher selectivity for CO_2 over N_2O , as evidenced by the experimental findings. The adsorp-

tion of CO_2 is predicted to be stronger on the N/S atoms of the TzTz^{2-} linker (interacting through its C/O atoms, respectively), as shown in Figure 9 and Table S6 (Supporting Information). The discrepancy between the experimental isosteric heat of adsorption and the computed interaction energy can be ascribed to the “ideal” computational models adopted for the calculations, which do not account for partial collapse of the framework pores, presence of defects, amorphization effects and other structural modifications that are present in the real samples, as suggested by the low BET specific surface areas reported in Table 3.

4. Conclusions

The heterocyclic linkers [2,2'-bithiazole]–5,5'-dicarboxylic acid and 2,2'-bipyridine-5,5'-dicarboxylic acid) have been exploited for the preparation of the two new cerium(IV) MOFs Ce_TzTz and Ce_TzTz_PyPy with UiO-67 3D architecture. Their performance as CO_2 and N_2O adsorbents has been analysed in detail through the combination of experiment and theory. Remarkably and to the best of our knowledge, these are the first cerium MOFs exploited for N_2O adsorption to date. When moving from the homo-linker to the mixed-linker analogue, a $\text{CO}_2/\text{N}_2\text{O}$ selectivity inversion occurs: Ce_TzTz shows higher capacity, thermodynamic affinity, and selectivity toward N_2O over CO_2 , while the opposite holds for Ce_TzTz_PyPy . Even the primary adsorption sites (as derived from DFT calculations) are different for the two MOFs: while N_2O preferentially interacts with the strongly acidic Ce^{IV} ions in the Ce_TzTz IBU, in Ce_TzTz_PyPy CO_2 is located close to the N/S atoms of the thiazole linker. This intriguing finding opens new horizons in the development of porous MOF materials able to discriminate between chemically similar (polluting) gases through a simple linker composition

modification, while keeping the same structural topology. This approach is alternative to the adsorption temperature tuning found by some of us in the past for the thiazole-decorated MOF NU-1000-PhTz.^[13] Reduction of greenhouse gases concentration in the Earth atmosphere is mandatory for the next future, and the discovery of new functional materials with tailored pollutants adsorption properties is a hot research topic of contemporary materials science research. Along this direction, current research activity ongoing in our laboratories is focused on the synthesis of other mixed-linker MOFs with high surface area to be tested in the adsorption and catalytic transformation of greenhouse gases.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Prof. Silvia Bordiga (Università di Torino, Italy) is acknowledged for fruitful discussions. A.R. would like to thank Dr. Enrico Berretti (ICCOM-CNR) for the SEM-EDX analysis carried out on **Ce-TzTz-PyPy**. A.R. and S.G. would also like to acknowledge the Italian Ministry of University and Research (MUR) and the European Union (Next Generation EU) for funding this research activity through the PRIN 2022 project LUMIMOF (2022A3XNWJ) "Wastewater treatment and monitoring with luminescent mixed-linker Metal-Organic Frameworks as chemical sensors and adsorbents of contaminants of emerging concern". S.G. also acknowledges Miss Lucrezia Madella and Miss Anna Mauri for help. The Department of Chemistry of the University of Turin acknowledge support through the Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023–2027" (CUP: D13C22003520001). L.D. and B.C. gratefully acknowledge the Gauss Centre for Supercomputing e.V. (www.gauss-centre.eu) for providing computing time on the GCS Supercomputer SuperMUC-NG at Leibniz Supercomputing Centre (www.lrz.de).

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Data Availability Statement

Research data are not shared.

Keywords

bipyridyl, bithiazole, carbon dioxide adsorption, cerium(IV), DFT calculations, EXAFS spectroscopy, IR spectroscopy, metal-organic frameworks (MOFs), nitrous oxide adsorption, powder x-ray diffraction (PXRD)

Received: February 19, 2024
Revised: March 14, 2024
Published online: May 10, 2024

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- angles, 128.0°; b) the DMF molecule: carboxylic C-O, 1.25 Å; C-N, 1.40 Å; C-H, 0.95 Å; bond angles for sp^2 and sp^3 atoms, 120.0° and 109.5°, respectively.
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Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

MIL-125-NH₂ functionalized chitin scaffold as dual sorbent and photocatalyst filter for degradation of trimethoprim

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ARTICLE INFO

Keywords:

Metal-Organic Framework
Chitin
MIL-125-NH₂
Emerging pollutant
Photocatalytic composite

ABSTRACT

A porous, photocatalytically active, and water-stable composite filter has been developed based on MIL-125-NH₂, a Titanium-based Metal-Organic Framework (MOF) and chitin polymeric scaffold. In order to tune the structure and functional properties of the CH/MOF composites, the loading degree of the MOF within the polymer was systematically varied. The composite material optimal performance was achieved with a 10% wt/wt loading of MIL-125-NH₂ into the chitin scaffold. This composite material was able to capture and photodegrade Trimethoprim (TMP) under acid and alkaline conditions with outstanding efficiency (82% within 180 min), as well as in waters collected from different geographical locations nearby Buenos Aires that were spiked with TMP. Furthermore, the chemical stability of MIL-125-NH₂ is significantly improved when incorporated into the chitin scaffold, maintaining its structural integrity even after four cycles of reactivation and reusability. The study outlines the experimental procedures for synthesizing MIL-125-NH₂, preparing chitin hydrogel and nanostructured composites, and details on the adsorption and photocatalysis experiments. The practical application of our approach can be further expanded to prevent degradation during gas or liquid adsorption processes of hydrolytically unstable MOFs.

1. Introduction

Water detoxification is becoming increasingly challenging in the 21st century due to intensifying anthropogenic activities and the advancement of global warming [1]. Today, wastewater treatment plants are responsible for removing common pollutants from densely populated areas, industry and agriculture [1]. However, substances of emerging concern or ECs (i.e. personal care products, pharmaceutical compounds, nanomaterials, pesticides, surfactants, caffeine) are particularly problematic to eliminate due to their lack of regulatory status, harmful effects at low concentrations, and the diverse nature of these compounds, making their removal from water exceptionally challenging [2]. Antibiotics exemplify these concerns: they continually enter our

environment through human activities, and their release contributes to bacterial resistance [1,3].

Many technologies have been proposed and assessed for detoxifying water from antibiotics, each with its strengths and weaknesses. Two main challenges persist: the selective capture of diluted antibiotic molecules amidst a complex chemical matrix and their effective disposal or neutralization. Here, porous materials and heterogeneous photocatalysts can play an important role in advancing state-of-the-art technologies to eliminate antibiotics from the environment [4]. These solutions offer cost-effective, renewable, and easy-to-apply techniques that can potentially revolutionize water treatment practices, especially when utilizing sunlight as an energy source for pollutant mineralization [5]. However, benchmark solutions, such as activated carbons and

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<https://doi.org/10.1016/j.jece.2024.113005>

Received 13 December 2023; Received in revised form 16 March 2024; Accepted 5 May 2024

Available online 8 May 2024

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certain photocatalysts, still need to improve antibiotic capture and degradation efficiency.

In this regard, Metal-Organic Frameworks (MOFs) offer a fresh perspective beyond traditional photocatalysts such as those based on TiO_2 and ZnO , where their efficiency in generating the oxygen-reactive species that trigger the mineralization of organic chemicals still needs to be improved far from the UV-Vis radiation range [6–8]. MOFs are hybrid compounds distinguished by their structural versatility, chemically codable porosity and semiconductor nature [4,9–12]. MOFs have been used in several applications, such as membranes (for purifications and separations), adsorption of pollutants, and control release systems, among others [13–18]. Since the discovery of the water-stable Zr(IV) and Ti(IV) based MOFs, their application as specific sorbents or photocatalysts for water remediation ends has been rapidly explored [19–21]. The chemical encoding of the inorganic and organic building blocks of MOFs has opened the room to the modulation of their light-harvesting [9,10], hole-electron pairs generation and transportation, and oxygen radical species production functions [22]. Overall, the adsorption and photo-degradation functions of archetypal semiconductor and porous MOFs, such as MIL-125- NH_2 , have been revealed to be very efficient for capturing and degrading myriad inorganic and organic pollutants, including antibiotics.

However, despite their efficiency, MOFs' powdered nature complicates their recovery and reactivation, consuming significant time, energy, and resources. Moreover, their long-term chemical stability in aqueous environments remains a concern. It was already known that the chemical stability of MIL-125- NH_2 is quite limited when exposed to acidic and basic conditions, which restricts activation processes to milder conditions. This often yields suboptimal results or requires MOFs metal doping for stability improvement [23].

This work outlines a research study focused on addressing the limitations associated with MOFs, specifically MIL-125- NH_2 , in water remediation applications. Two primary challenges have been identified. The first one is due to the powdered nature of MIL-125- NH_2 , which complicates its recovery after being used. The second challenge regarding the MIL-125- NH_2 is limited chemical stability in aqueous environments and alkaline and acid mediums. Thus, MIL-125- NH_2 reactivation and reuse as a photocatalytic system in an aqueous medium is hindered.

Consequently, we propose an innovative approach to immobilize MIL-125- NH_2 into a porous biopolymeric scaffold based on chitin (a biopolymer) (CH@MIL-125- NH_2). This biopolymer is non-toxic, biodegradable, chemically stable, and sourced from renewable raw materials, presenting an enticing alternative for water remediation [24–26]. Our research delves into blending the CH and MIL-125- NH_2 components into a photocatalytic composite filter, CH@MIL-125- NH_2 , that promises easy recovery and reactivation. This work is based on integrating MIL-125- NH_2 into a chitin-based biopolymeric scaffold, which will be significantly improved when embedded in the biopolymeric scaffold, thereby overcoming previous limitations related to its chemical stability, as well as easy recovery and reactivation in aqueous environments.

Furthermore, we examine its efficacy in concentrating and degrading the antibiotic trimethoprim under visible light and in various waters collected from different geographical locations in Argentina spiked with the antibiotic. Significantly, the investigation also probes the potential chemical stabilization of MIL-125- NH_2 when integrated into a polymeric scaffold. This novel approach could redefine how MOFs are applied and activated without disrupting their structural integrity. This work underscores the potential of integrating MOFs, such as MIL-125- NH_2 , into polymeric frameworks, emphasizing its significance to the research community.

2. Materials and methods

2.1. Materials

Chitin from shrimp shells was obtained from Sigma-Aldrich (USA), and the chitin degree of acetylation was 93%. Methanol and acetonitrile HPLC grade were purchased from Sintorgan (Argentina). Ethanol (99.5% purity) and calcium chloride dihydrate were purchased from Cicarelli (Argentina). Trimethoprim was acquired from Saporiti (Argentina). All chemicals employed in this work were used without further purification, and the reagent grade was analytical. N,N-Dimethylformamide (DMF) (purity 99.9%) and ethanol (purity 98%) were obtained from Labkem. 2-Aminoterephthalic acid (98%), and Ti(IV) isopropoxide solution (70%, Ti(iPrO)_4) were acquired from Aldrich.

2.1.1. Reflux synthesis of MIL-125- NH_2 (Ti)

7.70 g of BDC- NH_2 linker were dissolved in 100 mL of DMF under reflux and continuous stirring at 100°C for 1 h. Then, 28 mL of methanol was added to the solution and further stirred for one hour at the sample conditions. Afterward, 8.4 mL of Ti(iPrO)_4 was added drop by drop to prevent the formation of agglomerates. Samples were refluxed for three days, recovered, and thoroughly washed with DMF and ethanol to remove the non-reacted reagents.

2.1.2. Preparation of chitin hydrogel and chitin nanostructured composites

For the preparation of the chitin gel, 42.5 g of calcium chloride dihydrate were mixed in 50 mL of methanol and refluxed at 80°C to near-dissolution. Then, 1 g of chitin powder was added to the calcium/methanol solution and refluxed at 90°C for 2 h under constant stirring. Starting from the CH-xerogel, three different CH@MOF composites were assembled, loading different weight percentages of the MOF into the polymeric matrix. In a typical procedure, 1 g of CH, 42.5 g of calcium chloride dihydrate and 50 mL of methanol suspension were mixed with 111 mg of MIL-125- NH_2 -1% to obtain a hybrid material with 10% wt/wt of MIL-125- NH_2 (CH@MIL-125- NH_2 -10%). The weight percentage of the MOF added in the process was varied in order to obtain 1, 5 and 10 wt% (CH@MIL-125- NH_2 -1%, CH@MIL-125- NH_2 -5% and CH@MIL-125- NH_2 -10%) composites. Afterward, the CH-xerogel and CH/MOF composites were spun into a glass beaker with cold ethanol until gelled. Finally, the gels were subjected to several distilled water incubations to wash out all the methanol, ethanol, and CaCl_2 residues. All the materials were dried in an oven at 50°C , milled, and sieved between 250 and 500 μm before performing the adsorption and photocatalysis experiments.

Sections 2.3–2.5, with full experimental details concerning the characterization techniques employed, TMP quantification, photocatalytic assay specifications and kinetic mathematical models, are reported in the [Supporting Information](#) (SI).

3. Results and discussion

3.1. FT-IR and Raman results

The FT-IR and Raman spectra of MIL-125- NH_2 and CH components show the characteristic bands of both materials (Fig. 1(a) and 1 (b)), which are described in [Supplementary Information](#) [27–30]. For CH, 93% of acetylation was based on the IR signature [31,32]. Infrared spectra do not reveal any archetypal absorption bands related to the vibrational modes found in MIL-125- NH_2 in composite materials, but only the ones linked to the chitin scaffold. This is probably due to the combination of a relatively low loading of MOF into the polymer and the partial superposition of the most intense IR signals of MIL-125- NH_2 with the ones related to CH. On the other hand, Raman spectroscopy gives further insight in that respect since an absorbance increase of the bands located at 1626 and 1584 cm^{-1} is consistent with the increase in MOF loading (Fig. 1(c)). It is worth noting that neither IR nor Raman shows any significant displacement or alteration of the position or intensity of

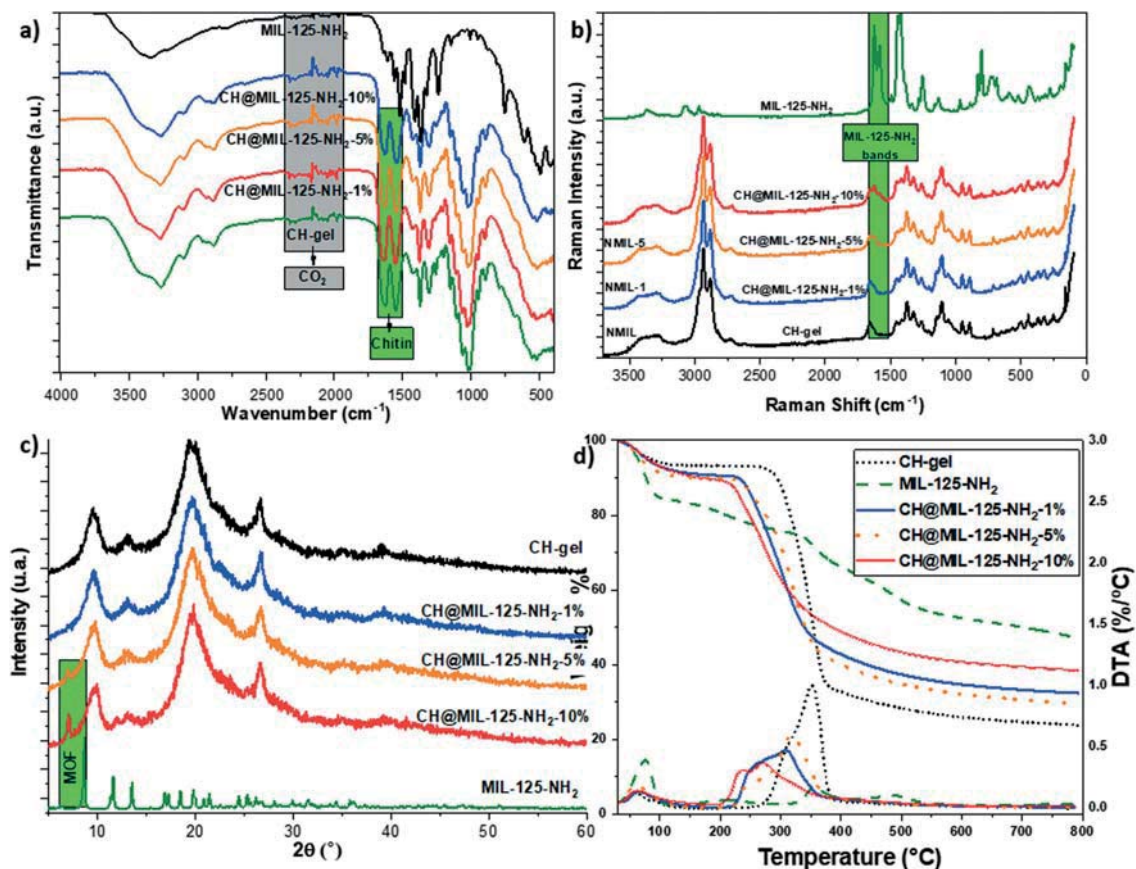


Fig. 1. FTIR spectra (a), Raman spectra (b), X-ray diffractograms (c), TGA and DTG thermograms (d) of CH, MIL-125-NH₂ and their composites.

the bands related to the vibrational modes related to CH.

Overall, the integration of the MIL-125-NH₂ particles does not imply a chemical or electrostatic interaction of enough energy to induce any change/alteration of the chemical structure or functions of the CH matrix. Thus, MIL-125-NH₂ particles would be dispersed by physical interactions into the polymeric scaffold.

3.2. XRD studies

The CH, MIL-125-NH₂ and CH@MIL-125-NH₂ samples were characterized in order to obtain a landscape of the chemical, textural, compositional and optical properties of the parent components and the three composites studied in this work (Fig. 1(c)). Firstly, X-ray diffraction data confirm that the reflux synthesis process of the MIL-125-NH₂ was successful since the experimental and simulated patterns are very similar in terms of diffraction maxima positions and relative intensities (Figure S1) [33,34]. XRD also confirmed the integration of the MIL-125-NH₂ into the CH matrix since the most intense diffraction maximum of MIL-125-NH₂, which is located close to 7° in 2θ, is detected as well in the diffraction patterns of the CH/MOF composites, as shown in Fig. 1(a). As expected, the higher the MIL-125-NH₂ loading in the composite, the higher the signal of its diffraction maxima in the composites. In the case of CH@MIL-125-NH₂-10%, a second maximum related to the MOF is also observed at 11.5°, as well as different shoulders along the diffraction pattern that coincides with the ones of the MIL-125-NH₂ compound. It is important to note that we expect a

homogeneous distribution of the MOF particles along the CH, which could induce attenuation of the XRD signal of the MOF when immobilized in the polymeric matrix. All in all, diffraction data indicates that the long-range ordering of the MIL-125-NH₂ structure resists the incorporation process into CH. In addition, it is relevant to mention that the XRD patterns of CH-xerogel and CH@MIL-125-NH₂ composites present as well the typical broad diffraction maxima related with α-chitin structure (i.e. 9.23°, 12.68°, 19.25°, 20.61°, and 26.77° [35]). Thus, the crystallinity of the α-chitin is slightly altered by the presence of MOF particles, in contrast to fillers of other natures, which can induce its amorphization [26,36]. These findings align with the crystallinity index values of CH and CH@MIL-125-NH₂ samples (Table S1). In summary, MIL-125-NH₂ nanoparticles were successfully immobilized in varying ratios into the chitin matrix. The MOF maintained its long-range ordering after its integration into CH, with no collateral alteration of the crystallinity of the α-chitin scaffold.

3.3. Thermal analysis

As revealed by thermogravimetric measurements, the thermal stability of the CH is slightly altered by the MOF (Fig. 1(d)). For MIL-125-NH₂, four decomposition steps are observed in the TGA profile. The first one is related to its dehydration (20–100 °C), the second is associated with the release of DMF molecules remaining in the pore space of the material after the washing process (150–250 °C), and the last one is linked to the pyrolysis of 2-amino terephthalate linkers and the

subsequent formation of an amorphous TiO_2 @carbon composite [37–39]. In comparison, CH exhibits a first dehydration step from 30 to 120 °C, followed by a complex deacetylation process and chitin structure depolymerization between 270 and 380 °C [36]. For CH@MOF composites, thermograms are similar to one of the parent's CH but with a slightly higher weight loss associated with the dehydration/desolvation (30–150 °C) and a subtle temperature reduction of the deacetylation and degradation of the CH. Even if it is not fully clear from the measurement profile, the degradation of the 2-amino terephthalate coming from

MIL-125-NH₂ needs to be overlapped with the thermal collapse of the CH [37,40]. The pyrolysis is completed above approximately 350–400 °C. The pyrolysis is completed with a slight weight loss observed during the last heating step up to 800 °C [41].

On the other hand, TGA analysis revealed that adding the filler into the chitin matrix affected the composites' degradation process and T_{max} . This would be due to the slight increase of amorphous regions during filler dispersion and the chitin gelling process, as indicated by the induced amorphization reflected in the XRD patterns. The disorderly

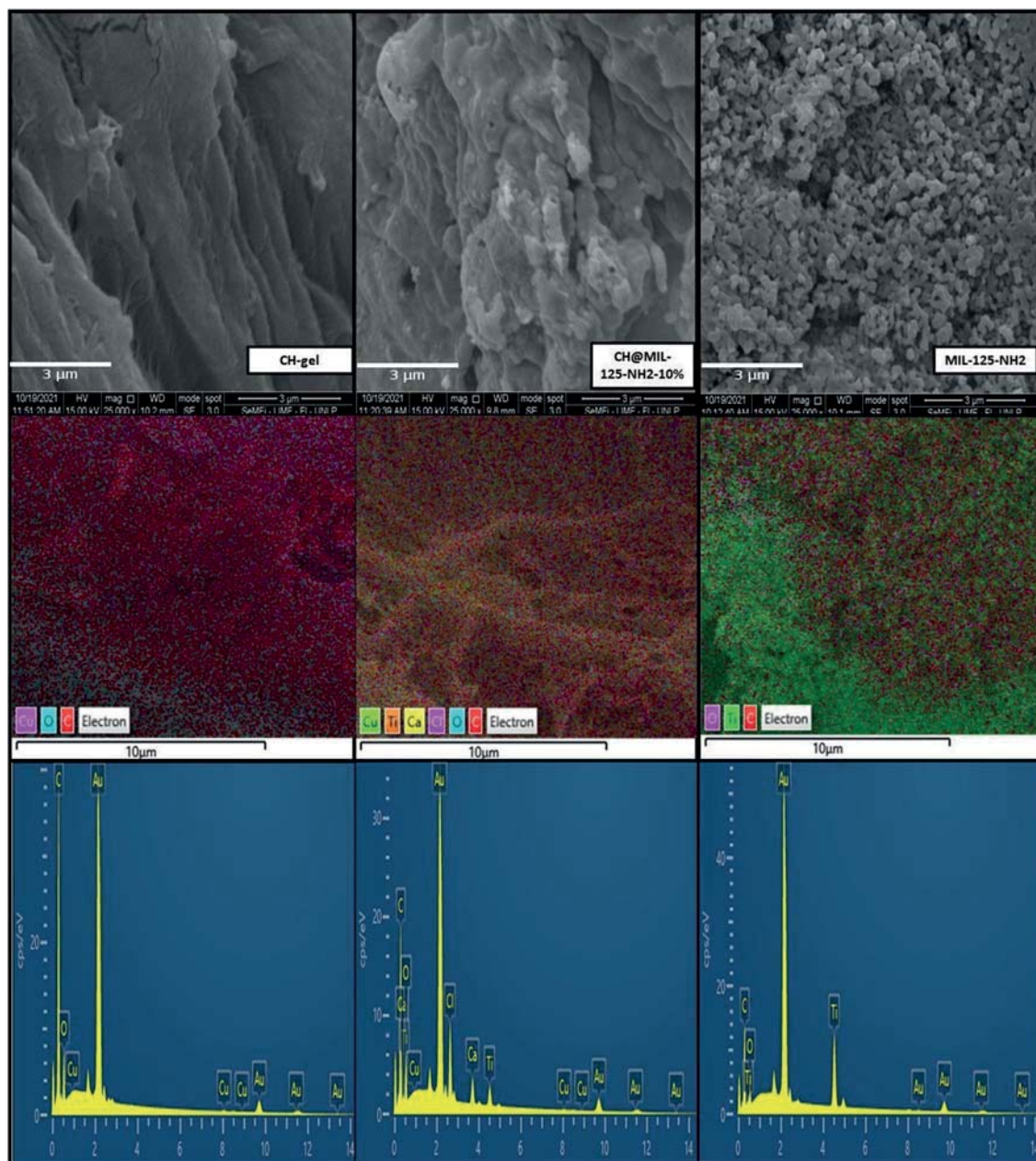


Fig. 2. SEM images and EDS of CH, MIL-125-NH₂ and CH@MIL-125-NH₂ composites.

structure of the composite enables heat transfer within the material more easily, resulting in reduced thermal resistance of the composites [26,36].

The differential scanning calorimetry experiment complements the information obtained by thermogravimetry, as shown in Figure S2. MIL-125-NH₂ exhibits an endothermic peak related to the evaporation of guest molecules adsorbed [42,43]. Similarly, CH-xerogel and CH@MOF composites show a broad endothermic transition attributed to water molecules release between 5 and 150 °C. The enthalpy (ΔH) and temperature (T_p) of this endothermic event are increased due to the contribution of the solvent release from MIL-125-NH₂ in the case of composite materials (Table S1). This behavior has also been observed for CH/bentonite composites [36]. Results from both TGA and DSC point towards significant variation in the thermal properties of CH after the MIL-125-NH₂ integration into the polymeric scaffold.

3.4. BET surface area analysis

The type I N₂-77 K isotherm of MIL-125-NH₂ confirms its microporous nature (Figure S3 – Table S2). The isotherm exhibits as well as a small hysteresis typical of type IV profiles that could be related to intraparticle mesoporosity [44]. The calculated BET surface (1097 m²/g (0.005 < p/p_0 < 0.03)) is close to the expected values compared with the literature [45,46]. In the next step, we also tried to determine the micro-porosity ascribed to the MOF installed within the CH matrix by softening the activation conditions employed for the MIL-125-NH₂ component. Unfortunately, the N₂-uptake at low partial pressures ascribed to the micro-porosity of the sample was negligible due to the soft-activation conditions imposed by the chemical stability of the CH, together with the low loading of the MOF into the polymer.

3.5. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis

TEM, SEM and EDS analyses were employed to elucidate the structural and compositional characteristics of CH-xerogel, MIL-125-NH₂, and CH/MOF composites, as illustrated in Figure S4 and Fig. 2. Figure S4 displays hexagonal nanospindle crystals of MIL-125-NH₂, which are 900–1000 nm in length and 400–500 nm in width. The SEM micrographs provided a detailed visualization of the surfaces, highlighting the morphological changes induced by the incorporation of MIL-125-NH₂ into the CH matrix. The chitin matrix initially exhibited an irregular and granulated surface texture. Upon integration of MIL-125-NH₂, these irregularities underwent a noticeable transformation, suggesting a significant modification in surface morphology attributable to the presence of the metal-organic framework components.

The effectiveness of the MIL-125-NH₂ incorporation was further substantiated through EDS analysis, which offered quantitative evidence of the elemental composition across the composites. Notably, the EDS compositional mappings demonstrated that the observed surface irregularities did not result from MOF agglomeration. Instead, they confirmed a homogeneous dispersion of MIL-125-NH₂ within the polymer matrix, indicating a successful integration without significant clustering of the MOF particles. This homogeneous distribution is critical for the desired material properties, as it ensures uniformity in the composite's structural and functional characteristics.

Furthermore, the combination of SEM imaging and EDS elemental mapping revealed that MIL-125-NH₂ could be successfully incorporated into the chitin matrix in various ratios, aligning with the observed morphological changes. This finding is corroborated by XRD results, which provide additional support for the successful synthesis of CH/MOF composites. The XRD analysis, not detailed here, likely indicates characteristic peaks corresponding to both the chitin matrix and the MIL-125-NH₂, further confirming the presence and uniform distribution of the MOF within the composite material.

On the whole, the integrated SEM and EDS analyses play a pivotal

role in understanding the microstructural and compositional intricacies of CH/MOF composites. These insights are instrumental in optimizing the synthesis process and tailoring the properties of the composites for specific applications, ranging from catalysis and adsorption to biomedicine and sensor technology. The uniform dispersion of MIL-125-NH₂ within the CH matrix, as revealed through these analyses, underscores the potential of these composites in enhancing material performance through structural design.

3.6. UV-visible DRS analysis

Fig. 3 presents the UV-visible DRS absorption spectra and plots of $[F(R)h\nu]^{1/2}$ as a function of the energy for the band gap determination (direct electronic transition) of CH, MIL-125-NH₂, and their composites. It can be noticed that MIL-125-NH₂ and composite materials absorb light in the UV and visible spectrum. The visible and UV light-harvesting capacity of MIL-125-NH₂ arise from: (I) the charge transfer process at the inorganic clusters (UV-Vis_{max} = 330 nm) and (II) the electronic structure of amino-terephthalate linkers (Vis_{max} = 400 – 450 nm). In parallel, CH is also active for light adsorption in the UV region due to the π -bond of the carbonyl functional group (C=O) (UV-Vis_{max} = 230 nm). On the basis of the Tauc plots of Fig. 3(b), the direct band gaps of the parent MOF and CH/MOF composites are between 2.55 and 2.71 eV. These values are within the reported range (2.55 eV); moreover, in the case of the composites, MIL-125-NH₂ incorporation into the CH matrix caused a slight increase in their energy band gap for the composites with the lower content of MOF. This effect was also reported in other semiconductors and polymer composites, and it probably arises from the

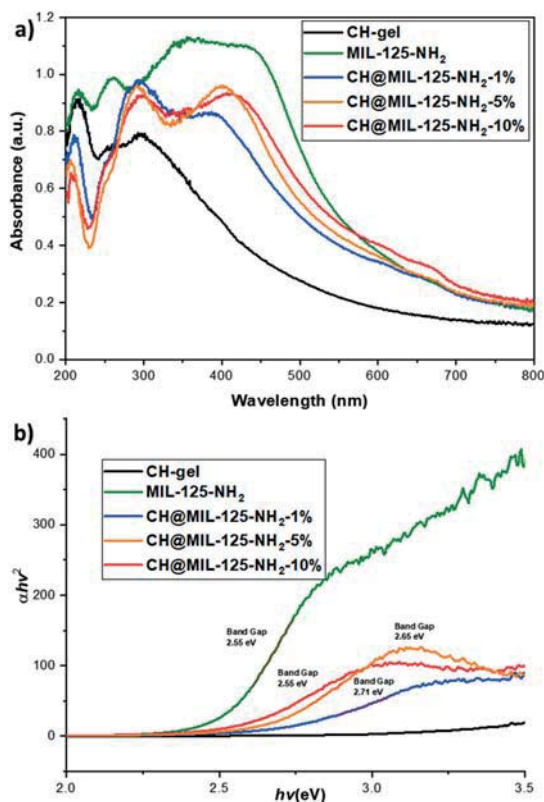


Fig. 3. Diffuse reflectance spectra (a) and Kubelka-Munk transform of diffuse reflectance data (b) for the CH-xerogel, MIL-125-NH₂ and their composites.

surface interfacial interaction between the two components of the system [47,48].

All in all, considering a scenario of illumination of a composite where the MOF nanoparticles are embedded into the CH matrix, the CH-scaffold could act as a filter of the ultraviolet, visible radiation accessible for the MIL-125-NH₂ nanoparticles and hence block or diminish the light adsorption by the titanium oxo-clusters. Therefore, the photocatalytic activity of the MIL-125-NH₂ within the CH arises mainly from the activation of the amino groups within the organic linkers by visible light radiation. It is interesting to mention as well that the assembly of MOF and CH components leads to a marginal rise in the energy band gap for the composites with lower MOF content.

3.7. Photocatalytic performance

Once our composite filters' chemical, structural, textural and optic properties have been assessed, their performance for the adsorption and photo-degradation of trimethoprim (TMP) antibiotic was assessed. First, it is important to note that the experiments were performed starting from an initial concentration of 100 mg/L since lower concentrations give rise to the almost full substrate adsorption into our composite membranes. Thus, in order to evaluate the photocatalytic activity of the CH@MIL-125-NH₂ system, it is necessary to end up with a value of TMP concentration after the adsorption step in dark conditions that enables follow up its degradation via photocatalysis once illuminated our composite porous photocatalyst with visible light source. The TMP

concentration variation during adsorption and photo-degradation for MIL-125-NH₂ powder and CH@MIL-125-NH₂ composites with different MOF loadings (from 1% to 10% wt./wt.) are shown in Fig. 4(a). First, it is important to note that the CH matrix did not present adsorption nor photocatalytic degradation capacity for TMP (data not shown). However, we have demonstrated in previous studies that it can act as an active polymeric scaffold that is able to retain organic, inorganic and biological targets with different characteristics. In this case, MIL-125-NH₂ is the active component of the system, with almost 78% of TMP adsorbed under dark conditions and close to 100% of TMP degraded after photocatalysis. In the case of the CH/MOF composites, the adsorption capacity/photo-degradation efficiency increased from 12/13–75/85% when the loading of MIL-125-NH₂ from 1% to 10% was increased into the CH matrix. At this point, it is important to mention that the TMP removal and photo-degradation with MIL-125-NH₂ and CH@MIL-125-NH₂-10% composite were performed with the same overall weight of MIL-125-NH₂ in the media. Thus, since the TMP adsorption capacity remained the same for both parent MOF and CH/MOF composite, it can be concluded that the TMP has full accessibility to MIL-125-NH₂ when it is immobilized into the CH scaffold. On the contrary, this behavior is not maintained during photocatalysis. This tendency is also observed for the 1 and 5 wt./wt% composites, with residual C/C₀ values significantly different after adsorption and photocatalysis. Since a proportional decay in C/C₀ with the increase of MOF loading was observed, it is proposed that the reduction in the photocatalytic efficiency observed, in comparison with free MIL-125-NH₂,

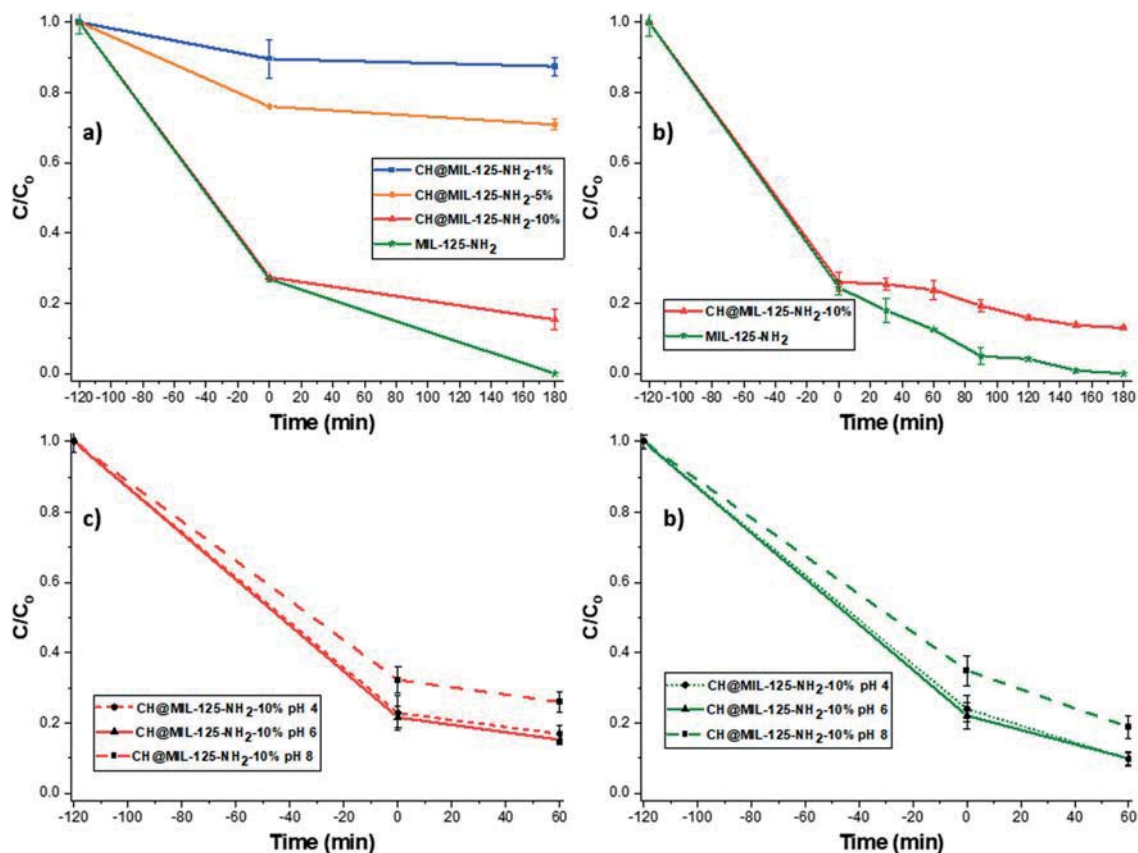


Fig. 4. TMP adsorption ($C_0 = 100$ mg/L) and photo-degradation capacity (a) and photocatalytic degradation kinetics (b) of CH, MOF and CH/MOF composites. Comparison between the adsorption and photocatalytic degradation of TMP by CH@MIL-125-NH₂-10% (c) and MIL-125-NH₂-10% (d) at different pHs (c and d).

originated only in CH matrix-associated factors.

Elucidating the factors that can affect the photocatalytic activity of MIL-125-NH₂ into CH is not straightforward. To mention some, the efficiency of the illumination of MOF particles into the composite can be reduced since the retained by the CH-scaffold is a significant fraction of the light radiation. In addition, once the oxygen reactive radical species are generated on the surface of the MIL-125-NH₂ particles, they can be partially consumed by an oxidation process affecting CH polymer. Even though there is room for improvement in MOF loading, CH/MOF structuration as a multilayered or core-shell system and even shaping the composites as thin membranes could improve the illumination and photo-degradation efficiency. All in all, the biopolymer's three-dimensional network that supports the MIL-125-NH₂ active material is easy to recover, reactivate and reuse (which is not the case for the MIL-125-NH₂).

At this point, the composite material with the highest MIL-125-NH₂ loading (CH@MIL-125-NH₂-10%) was selected as the optimal dual sorbent and photocatalytic filter to study with more detail the kinetics of trimethoprim degradation in comparison to the active material (Fig. 4 (b)). A significant difference can be appreciated when comparing the TMP degradation kinetics between MIL-125-NH₂ and CH@MIL-125-NH₂-10%. In the case of MIL-125-NH₂, TMP degradation turned out to be more efficient and faster (near to complete adsorption and degradation of TMP in 180 min) when compared to CH@MIL-125-NH₂-10% (82% of TMP adsorption and degradation). Still, the composite shows an interesting reduction of the TMP concentration under illumination that could be improved by tuning the composite design.

3.7.1. Photodegradation kinetics

Non-linear regression was applied to evaluate the degradation kinetics, employing pseudo-zero-order, pseudo-first-order, and pseudo-second-order models to fit the experimental data. The fitted parameters are summarized in Table 1. Most of the reported photocatalyst degradation reactions of organic pollutants by MIL-125-NH₂ in water fit pseudo-first-order kinetics [30,49,50], a general tendency that agrees with our fitting to a 1st-order kinetic for the TMP photo-degradation. In turn, the kinetic of TMP degradation when MIL-125-NH₂ is immobilized in CH is better fitted to a pseudo-zero order (Fig. 4b and Figure S5). However, when looking at the tendency in more detail, it seems that it is an activation/latent period of 60 min after the illumination where the TMP concentration is maintained almost stable. Afterward, the kinetics of degradation for CH@MIL-125-NH₂-10% started to fit better with the 1st-order model proposed for MIL-125-NH₂ but still had a lower overall rate in comparison to the MOF obtained.

The photodegradation of trimethoprim using various reported metal-organic frameworks fitted to the pseudo-first-order degradation kinetics [51,52]. This adherence is further validated by the high R-squared values associated with these MOFs, affirming the suitability of the pseudo-first-order model in describing the photodegradation reaction.

The photo-degradation capacity of a complex composite system studied in this work depends on various parameters, including the amount and type of photocatalyst oxygen species produced, the geometry, the light absorption, and the porosity of the catalyst [53,54], to mention the most relevant ones. Thus, the complex kinetics observed in our experiments might arise from the sum of two effects: (i) chitin is not a semiconductor and reduces the light transmission to the active material, and (ii) the degradation kinetic behavior would also probably be

derived from the diffusion process of TMP and reactive oxygen species within the CH/MIL-125-NH₂ composite and (iii) the CH matrix could partially consume the reactive oxygen species generated at the surface of the MOF particles.

3.7.2. Effect of pH on adsorption capacity and photodegradation performance

The adsorption behavior of a composite was studied in aqueous solutions of different pH values ranging from 4 to 8. The composite exhibited adsorption capacity at all pH levels. However, acidic pH was identified as the most effective condition for adsorbing TMP, probably due to its weak base nature (pK_a = 7.2) [55]. At acidic pH, TMP was protonated and could be adsorbed by physical interactions such as electrostatic interaction and hydrogen bonding [56]. The interplay between the protonation state of the adsorbate and the surface charge of our CH@MIL-125-NH₂ composite at acidic pHs can play important roles during adsorption [57]. This process was confirmed by the presence of significant adsorption capacity at pH 4 compared to pH 6. At pH 8, as the protonation of TMP is lower than its pK_a, the negatively charged surface sites on the composite were not able to adsorb neutral TMP. Thus, the adsorption capacity of the composite at a basic medium presented the contribution of hydrophobic interactions (Van der Waals forces), which resulted in lower adsorption capacity at pH 8 compared to acidic pH. Additionally, the adsorption capacity of MIL-125-NH₂ and CH@MIL-125-NH₂-10% were similar. Therefore, incorporating the MOF into the chitin structure does not affect the adsorption capacity of the MIL-125-NH₂.

The effect of the pH of the media on the photocatalytic degradation of TMP by MIL-125-NH₂ and CH@MIL-125-NH₂-10% was analyzed as the next step of the research (Fig. 4(c) and (d)). Acidity or alkalinity does not significantly change the photo-degradation efficiency rate. According to the results, both the parent MIL-125-NH₂ and the one immobilized within the CH matrix continue to exhibit the same performance in terms of adsorption. At the same time, the CH@MOF composite shows slightly lower photo-degradation kinetics, independently of the pH of the media.

3.7.3. Effect of water composition on adsorption capacity and photodegradation performance

This research also considered the practical application of our composite photo-degradation performance on waters collected from different geographical locations in Argentina and spiked with TMP. The water samples were collected from Luque, Colón, Santa Clara, and Roque Perez cities in Argentina, and their physicochemical characteristics are summarized in Table S3 of the supplementary information file. In brief, all the water samples share similar pH values but differ in ionic strength and composition. The TMP was dissolved in these water matrices until a concentration close to 100 mg/L⁻¹ was obtained, as corroborated by liquid chromatography. Despite the compositional complexity of the waters, several general tendencies of the TMP removal efficiencies were observed during the adsorption and photocatalysis steps, as shown in Fig. 5(a) and (b). Firstly, the MIL-125-NH₂ and CH@MIL-125-NH₂-10% adsorption capacity in all spiked water samples decreases compared to the experiments performed in distilled water. The concurrence of TMP with other organic and inorganic competitors partially blocks the access of the antibiotic to the adsorption sites. In turn, this adsorption-capacity loss seems to be related to the organic components of the water since both the active material and the

Table 1
The calculated parameters of the pseudo-zero-order (equation (5)) pseudo-first-order (equation (6)) and pseudo-second-order (equation (7)) model for MIL-125-NH₂ and CH@MIL-125-NH₂-10%.

Materials	Pseudo-zero-order			Pseudo-first-order			Pseudo-second-order		
	R ²	χ ²	k ₁ (mg/L min)	R ²	χ ²	k ₂ (min ⁻¹)	R ²	χ ²	k ₂ (L/mg min)
MIL-125-NH ₂	0.926	7.059	0.132±0.02	0.966	3.190	(1.5±0.2)×10 ²	0.868	12.55	(1±0.38)×10 ³
CH@MIL-125-NH ₂ -10%	0.957	1.443	0.08±0.001	0.941	1.984	(4±0.4)×10 ³	0.900	3.358	(2±0.3)×10 ⁴

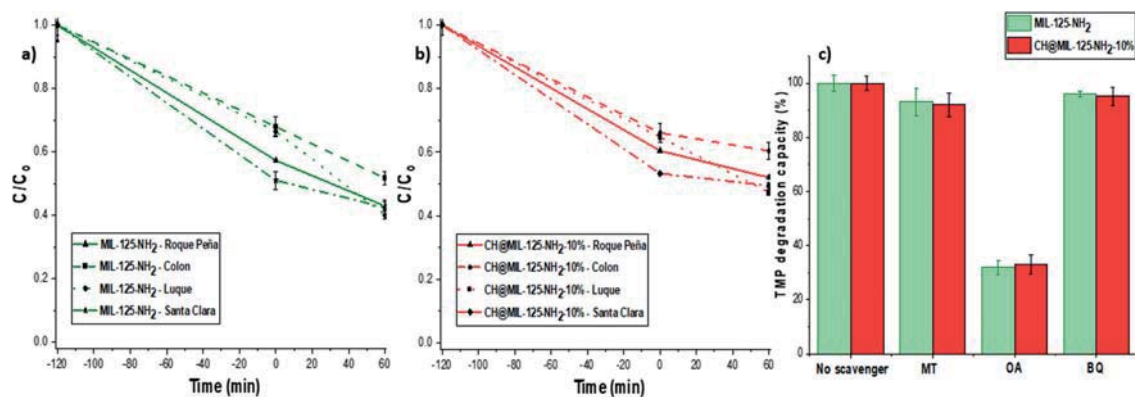


Fig. 5. Photocatalytic degradation of TMP ($C_0 = 100$ mg/L) in waters collected from different geographical locations of Argentina with MIL-125-NH₂ (a) and CH@MIL-125-NH₂-10% (b). Evaluation of the scavengers on the photocatalytic efficiency.

composite work slightly better in water matrices with higher contents of total dissolved solids and inorganic ions as K⁺ and Cl⁻ (i.e. Santa Clara and Roque Perez) presented higher adsorption capacity. In contrast to the observed adsorption behavior, the presence of inorganic cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and anions (Cl⁻, NO₃⁻) (Supplementary Table 3) in the water does not interfere with the photocatalysis process except when Luque-water was assayed. In this case, the kinetics of the photo-degradation are accentuated. Although many possible factors could give rise to this trend when it was used with complex ionic composition, the sulfate content of Luque-water could play a promoter role during the photooxidation of TMP, as reported in the literature for other photocatalysis organic pollutant degradation processes [58–60].

3.7.4. Mechanism of photodegradation

In order to investigate the mechanism and reactivity paths involved during the photocatalysis, methanol (MT), oxalic acid (OA), and benzoquinone (BQ) were employed as a scavenger for hydroxyl radicals (OH[•]), positive holes (h⁺), and superoxide radicals (O₂^{•-}), respectively (Fig. 5(c)). The photo-degradation of TMP was scarcely affected by MT and BQ. In contrast, the photocatalytic degradation of TMP declined significantly with the addition of OA. Although OH[•], h⁺, and O₂^{•-} can possibly be involved in the TMP photo-oxidation, h⁺ seems to have an essential role. Furthermore, the CH scaffold does not alter the TMP

photo-degradation mechanism as derived from ANOVA one-way test analyses between photocatalytic efficiencies among scavengers for MIL-125-NH₂ (a) and CH@MIL-125-NH₂-10% ($p > 0.05$).

3.7.5. Reutilization cycles and regeneration

The recyclability and stability of our system were rigorously assessed (Fig. 6(a)). In order to standardize the photocatalytic process, we set the TMP degradation fraction of the first cycle as the 100% reference point for both MIL-125-NH₂ (a) and CH@MIL-125-NH₂-10% (Fig. 6(a)). Here is where the integration of the MOF into the CH scaffold makes the difference, since the overall performance of CH@MIL-125-NH₂-10% is maintained after four photocatalytic and activation cycles (i.e. 97% (ANOVA one-way ($p > 0.05$))), while the activity of the MOF in dispersion decay significantly down to a 70% of the initial value. In fact, the XRD data points towards a complete structural collapse of the MOF framework. In contrast, the structural stability of some fraction of the MIL-125-NH₂ sample is still maintained after four cycles, although a significant degradation was also observed by XRD (Fig. 6(c)). Furthermore, no meaningful changes were observed in the structure of α -chitin by XRD after use. Moreover, if the composite structure is altered or disassembled during the photocatalytic process, leading to the release of MIL-125-NH₂, its photocatalytic performance would be significantly reduced, in contrast to our data.

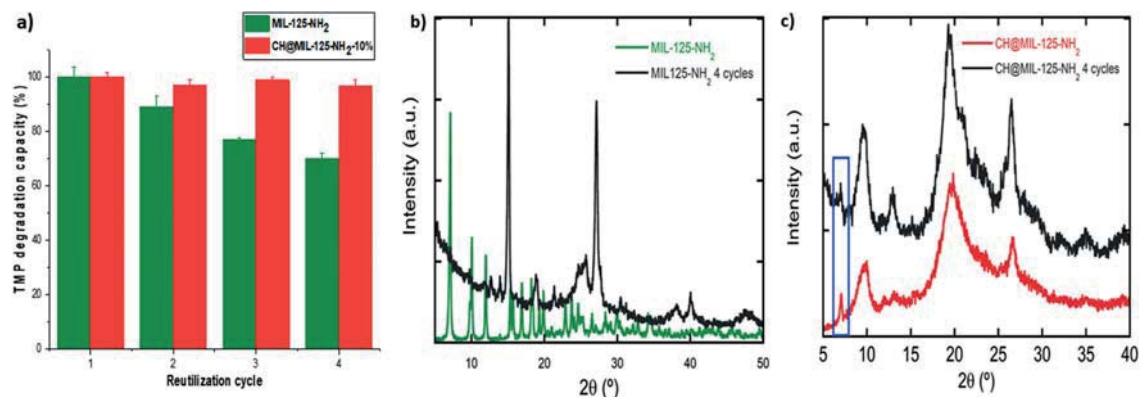


Fig. 6. TMP degradation efficiency ($C_0 = 100$ mg/L) of MIL-125-NH₂-10% and CH@MIL-125-NH₂-10% on different degradation cycles (degradation efficiency was normalized using the degradation fraction of the first cycle as 100%) (a). XRD diffractograms of MIL-125-NH₂-10% and CH@MIL-125-NH₂-10% after and before the photocatalytic experiments (b and c).

Seldom works assessing pristine MIL-125-NH₂ (without any further covalent MOF modification) for photocatalytic degradation report the reusability of the material. On the other hand, modifications of this MOF showed to be stable upon several reuse cycles [45,61]. Stability upon reusability has been tested as well on homolog systems as MIL-125-NH₂ doped with Ag₃VO₄ and Ag₂WO₄ nanoparticles, but the significant decay of the photo-degradation (~20% after four reuses) points towards a certain chemical instability of the initial material [62]. On the other hand, the degradation efficiency performance achieved in the present study was comparable or superior to the reported in the literature for other composites that tested their photocatalytic performance with TMP [26,52]. It is worth noting that the TMP initial concentration was above the usual values that can be found in polluted waters for all the studied systems, but still, the works in literature employed concentrations much lower initial concentrations, between 10 and 20 mg/L, compared to this study, which employed 100 mg/L. Hossam et al. tested the photocatalytic system of a MOF (MIL-53(Al)/ZnO) for trimethoprim degradation (starting concentration of 10 mg/L) with an efficiency of around 80% achieved after four recycles [52]. While chitin with TiO₂ or ZnO nanocomposites were tested for trimethoprim degradation, and the efficiency was almost 100%. However, the initial concentration of TMP was 20 mg/L, and the testing lasted 7 hours with four reuse cycles [26].

As depicted in Fig. 7, the overall functional mechanisms of CH/MIL-125-NH₂ composites need to be explained, taking into account different factors. First, CH acts as a filter for the ultraviolet radiation for the MIL-125-NH₂ and, thus, limits the light adsorption to the amino groups of the organic linkers. The electron/hole separation is likely to be triggered at this point, where both can generate radical oxygen species via oxidation and reduction processes in water. Nevertheless, as revealed by the experiments performed with the presence of scavengers, the oxidation of TMP seems to be driven by positive holes instead of ROS.

In addition to protecting against UV-Vis light, the CH shield seems to have an important role in preventing or minimizing the contact of acidic or basic species generated during the operation or activation of the MOF nanoparticles. This shielding effect delays the MIL-125-NH₂ degradation, even when exposed to the stringent conditions of the activation process.

To summarize, the CH@MIL-125-NH₂-10% composite demonstrates superior and sustained photocatalytic performance in terms of stability after degrading trimethoprim four times, making it an efficient and durable sorbent and photocatalyst filter. This achievement was thanks to the chemical stability of MIL-125-NH₂ when incorporated into the CH matrix.

4. Conclusion

This study presents a novel technique for generating photocatalytic composites using photoactive MIL-125-NH₂ and chitin. This method surpasses conventional approaches in literature owing to its simple process and absence of chemical alteration. The composites were effectively developed and evaluated, exhibiting their remarkable potential to eliminate TMP from different genuine water samples. Furthermore, this extensive analysis verifies the consistent photocatalytic performance of the composites in diverse waters collected from different geographical locations in Argentina. The most promising combination of MOF/CH exhibited an efficiency of approximately 85% in removing trimethoprim from water through adsorption and photo-degradation. Even though the MIL-125-NH₂ remains accessible for TMP adsorption after being immobilized into the CH porous scaffold, its effectiveness in photodegrading trimethoprim is greatly reduced. This is likely due to a combination of restrictions caused by interparticle interactions and partial light absorption by the CH matrix. Moreover, the

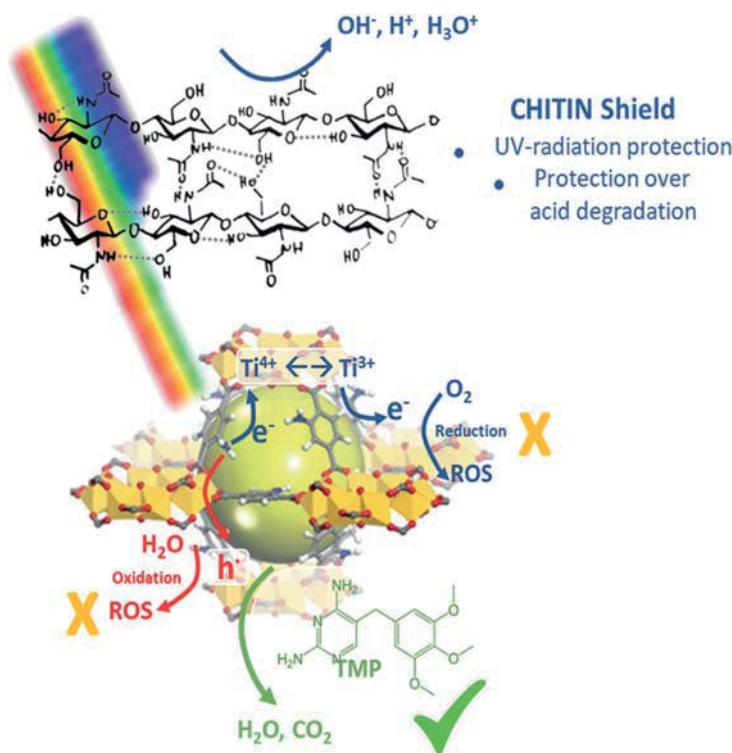


Fig. 7. Functional mechanisms involved in the photocatalytic degradation of TMP by CH/MIL-125-NH₂ composites.

chitin framework allows for the regeneration and reutilization of MIL-125-NH₂ after multiple cycles. It was determined that 10% wt/wt of MIL-125-NH₂ was the recommended load into the chitin matrix. The CH@MIL-125-NH₂ displayed excellent performance across a wide range of pH and compositional variations found in waters collected from different geographical locations in Argentina. In addition, the CH scaffold effectively protected MIL-125-NH₂ from chemical degradation. The CH stabilizes the MIL-125-NH₂ even after multiple reuses. This is the first photocatalytic composite based on MIL-125-NH₂ and chitin using a straightforward and green-based method for its assembly, in contrast with previous reports. In fact, advanced manufacturing processes applied to this system can balance the light harvesting and photocatalysis function to the sorption of the intermediate products generated during the water treatment of antibiotics or alternative organic contaminants in water.

CRedit authorship contribution statement

María Luz Peralta Ramos: Writing – original draft, Methodology, Investigation, Data curation. **Ainara Valverde:** Writing – original draft, Methodology, Investigation. **Jonas Perez Bravo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Funding acquisition, Conceptualization. **Roberto Fernández de Luis:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis. **Francesca Bonino:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Margherita Cavallo:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Guillermo Javier Copello:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests. Jonas Jose Perez Bravo reports financial support was provided by University of Mons. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Acknowledgments

J.J.P.B. is grateful for his postdoctoral fellowship granted by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). The authors thank Dr. Giorgieri for assisting with waters collected from different geographical locations and their composition determination. This work was supported by grants from Universidad de Buenos Aires (UBACyT 20020170100125BA, UBACyT 20020190100265BA) and Agencia Nacional de Promoción Científica y Tecnológica (PICT 2018–01731, PICT 2019–03757). The authors thank the financial support from the Spanish Agencia Estatal de Investigación (AEI) through EVOLMOF PID2021–122940OB-C31 (AEI/FEDER, UE) (including FEDER financial support). The MSCA-RISE-2017 (No 778412) INDESMOF project, which received funding from the European Union's Horizon 2020 research and innovation programme is also acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.113005.

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