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Chapter 10

Design and characterization of MOFs (Metal Organic Frameworks) for innovative applications

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1. INTRODUCTION

1.1. Metal-Organic Frameworks as hybrid materials

Hybrid framework materials are constructed from a combination of organic and inorganic units at the molecular/nanoscale level. The incredibly rich structural diversity and chemical versatility of such materials can lead to the emergence of unique and novel properties at the meso- and macroscale that open access to a wide spectrum of multifunctionalities not present in traditional materials. The exploration of structure-function relationships has then attracted considerable interests in broadening the combination of chemically bound organic and inorganic building blocks to yield an increasingly large number of 1D, 2D and 3D frameworks. In this respect, metal-organic frameworks (MOFs) are amongst the most extensively studied hybrid framework materials and they have garnered major developments in the last decades mainly because of their nanoporous and tunable architecture (1–4).

Basically, MOFs are comprised of an inorganic part, usually formed by either metal ions or small clusters (e.g. metal-oxide) that acts as a node in a network, and an organic ligand that operates as a linker, or a spacer, among the nodes to form the framework through metal-ligand coordination bonds. This is schematically sketched in Figure 10.1. In a broader sense, they correspond to

coordination polymers but with a porous (and in most cases crystalline) structure that is architecturally stable and rigid, as zeolites. In addition, they show a high and ultra-high porosity that, in some cases, is even larger than common adsorbents (5). Furthermore, post-synthetic modifications of the organic linkers (6), multivariate structures (i.e. multiple functionalities in a single MOF) (5,7) and host-guest interactions have been achieved (8).

Therefore, MOFs with their unique structure and the tunability of their organic and inorganic components show an incredible chemical versatility, such that they have been defined as nano-laboratories. It is not unexpected then that these materials have attracted a lot of interests in the last decades for their potential application in many areas: from capture, storage, separation and conversion of gases (5) to (photo-)catalysis (9) and drug delivery (10), from optoelectronic (e.g. low-k dielectric materials) (11) to sensors (12), from magnetism and ferroelectricity (13) to light harvesting and energy transfer (14).

Other kinds of materials with a porous framework that have recently attracted an increasing interests such as Zeolitic Imidazolate Frameworks (ZIFs), Covalent-Organic Frameworks (COFs) and Porous Aromatic Frameworks (PAFs), to mention a few, will not be discussed in the present work.

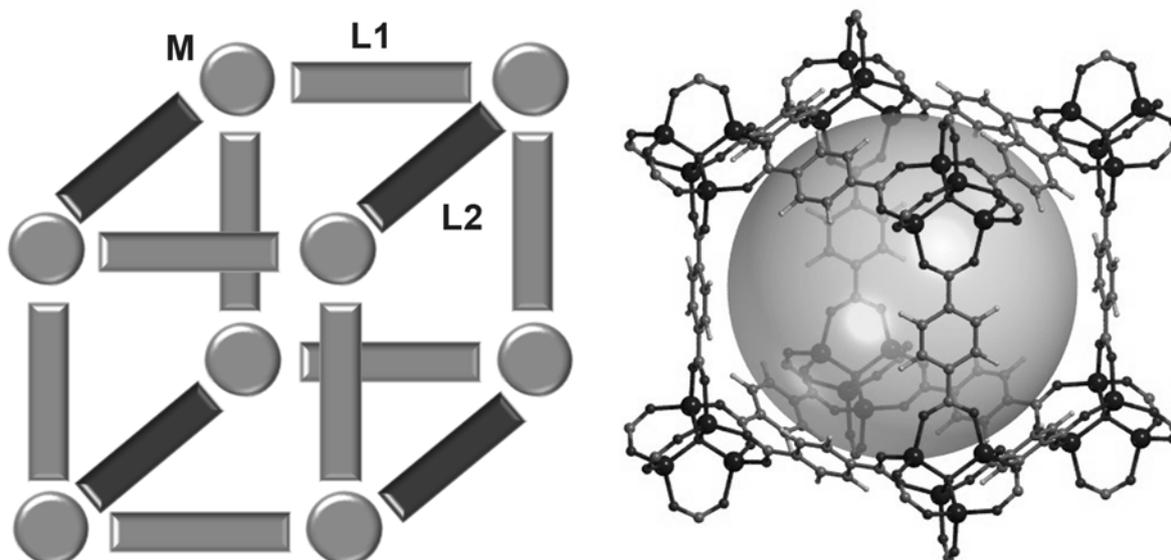


Figure 10.1: (left) a schematic representation of a metal-organic framework with the metal ions (M) acting as nodes and the organic ligands (L1, L2) acting as spacers to form a robust and porous

crystalline structure. (right) The porous crystalline structure of IRMOF-1 (also known as MOF-5). The grey sphere shows the large accessible volume in the structure. [Adapted from Ref. (15) with permission of The Royal Society of Chemistry 2006]

In the following, we will discuss firstly basic concepts on the design (see Section 1.2), synthesis and characterization of MOFs (Section 2). The use of MOFs for gas capture/storage (Section 3.1) and catalysis (Section 3.2) will be then presented, along with a brief overview of innovative applications of MOFs as energy related materials (Section 3.3) and biomaterials (see Section 3.4).

1.2. Structure and design

O’Keeffe and co-workers have rationalized MOFs structures on the basis of a network analysis in several exemplary works (see ref. (16) and references therein). The inorganic and the organic components of the structure can be considered as secondary building units (SBUs) from which the whole framework can be built. Some examples of most common SBUs and crystal structures of MOFs are shown in Figure 10.2 and Figure 10.3, respectively.

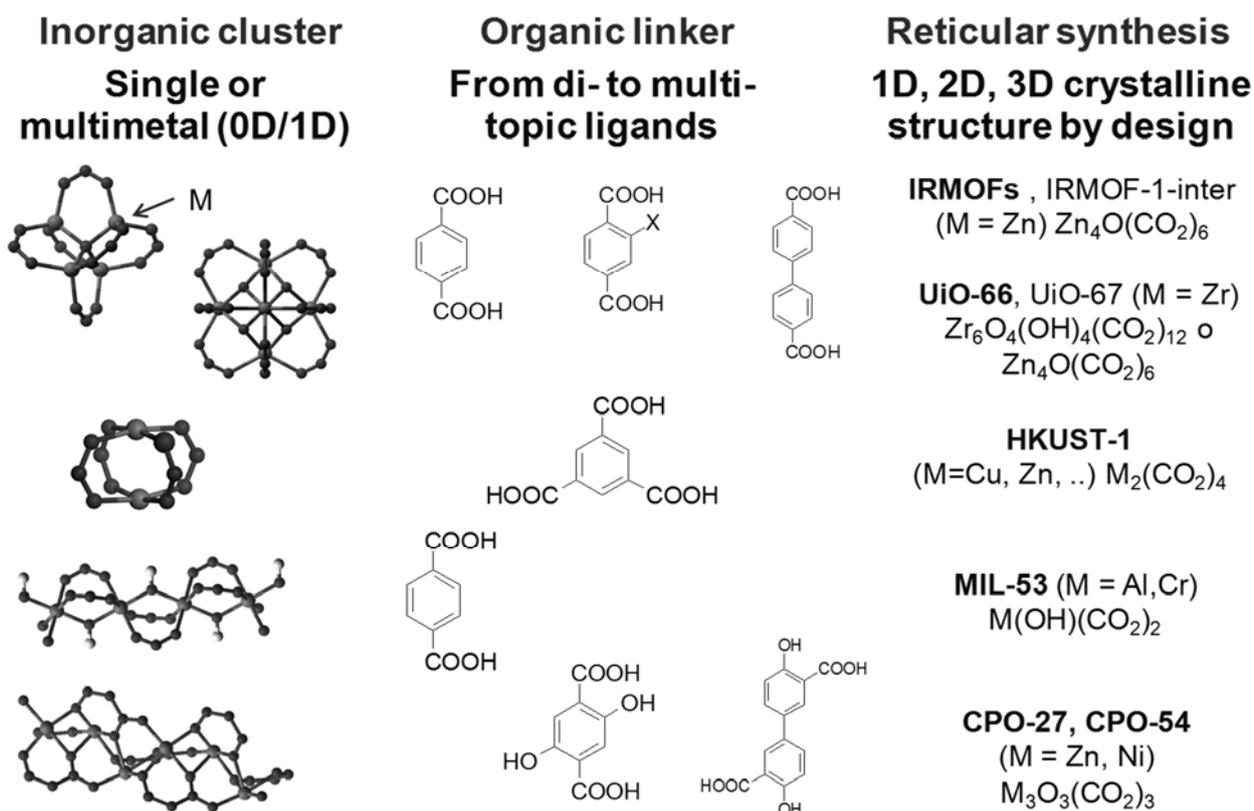


Figure 10.2: Examples of inorganic and organic components of most common MOFs. The two components represent the secondary building units from which the framework is built.

Therefore, the identification and description of the nets that describe the underlying topologies of the structure of MOFs have allowed the design of targeted networks and the use of combinatorial chemistry for a rational design of the structures. For instance, the Reticular Chemistry Structure Resource is a collection of more than 2000 different nets (17). On a practical viewpoint, such knowledge has been crucial to guide and tailor the synthesis of MOFs through a modular process that has been denoted as reticular synthesis. This has led to the synthesis of a paramount number of MOFs with different structural topologies and chemical diversity.

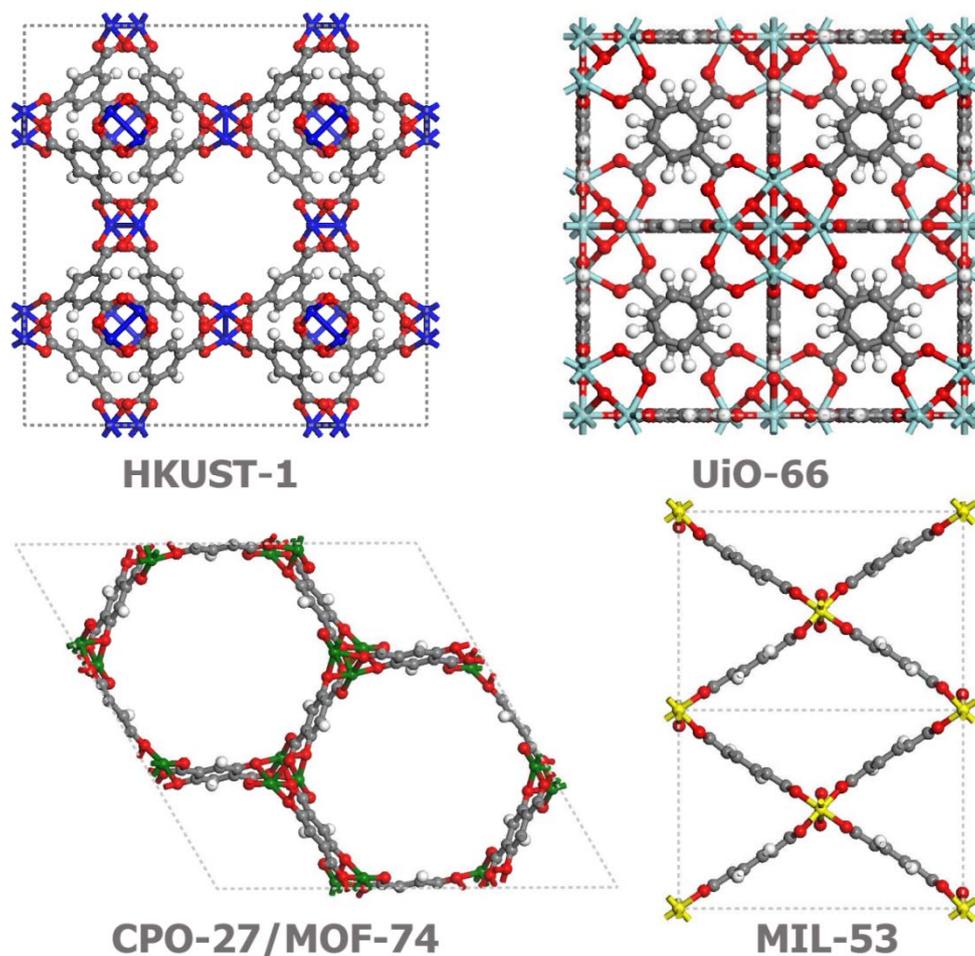


Figure 10.3: Crystalline structures of common MOFs built with secondary building units depicted in Figure 10.2.

MOFs' unique properties can then be tuned by playing with their three main structural features: the metal, the organic ligand and the framework (see Scheme 10.1).

MOFs properties

Design			
How to change	Structural units to be modified		
	linker	metal	guest molecules
specificity of the interaction	x		x
breathing	x	x	x
pore size	x		
pore volume	x		
working capacity	x	x	x

Property	Techniques		
capacity	Volumetry Gravimetry	Breakthrough measurements	Modeling
selectivity	Volumetry Gravimetry	Breakthrough measurements	Modeling
energetic of interaction	Volumetry Gravimetry	Microcalorimetry, DSC, VTIR	Modeling
adsorption sites	IR, NMR, UV-Vis, XAS- XES,	fluorescence, NMR,...	Modeling

Characterization

Scheme 10.1. Design strategies applied to MOFs and characterization techniques to determine the properties in different application fields.

Alternatively, the structural complexity of MOFs have been compared to the structure of proteins and rationalized according to four hierarchical levels (18,19):

- *Primary structure*: organic ligands, metal cations and the coordination sphere. This represents the first structural level that refers to the basic bricks of the framework: the building blocks or secondary building units.
- *Secondary structure*: the way the SBUs assemble to form the crystalline structure can lead to the different topologies of the net and this represents the second structural level.
- *Tertiary structure*: the next level includes the inter-linker interactions and the formation of intertwined networks. It can be regarded as a first supramolecular level. This structural level is related to important effects such as framework dynamics and structural flexibility.
- *Quaternary structure*: this level refers to the possible interaction with other structural elements such as framework-guest interactions and can be considered as a second supramolecular level.

Structural complexity then acts at different length scales and influences the functionality of the material. It is clear then why MOFs have an enormous potential for many practical applications as will be discussed in Section 3.

2. SYNTHESIS

A great amount of effort was spent in the last two decades on the bottom-up synthesis of metal-organic frameworks (18,20,21): the ability to tune the performances of these materials for selected applications has in fact to pass through the sieve of a successful and reliable synthesis.

Generally speaking one has to find the synthetic conditions that lead to a defined inorganic unit without decomposing the organic linker. Moreover, at the same time the material has to nucleate and grow with an appropriate kinetics in order to have a crystalline product. To overcome this

complex series of requirements, several synthetic methods have been used going from Conventional Electric (CE) to Microwave Heating (MW), Electrochemistry (EC), Mechanochemistry (MC) and Ultrasonic (US) methods as depicted in the top part of Figure 10.4.

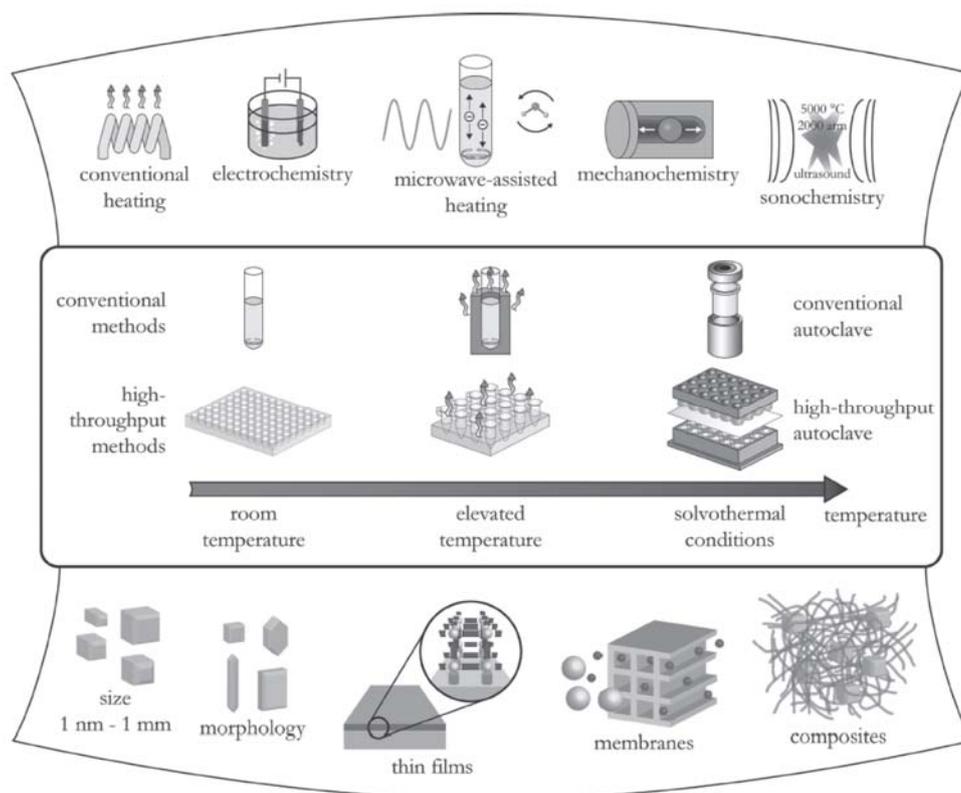


Figure 10.4: A pictorial representation of the most common synthetic methods (top), synthetic conditions (middle) and final products (bottom) in MOF synthesis. [Reproduced from Ref. (20) with permission, copyright ACS 2012]

The most common synthetic procedure for a MOF considers to put the linker and the metal precursor in a closed vessel with a suitable (commonly polar) solvent, and heat the solution in a controlled way, often with programmed heating and cooling ramps. Among the others, the most commonly used non protic solvents are dimethylformamide (DMF) and diethylformamide (DEF) whereas water or methanol are the most common choices among protic solvents. The synthetic reactions can be distinguished in solvothelmal or nonsolvothelmal, if the temperature is above or beyond the boiling point of the used solvent. The controlled additions of reagents like modulators,

Structure-Directing Agents (SDAs) or mineralizers is widely used in MOF synthesis. A modulator is a monodentate ligand having the same chemical functionality of the linker and which is able to compete with it during the synthesis, thus modifying the process of nucleation and growth: the crystal size and morphology are greatly influenced by modulators as studied by Hermes et al. (22). SDAs are also used (in a tight comparison with their usage in zeolite synthesis) (23) to fill the pore space and so “support” the formation of the framework. An example can be found in the synthesis of the DUT-8 (24,25) ($\text{Ni}_2(2,6\text{-ndc})_2(\text{DABCO})$) MOF which requires the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) in the synthetic solution to get this kind of structure. SDAs can be removed in some cases during activation. Mineralizers, on the other hand, are added in order to help the dissolution of the starting materials in the reaction mixture. Common mineralizers are for example acids, bases or fluoride salts.

Such an extremely wide set of synthetic parameters (concentration, temperature, reaction time and additives) has to be optimized through exploratory synthesis and reasoned guesses. To overcome this time-consuming work a so-called High-Throughput (HT) synthesis approach has been developed by Stock et al. (26,27) in order to accelerate the discovery of new compounds and the optimization of the synthetic parameters. This is done generally filling multi-welled reactors with reaction mixtures and varying systematically the parameters, like the linker-metal ratio, the concentration or the addition of modulators, SDAs or mineralizers. The products, after filtration, are characterized by fast and automated PXRD measurements and the patterns are compared to databases containing simulated diffractograms of the known reagents used in the synthesis. Through the analysis of large sets of data, relevant trends and crystallization fields can be found. The whole procedure is depicted in Figure 10.5.

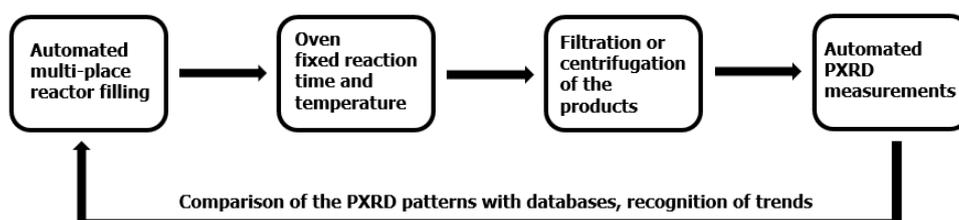


Figure 10.5: Flowchart showing a High-Throughput (HT) approach to the MOFs synthesis.

2.1. Basic characterization

Once the synthesis has been optimized (that is, it is able to give rise to a phase-pure product with a acceptable yield) the classical basic characterization steps that can be followed are: (i) structure determination by X-ray diffraction (Section 2.1.1), (ii) assessment of the thermal stability by Thermogravimetric Analysis (TGA, Section 2.1.2) and (iii) surface area measurements by means of N₂/Ar adsorption volumetry (Section 2.1.3). NMR spectroscopy of the solubilized MOF can be also useful to obtain quantitative information about the organic moieties present in the final material as the relative ratio between linkers and modulators (see Section 2.1.4).

2.1.1. X-ray diffraction

The determination of the crystal structure is favorably and preferentially obtained through single-crystal X-ray diffraction (SCXRD) experiments: this technique requires to grow a crystal of suitable dimensions and collect a diffractogram in order to solve the structure with the powerful techniques of the modern X-ray crystallography. A suitable crystal size for this kind of analysis is in the hundreds of micrometers range, for laboratory diffractometers, meanwhile for synchrotron sources also smaller crystals are adequate. Besides the optimization of the synthetic parameters (20), also more advanced strategies have been exploited like reverse microemulsions or diffusion-limited growth (20) in order to grow a single crystal of sufficient dimensions. For those materials all the efforts have failed in this sense, the less straightforward work of solving the structure from a powder diffractogram can be tempted. In this case, complementary information coming from elemental analysis (by ICP-MS measures), oxidation state determination (from XAS, XPS and UV experiments) or ab-initio modeling are even more important to drive the structural determination toward a correct structure.

2.1.2. Thermogravimetry

TGA methods are very useful in the first steps of the characterization of MOFs: beyond the ultimate thermal stability (i.e. the maximum temperature the framework can withstand without collapsing) information about loss of guests inside the pores (for example adsorbed solvent molecules) or about defectivity can be easily extracted from TGA data, as shown by Shearer et al. (28). In particular, they quantified the concentration of defects in UiO-66 materials through TGA data that allowed also to correlate the concentration and nature of the defects with the thermal stability of the materials. Hyphenation of thermogravimetry with mass spectrometry (TGA-MS) can be very useful to extract chemical details on the nature of the desorbed species. The combined use of thermogravimetry with variable-temperature X-ray diffraction studies (VTXRD) allows to understand how the structure changes during thermal treatments. This was exploited by Ethiraj et al. (29), where the progressive loss of guest solvent molecules inside the pores was correlated with modifications of the crystal structure.

2.1.3. Gas adsorption volumetry

Being MOFs porous materials, an evaluation of their porosity can be done from adsorption isotherms of probe molecules (i.e. N₂, Ar, or CO₂) physisorbed on the surface of these frameworks. An overview of what can be measured with this kind of experiments is published by Thommes et al. (30). Volumetry can be also used as a technique to optimize the activation procedure for a MOF. The increase of the surface area is the most obvious evidence that activation (i.e. the removal of guest molecules trapped inside the pores) is successful and gives rise to accessible voids inside the framework without causing its collapse. Coupling of these data with structural information coming from crystallographic techniques can be very useful as highlighted in the work by Ethiraj et al. (29) which rely on the solvent-removal driven structural changes and their effects on the adsorption and separation properties of N₂ and CO₂.

2.1.4. NMR spectroscopy

Solution NMR spectroscopy involves the dissolution of the MOF in a suitable deuterated solvent, like NaOD/D₂O, and the analysis of the resulting spectra to quantify the organic components

(linker, modulator and pore-filling solvent) present in the sample. A quantification of the defects present in an acid modulated UiO 66 can be found in the work by Shearer et al. (31).

2.2. Linker functionalization

Slight different linkers leading to different chemical functionalities can be used in MOF synthesis to obtain isostructural MOFs having peculiar and tunable properties (5): examples can be found in mixed-linker amino-functionalized Fe-MIL-101 (32) or UiO-66 (33) with $-NH_2$ groups dangling on the linkers. The tuning of the $-NH_2$ concentration in the MOFs allowed to modify in a controlled way the sorption properties of these materials especially towards for example carbon dioxide.

2.3. Post-synthetic functionalization

Chemical modifications of the MOF framework after the synthesis can be exploited to tune their properties: this area has been extensively reviewed in literature (34,35). Shearer et al. (36,37) succeeded to introduce the monoethanolamine (MEA) moiety into a UiO-66 framework through a two-step procedure: first the framework has been synthesized with a huge number of “missing cluster” defects through the presence of benzoate moieties, then these have been exchanged firstly with formiates and then with MEA moieties in a post-synthetic ligand exchange (PSE). The CO_2 sorption properties of the material have been extensively characterized.

Other approaches consider the coordination of metallic species (as Pt and Cu) to bipyridine-functionalized UiO-67s, like the one followed by Øien et al. (38) and Braglia et al. (39), to create potential candidates to be used in heterogeneous catalysis.

3. CHARACTERIZATION AND INNOVATIVE APPLICATIONS

3.1. Gas storage

Gas storage is a crucial technology in applications related to energy (see Section 3.3), environmental, and health care (see Section 3.4). MOFs flexibility in design makes them an ideal

class of materials for gas storage that in fact constitutes their most common field of application and the most studied one by the authors. For this reason, this topic has been deeply treated in the present chapter. The possibility to change the linker and the metal nodes has, as direct consequence, the possibility to tailor during the synthesis the surface area, pore volume, pore shape and functionality of the material toward a specific adsorbate. For this reason MOFs have been proposed for gas storage and purification of a very large number of systems, going from H₂(40) to gasoline(41,42) and air.(43,44) The design strategies and the characterization techniques applied to MOFs for gas storage applications are reported in Scheme 10.1.

Another peculiarity of MOFs, that makes them particularly suitable for gas adsorption, is their structure flexibility: in fact, MOFs structure not only responds to the presence of adsorbates more than what observed for other classes of materials but also they can undergo to structural transitions upon pressure or temperature change.(45) This means that during the adsorption process, a MOF can change drastically its porosity,(46) a property with no analogy with any other crystalline material. It is interesting that in most cases the modification is fully reversible, and for this reason the word “breathing” is used to describe this reversible structural modification. One of the most famous examples of breathing MOFs is MIL-53,(45,47,48) where the volume cell decreases of about 30% upon adsorption, that is it shows an opposite behavior with respect to the most part of breathing MOFs, that expand for coverage higher than a threshold value,(45) as for example M(bdp) (M = metal, bdp²⁻ = 1,4-benzenedipyrazolate).(49) The most part of breathing MOFs, as for example Fe(bdp), are almost no porous up to a certain threshold gas pressure at which a sudden structure expansion is observed. It is interesting that the phase transition in breathing MOFs is observed only if the adsorbate is able to develop an interaction with the framework of a sufficient strength. In MIL-53(Al), for example, while CH₄ shows a monotonic isotherm, CO₂ is able to cause the phase transition. This difference is related to the fact that CO₂ has a significant quadrupole moment while CH₄ has not (50). Although these are limit cases, the so-called breathing of the structure is a behavior typical of all MOFs, also of the ones topologically equivalent to structures

that are generally considered quite rigid. This is the case of $M_2(\text{dobdc})$ family, having the same topology of MCM-41, a mesoporous siliceous nanoscaffold. Nevertheless, while MCM-41 is considered a rigid material, $\text{Ni}_2(\text{dobdc})$ structure, although not changing phase, has been proven to respond to gas adsorption, being all the IR modes of the framework modified also at low gas pressure (<50 mbar) (51). MOFs structure flexibility is an advantage in gas storage applications: in this way, part of the heat evolved (or required) by the adsorption (desorption) process can be managed by a contemporaneous modification of the framework, allowing an intrinsic, although partial, heat control of the process (49) (see Section 3.1.1.).

The earliest report of a gas adsorption isotherm and permanent porosity in MOFs dates only 1998 for MOF-2.(52) Since then, several systems have been proposed and it is not surprising that, as noted by Furukawa (5), all the world record materials for gas storage belong to the MOF class. An expanded and updated version of the review reported in Ref. (53) is shown in Table 10.1.

In Table 10.1, the highest capacities ever reported for CO_2 , O_2 , CH_4 and H_2 are present, that is the four gases having the highest importance for energy and environmental applications. It is impressive that materials belonging to a class characterized by very low bulk densities are the ones showing the highest volumetric capacities for both CO_2 and methane (54,55). Besides gas storage, MOFs have also shown outstanding performances for gas separation. This is the case of $\text{Cr}_3(\text{btc})_2$ ($\text{btc}^{3-} = 1,3,5\text{-benzenetricarboxylate}$) showing the highest value of 22 for O_2/N_2 selectivity at RT (56). These results all rely on the possibility, starting from a MOF platform, to tune its gas capacities rationally by changing (i) the polarizing effect of the metal (55,57–64), and (ii) the length of the linker;(50,63,65) or by introducing functional groups in the material by (iii) modifying the linker (pre- or post-synthesis modifications) (33,66–68) or (iv) by grafting molecules bearing a certain functionality. (29,59,69,70) The influence of the different structural modifications on the gas storage performances in MOFs is discussed in the following sections. The way these different strategies influences the adsorption are schematized in Figure 10.6. Whereas at high pressures ($>4\text{-}5$ bar) and/or low temperatures ($T \leq$ condensation temperature of the adsorbate) the capacity is

strongly bounded up only with the MOF porosity,(66) at low pressure and/or high temperatures the situation is more complicated being the stored amounts dependent by the interbalance of all these factors,(66) as schematized in Figure 10.6. Moreover, it is evident that a high heat of adsorption corresponds to a higher uptake at low pressure. Nevertheless, it is important to stress that in order to have a material suitable for applications, the adsorption heat has to be as close as possible to the latent heat of evaporation.(65)

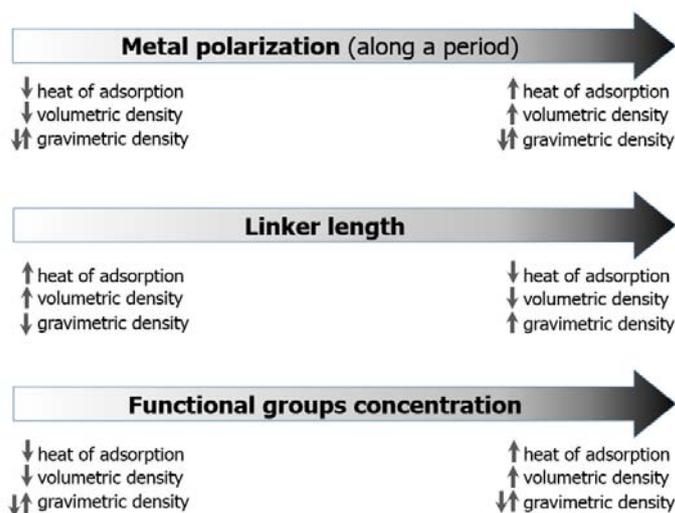


Figure 10.6: Effects of the MOFs structural modifications on the gas adsorption properties. The ↑ and ↓ arrows indicate an increase or a decrease in the associated property, respectively.

Table 10.1: Metal organic frameworks reporting the highest values of important properties for gas storage applications.

Highest value reported	value	material	Ref.
pore volume for a crystalline material	98 Å	IRMOF-74-XI	(71)
number of organic linkers	8	MTV-MOF-5	(72)
degree of interpenetration	54	Ag ₆ (OH) ₂ (H ₂ O) ₄ (TIPA) ₅	(73)
BET surface area	7140 m ² g ⁻¹	NU-110	(74)
pore volume	4.40 cm ³ g ⁻¹	NU-110	(74)
excess H ₂ gravimetric uptake (77 K, 56 bar)	99.5 mg g ⁻¹	NU-100	(75)
excess CH ₄ gravimetric uptake (298 K, 35 bar)	260 mg g ⁻¹	Al-soc-MOF-1	(65)
CH ₄ gravimetric working capacity (298 K and 5-65 bar)	360 mg g ⁻¹	Al-soc-MOF-1	(65)
CH ₄ volumetric working capacity (298 K and 5-65 bar)	210 cm ³ STP cm ⁻³	MOF-519	(54)
excess CO ₂ gravimetric uptake (298 K, 50 bar)	2347 mg g ⁻¹	MOF-200 and MOF-210	(53)
excess CO ₂ gravimetric uptake (298 K, 1 bar)	352 mg g ⁻¹	Mg ₂ (dobdc)	(55)
excess CO ₂ volumetric uptake (298 K, 1 bar)	174 cm ³ STP cm ⁻³	Mg ₂ (dobdc)	(55)
CO ₂ working capacity (1-40 bar)	1900 mg g ⁻¹	Al-soc-MOF-1	(65)
O ₂ working capacity at 298 K (5-140 bar)	880 mg g ⁻¹	Al-soc-MOF-1	(65)

3.1.1. Effect of the metal

The nature of the metal nodes has an important impact on the adsorption process. Metal ions with a higher charge to radius ratio, in fact, have a stronger withdrawing effect on the electrons of the organic ligand, thus increasing the polarity of the whole framework and then the gas uptakes.(47) Besides that, changing the metal node can simply change the conditions for the framework breathing or prevent it.(45–47,49,76,77) In M(bdp) MOFs, the “gate opening effect” is regulated by the π - π interactions among the central benzene rings of the pyrazolate linkers.(49) Co(bdp) and Fe(bdp) breath also upon adsorption of a low interacting molecule as CH₄, with a structure expansion at about 17 and 26 bar for Co(bdp) and Fe(bdp), respectively, during the adsorption and a structure contraction at about 10 and 15 bar in desorption.(49) The different threshold pressure indicates that the structure transition is more energy demanding for Fe than for Co. Although the working capacity is slightly lower than those reported for MOF-519 (197 and 190 cm³ STP cm⁻³ at

25°C in the 5-65 bar range for Co(bdp) and Fe(bdp), respectively, see Table 10.1), M(bdp) possesses an invaluable advantage related to the ability to breath during the adsorption/desorption cycle. In fact, the heat management in gas storing systems during the charge (exothermic process) and the discharge (endothermic process) is quite an important task in the implementation of such systems, requiring the presence of dedicated devices, that increase the total weight and volume of the total system, besides its cost and complexity.(49) Materials as M(bdp) offer the possibility to intrinsically manage this heat (fully or partially) using it for the structure transitions. Between the two isomorphs, the most effective heat management was obtained for Fe(bdp), for which only 64.3 kJ of heat was released per liter of CH₄ during adsorption at 35 bar, that is 41% lower than for a more rigid MOF, as HKUST-1.(49)

Metal sites can have a more direct effect on the adsorption process if they show one or more coordinative insaturations. This is possible in the case that the temperature necessary to remove precoordinated solvent molecules is lower than the decomposition temperature of the material (50). Open metal sites can be present as part of the framework (e.g. in MOF-74 and its isomorphs, see Figure 10.3) or, more rarely, as extraframework species (e.g. UTSA-16,(78) rho-MOFs,(79) and M₃[(M₄Cl)₃(BTT)₈]₂, BTT³⁻ = 1,3,5-benzenetristetrazolate; M = Mn, Fe, Co, Cu, Cd).(80) A complete activation of the material is in these cases even more important to be achieved in order to fully exploit their potentialities.(66) A characterization technique aimed to evaluate this, as IR spectroscopy, would have to be part of any gas adsorption study.(81)(68) A more exotic way to create open metal sites in MOFs having completely shielded cations is by metal exchange. This is the example of MOF-5, a Zn-based MOF where the metal ions are not accessible to incoming adsorbates being all the ligands oxygen atoms belonging to the structure.(82) Nevertheless, by leaving MOF-5 in presence of a solution of different metal salts, it is possible to substitute the Zn²⁺ ions with several other metals (Ti, V, Cr, Mn, Fe, Co, or Ni),(83,84) all of them coordinated within an unusual all-oxygen trigonal ligand field and, for this reason, accessible to both inner- and outer-sphere oxidants. Obviously, different metals are the optimal match for different adsorbate: in the

M₂(dobdc) series (also known as M-MOF-74, M-CPO-27 or IRMOF-74-I-M), nickel showed the highest affinity towards C₂H₂,(60) Xe (57), Kr,(57) CO (58) and H₂ (62), Mg for CO₂ (59,55) and CH₄,(61) whereas for O₂ the highest interaction energy was reported for the Fe-based material.(85)

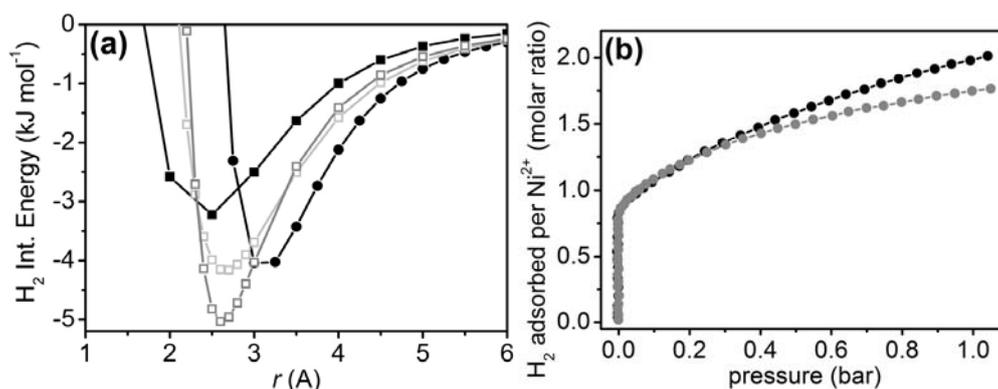


Figure 10.7: (a) Dihydrogen interaction energy on siliceous and carbonaceous rings.(86) Data obtained at the MP2 level of calculation for the interaction of a hydrogen molecule with C₆H₆ (circles), Si₆O₆H₁₂ (full squares), LiSi₅AlO₆H₁₂ (light grey squares), NaSi₅AlO₆H₁₂ (grey squares). Basis sets used: TZVp on the rings and aug-cc-pVQZ on the H₂ molecule. Data from Ref. (86). (b) Dihydrogen adsorption isotherms recorded at 77 K on Ni₂(dobdc) (grey circles) and Ni₂(dobpdc) (black circles). Data digitalized from Ref. (63).

3.1.2. Effect of linker dimension

Increasing the linker dimension is an easy way to increase both the pore volume and pore size in a MOF, maintaining the topology and its local properties. This has two evident effects on gas storage: an increase in both the maximal gravimetric gas capacity (because of the larger pore volume) and the gas diffusion (due to the larger pore size). Nevertheless, the increase in the pore size has another important effect, that is a decrease in the adsorption energy. In fact an increase in the pore size would correspond to a decrease in the superposition range between the van der Waals component of the potential energy from two opposite walls of the pore.(86) The superposition is null for pore dimensions larger than a certain threshold size, size that is different for different adsorbate and for different materials. In Figure 10.7a, it is reported as an example the energy potential calculated for

H_2 at different distances from an organic wall (black circles) and a siliceous one (black squares), in the case that no open metal sites are present (86). H_2 would adsorb at a distance of about 3-4 Å from a pore wall having no metal site. Assuming as threshold for the adsorption energy the value of 1 kJ mol⁻¹, it is evident that for size larger than 8-10 Å, there will be no efficient contribution to the adsorption energy from the opposite side of the wall for pores larger than 10 Å. This means that using a linker larger than a monophenyl one would cause a significant drop in the H_2 adsorption energy and then a decrease in the H_2 capacity get at a fixed pressure. The importance of micropores to have efficient H_2 storage has been repeatedly stressed in the literature. The presence of an open metal site causes itself an increase in the adsorption energy (see light grey and grey curves in Figure 10.7a). This means that in MOFs having strong adsorption sites, no significant effect on the adsorption isotherm is observed up to the saturation of these sites. At higher coverage a decrease of the incremental uptake is expected, in the same manner observed for MOFs without open metal sites.(63) This has been actually verified in a recent study for dihydrogen storage in $M_2(\text{dobdc})$ and $M_2(\text{dobpdc})$ with $M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$. Going from the monophenyl linker (dobdc^{2-}) to the biphenyl one (dobpdc^{2-}), the pore size is enlarged from 13-15 to 18-22 Å (crystallographic dimensions). For this reason, although the larger maximal capacity and an almost doubled surface area, all the $M_2(\text{dobpdc})$ are characterized by a gravimetric adsorption capacity only slightly higher than the corresponding $M_2(\text{dobdc})$ at 77 K and 1 bar (see Figure 10.7b). At RT and 100 bar, because of the larger thermal energy of the molecules that makes H_2 essentially unbound by the structure, the uptake scales with the surface area, having about 1.5 wt% of H_2 stored in $M_2(\text{dobpdc})$ and 0.7 wt% in $M_2(\text{dobdc})$.(63) Nevertheless, the lower material density of the $M_2(\text{dobpdc})$ makes the $M_2(\text{dobdc})$ more favorable on the volumetric storage point of view in all the temperature and pressure conditions considered in the study. Analogue results were reported for CO_2 (50), where the $\text{Mg}_2(\text{dobpdc})$ (black triangle scatters in Figure 10.8b) shows only slightly lower gravimetric capacities than $\text{Mg}_2(\text{dobdc})$ at RT an 1 bar (circles). For the isomorphous MOFs obtained with a triphenil linker, very low CO_2 uptakes where obtained (stars in Figure 10.8b).(87)This can be

associated to the significantly lower superposition of the potential energy for this MOF with respect to the other two. Nevertheless, this was not expected, being the adsorption enthalpy of the magnesium ion sufficient to guarantee an high affinity toward CO₂ at low coverage in these conditions. In this latter study, a significant low activation temperature was adopted (87) (120°C (69) versus and 250°C (88)) that it is known to be not able to free all the Mg²⁺ from the solvent for both Mg₂(dobdc) (88) and Mg₂(dobpdc) (89). In this study, the material was not checked after the activation by, for example IR. It is evident from this that the use of spectroscopies (as for example infrared spectroscopy) is mandatory to check the activation degree of a MOF material before to carry out quantification of the gas capacity.

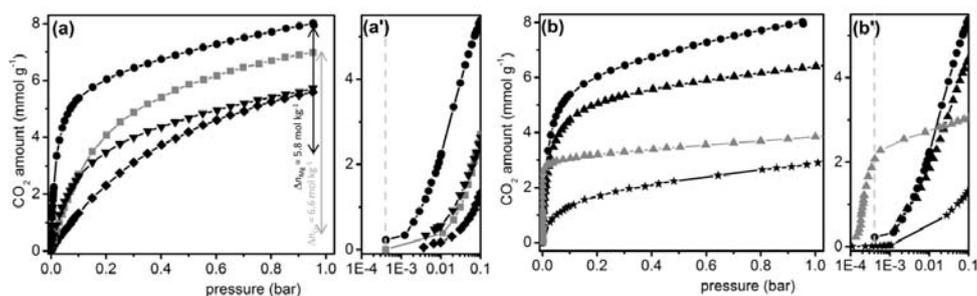


Figure 10.8: CO₂ excess adsorption isotherms on (a) M₂(dobdc) with M = Mg (circles), Co (squares), Zn (diamonds), Ni (triangles); (b) Mg₂(dobdc) (circles), Mg₂(dobpdc) (black triangles), mmem-Mg₂(dobpdc) (gray triangles) and IRMOF-74-III-Mg (stars). The vertical dashed line is placed at 0.4 mbar, that is at the atmospheric CO₂ partial pressure. [Adapted from Ref. (50) with permission of The Royal Society of Chemistry 2015]

For what concerns MOFs having no exposed metal sites, a comparison of the effect on the adsorption of the increase of the linker dimension is allowed by a recent study on the Al-soc-MOF family (65). The parent structure is in this case Al-soc-MOF-1, having as formula [Al₃O(TCPT)_{1.5}(H₂O)₃]Cl⁻, with TCPT = 3,3'',5,5''-tetrakis(4-carboxyphenyl)-p-terphenyl. This MOF is characterized by cages having aperture of 5.6 x 8.4 Å and by channels of 14 Å width (van der Waals dimensions). Its naphthalene and anthracene analogues have been also synthesized. Having Al-soc-MOF-1 pore dimensions close to the border between micro- and mesopores, it was expected

and verified that increasing the linker dimension caused a drop in the gas uptake for CO₂, CH₄ and O₂ (65). Al-soc-MOF-1, on the contrary, seems to possess the correct linker length to allow a simultaneous high gravimetric and volumetric capacities. This material actually showed record capacities for all the adsorbates considered (see Table 10.1).

3.1.3. *Effect of functional groups on the linker*

To increase the gas uptake of a material maintaining fixed the temperature, it is necessary to increase the adsorption heat. As stated above, starting from a certain MOF platform, this can be achieved by decreasing the pore size or introducing strong adsorption sites. Besides the introduction of open metal sites, a more flexible choice is to modulate the affinity of the material by tuning the concentration of ligands bearing a desired functionality (68). This was shown in a recent study on CO₂ adsorption in UiO-66 materials, synthesized with different relative concentrations of unfunctionalized linkers (1,4-terephthalate) and amino-modified ones (2-amino-1,4-benzenedicarboxylate). In these materials, the CO₂ uptake at RT and pressures lower than 1 bar was found to be directly related to the concentration of the amino-groups in the material (33). In particular, an increase in the uptake was verified with the –NH₂ content and it was related to a corresponding increase in the adsorption energy (33).

Introduction of the suitable functional group can be achieved not only by pre-synthesis reactions as in UiO-66-NH₂ (33,90), but also by means of post-synthesis reactions (67,87). Post-synthetic reactions are sometimes necessary because of the high reactivity of the desired functional groups that would make them suitable for side reactions during the MOF synthesis (67).

It is important to stress that the presence of functional groups modifies other materials properties. For example the breathing behavior in MIL-53(Al) is strongly modified not only by changing the metal (see Section 3.1.1) but also if amino groups are present on the linkers, because the strong H-bonding between the linker groups of opposite pore walls (76). A similar study was also reported for a pyrazolate-based MOF, in which the possibility to fine-tune the gate opening pressure was exploited by changing the alkyl substituent on the linker.(91) The introduction of fluorophoric

functional sites on the linker can modify also their electronic and fluorescence properties and the way these properties are modified by the presence of specific adsorbates. CO₂ sorption and contemporaneous CO₂ detection and quantification was for example reported in amidine modified NH₂-MIL-101.(92)

3.1.4. Effect of hosted molecules in the pores

Functional groups can be alternatively introduced in the MOFs by adsorbing molecules bearing such functionalities. Guest molecules are known to be able to change also dramatically the MOF properties,(8) influencing their properties largely than what observed previously for any other class of materials (see discussion in Section 3.3).

The presence of guest molecules, obviously, has as first effect the change of the MOF textural properties, that is an increase of their bulk density and a decrease of their surface area, pore volume and size. Being extra-framework entities, stability upon use of the material can arise. Moreover, the operational conditions cannot exceed the ones fixed by the stability of the composite.

Among the possible options, the more straightforward one, although often disliked or simply forgotten, is to use solvent molecules as guest molecules to modify the MOF storing properties (70). The presence of residual solvent molecules, for example due to an unperfect activation, can enhance the hydrophilicity of MOFs (29)(70), decreasing or enhancing the affinity of a MOF toward a certain adsorbate. For example, the pre-adsorption of low amount of water on HKUST-1 has shown to increase the adsorption energy toward CO₂ (93). The presence of residual solvent molecules can also have a strong effect on the structure of the MOF. A spectacular example of this is given by MOF-76-Ce (29). This MOF showed two structural transitions upon the removal of different amount of the solvent: (i) at 150 and (ii) at 250°C in vacuum, corresponding to the removal of half (MOF-76-Ce-hs) and the totality (MOF-76-Ce-ds) of the solvent. Local symmetry of Ce ions in the fully solvated MOF-76-Ce is a distorted trigonal prism. Removing half of the solvent molecules, a transition to a distorted pentagonal bipyramid symmetry is observed. In the fully desolvated structure, the distorted trigonal prism symmetry is restored (29). The change in the Ce symmetry

causes in the first step a structure collapse, possessing MOF-76-Ce-hs no surface area for N₂. The complete removal of the solvent causes an expansion of the structure, that is testified by the increase in the surface area to 1000 m² g⁻¹. The most interesting property of MOF-76-Ce-hs is that due to its smaller pore shape, MOF is permeable to CO₂ and not to N₂, conferring to this material a CO₂/N₂ selectivity double with respect to MOF-76-Ce-ds (34 vs. 15) (29). This study then suggests to test the selectivity of a material for different degrees of solvation, in particular the retesting of the best performing microporous structures reported so far in the literature (29).

Another possibility is to disperse molecules in the MOF pores, molecules that can have with the adsorbate a stronger interaction than the bare MOF. A uniform dispersion can be obtained if the MOF possesses strong adsorption sites that can strongly interact with functional groups present on the guest molecule. Alkylamines are able to reversibly and selectively chemisorb CO₂, also in presence of water. Several silica-based systems where the alkylamines were grafted have been reported, but these systems were degrading upon cycling (94). Recently, exploiting the presence of open metal sites, McDonald et al. (59,69) have introduced di-alkylamine in the M₂(dobpdc) frameworks obtaining systems characterized by a quite peculiar isotherm. In fact, all the systems were presenting an almost zero uptake until a threshold pressure was reached, in correspondence of which a steep increase in the uptake was observed. The threshold pressure was observed to change by changing the metal (59) or the amine (95). X-ray diffraction measurements coupled with density functional calculations revealed that at the basis of the steep increase was a cooperative effect among all the amines propagating through the MOF pore at a well defined pressure, which value was determined by the strength of the metal-amine bond (59).

3.2. Catalysis

The first results reporting catalytic application for MOFs were essentially proof of concept. After the identification of some robust frameworks, together with their limitations, MOFs were fully

introduced in catalysis field, revealing similar or, in some cases, better performances in comparison with conventional catalysts (9,96–100).

In principle MOFs should reveal very interesting characteristics for catalysis (98): (i) the pore dimensions in the nanoporosity-mesoporosity range, bridging the gap between zeolites and mesoporous systems; (ii) the combination of polynuclear sites, dynamic host-guest response and hydrophobic cavity environment, bridging the gap between zeolites and enzymes.

Gascon et al. (9) reported by means of the pictorial representation shown in Figure 10.9 the different possibilities to have catalytic sites in MOFs. In fact these sites can occur both at the organic and inorganic component and they can be inserted directly during the synthesis or by Post-Synthetic Modification (PSM).

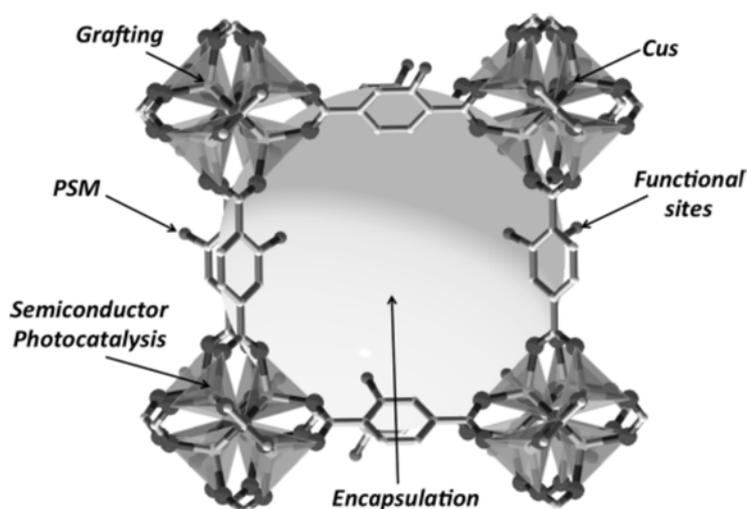


Figure 10.9: Catalytic moieties differently included in MOFs. [Adapted from Ref. (9) with permission, copyright ACS 2014].

The use of coordinatively unsaturated sites (cus) as active catalytic centers is probably the most common case. Cus can be also used as anchoring points for grafting of different functionalities. The active site can be located also at the organic linker and in this case it exposes a reactive functional group, besides containing the functionality able to coordinate the metal sites. When metal oxide

nanoclusters present in the MOF structure show the electronic configuration proper of a semiconductor, then, in particular conditions, some photocatalytic activity can be exploited.

Finally, encapsulation of different moieties (*e.g.* metal or metal oxide nanoparticles, metal coordination complexes, or molecular species) can be also exploited, dealing with high porous structures. Different strategies are followed, depending on the characteristics of the MOF and the species to be encapsulated. Usually the encapsulation can happen by a “ship in the bottle”, *i.e.* by forming the active species inside the pores, or a “bottle around the ship – templated synthesis” route, *i.e.* building the hosting structure around the encapsulated species. MOFs themselves can also have, in some cases, an active role in the catalytic reaction, *e.g.* by stabilizing transition states, orienting molecules or adding active sites.

The main limitation encountered in catalysis field by MOFs is the low relatively thermal and chemical stability. Many MOFs are unstable at the high temperatures required for some reactions. Moreover, a lot of structures collapse if exposed to air or to moisture, particularly when the solvent used in the synthesis is removed. PXRD and surface area analysis are fundamental techniques to check the structure of the MOF catalyst after the reaction.

Gascon et al. (9) claimed the guidelines to be followed when a MOF is taken in consideration as the catalyst in a reaction: (1) consider an ideal reactor and use isothermal conditions; (2) compare catalysts at low conversions in continuously operated reactors; (3) compare the selectivities at the same conversion value; (4) take into account kinetic curves in case of batch experiments; (5) compare the performance of MOFs with those ones of standard catalysts by considering TurnOver Frequency (TOF) and Total Number of Turnovers (TON).

Farrusseng et al. (98) recognized the activity of MOFs in different kinds of catalysis: (i) Lewis acid, (ii) Brønsted acid, (iii) Base, (iv) Enantioselective, (v) C-C bond formation and polymerization, (vi) Nanosized metallic particles supported on MOFs and (vii) Organometallic complexes supported on MOFs.

For sake of brevity only points (i) and (ii) of the previous list will be discussed in the following being those ones in which the authors gave major contributions.

3.2.1. Lewis acid catalysis

One of the most famous MOFs showing Lewis acidity is, without doubt, HKUST-1 (101–106). $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$ (BTC = benzene 1,3,5-tricarboxylate) is characterized by the so-called paddle-wheel units formed by four carboxylate groups coordinating two antiferromagnetically coupled Cu(II) ions. The Cu(II) dimers are connected by the BTC linker to form a three-dimensional porous framework. H_2O molecules are weakly adsorbed at the residual axial vacant position of the Cu(II) sites and they can be easily removed upon mild treatment in vacuum, giving rise to Cu(II) Lewis sites able to coordinate basic molecules being the reactants of a catalytic reaction. In Refs. (101)(102) a multitechnique characterization (PXRD, EXAFS, XANES, mid- and far-IR, DRUV-vis, and EPR) of Cu(II), as possible catalytic site, has been reported.

Piscopo et al. (106) reported very recently a study concerning the acetalization reaction of benzaldehyde with methanol by adopting HKUST-1 as catalyst. The reaction was done in batch and continuous flow conditions; the authors claimed that the conversion of benzaldehyde into 1,1-dimethoxytoluene proceeded efficiently in the presence of a small quantity of water.

Another recent example reporting the catalytic activity of a Lewis site inserted in a MOF is the Zr-based NU-1000 (see Figure 10.10a) (107,108). NU-1000 consists of eight connected $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_4(\text{OH})_4$ nodes and tetratopic 1,3,6,8(p-benzoate)pyrene linkers (TBAPy^{4-}). The structure presents ultra-wide (31 Å) and smaller (10 Å) channels. The first typology of pore system can be very useful when bulky molecules are considered. In fact NU-1000 has been reported to be a very active catalyst in the destruction of the nerve agent simulant dimethyl 4-nitrophenyl phosphate (DMNP) and, the highly toxic chemical warfare agent GD (O-pinacolyl methylphosphonofluoridate, also known as Soman, see Figure 10.10b,c). Experimental and computational data evidenced the presence of a highly accessible Zr (IV) Lewis site, responsible of

the MOF efficiency as catalyst. Particular attention was devoted to MOF characterization (PXRD, Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) and TGA) also in forced dehydration conditions, in which the material revealed a higher catalytic activity, in order to understand well the structure of the modified active site.

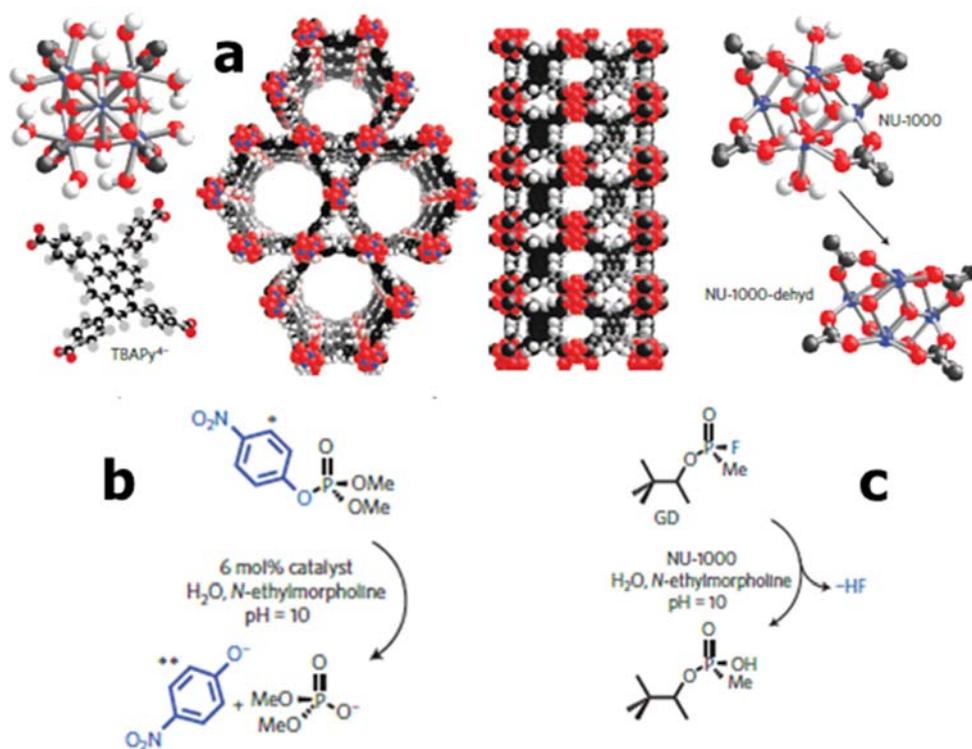


Figure 10.10: Part a: structure of the NU-1000 node and linker (left), MOF structure (two views, centre), and the dehydration of the NU-1000 node (right). Colour code: Zr (blue); O (red); C (black); H (white); part b: decomposition reaction of DMNP; part c: decomposition reaction of GD. [Adapted from Ref. (108) with permission, copyright Nature Publishing Group 2015]

3.2.2. Brønsted acid catalysis

Farrusseng et al. (98,109) reported that bridging OH groups in MOF-53 (M(OH)(bdc) (M= Al, Cr, Fe, Ga or In, bdc= terephthalate), see Figure 10.3) revealed Brønsted acidity (110). Corner-sharing MO₄(μ₂-OH)₂ octahedra make infinite chains giving rise to 1D lozenge-shaped channels.

MIL-53(Al) and IM-19 (also named MIL-53(Ga)) were tested in Friedel–Crafts alkylation reactions (109). While IM-9 demonstrated to be very active in the reaction of both monosubstituted benzenes (cyano-, chloro-, bromo-, methyl) and biphenyl with tBuCl, MIL-53(Al) did not show any catalytic activity. This fact has been demonstrated by means of CD₃CN and CO probe molecules adsorption study by means of FTIR spectroscopy (109).

To find the best shaping of MOFs in order to optimize their performance in the final application (catalysis, storage, separation, etc.) is an interesting challenge. Tablets, rings, spheres, extrudates, lumps are the most common shape for industrial porous materials (9). In catalysis, usually, crystallites from 5 to 500 Å are aggregated in bigger particles in the 50 µm to 10 mm range of size, in order to optimize on one side the contact between the catalyst and the reactants in liquid or gas phase and on the other side the separation of the reaction products. Concerning MOFs, this step can be a critical point as the powder aggregation can partially destroy their structure with the obvious consequence of surface area loss. A possible way to prevent the framework collapse can be the immobilization of MOFs on different supports.

Ramos-Fernandez et al. (100) presented one of the first synthesis of MOFs monolith where MIL-101(Cr) is immobilized on a monolithic cordierite structure and a uniform coating of ~9 wt.% inside the monolith channels is obtained (see Figure 10.11).

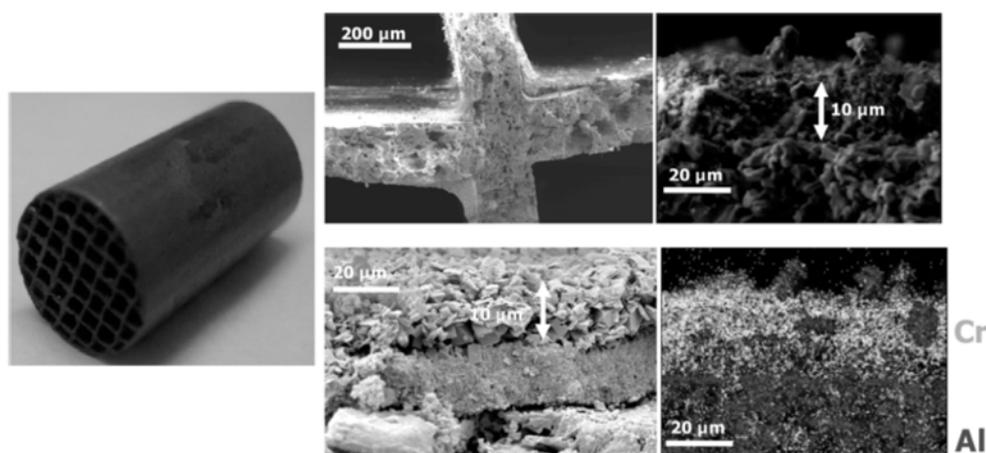


Figure 10.11: A MIL-101(Cr)-coated monolith. [Adapted from Ref. (9) with permission, copyright ACS 2014 and from Ref. (100) with permission, copyright Elsevier 2011]

3.3. Energy (related) applications

The actual urgent quest for sustainable innovative solutions, in the field of clean energy technologies, has boosted the research in novel materials with unprecedented properties. MOFs, as already discussed in the previous Sections, offer a unique combination of properties, such as synthetic versatility and possibility of a rational design, that make them attractive as new materials for a series of energy related applications. (111) Two main approaches have been successfully explored in order to finely tune the molecular properties for specific applications: the more classic use of specific functionalized (in synthesis or post synthesis) ligands, bearing the desired property (112) and the exploitation of selected guest/host interactions (Guest@MOF, see Figure 10.12) (8).

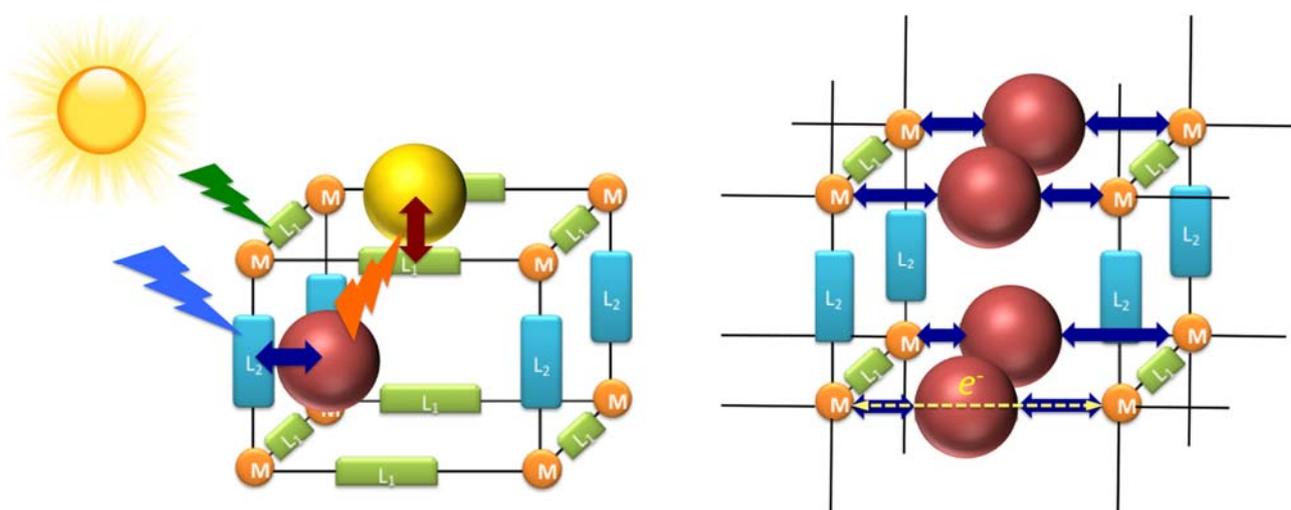


Figure 10.12: Schematic illustration of two types of Guest@MOF systems. Left: light harvesting process is facilitated by guest molecules (red and yellow spheres) interaction with each other and framework linkers (L1 and L2). Right: the pathway for charge transfer is created through the binding of guest molecules (red spheres) with open metal sites (M) in the framework. [Reproduced from Ref. (8) with permission, copyright ACS 2012]

Recent examples showing the effect of these two approaches in the field of light harvesting, (113) energy storage (114) and conductive properties (115), will be briefly reviewed in this Section, while hydrogen gas storage and carbon dioxide sequestration have been already discussed in Section 3.1. Pioneering studies in this area were related to the study of the classic Ru to Os energy transfer processes within an isomorphous mixed-metal MOF based on a 4,4'-(HO₂C)₂-bpy ligand. These first results demonstrated a rapid and efficient energy migration within a long distance transfer in isomorphous MOFs, showing their potential impact in the field. (116)

3.3.1. Light harvesting and Photovoltaic applications

The emerging field where MOF structures are designed as light harvesting materials and used as photovoltaic materials has been recently critically reviewed by Hupp, Fahrenholtz and coworkers (14). Thanks to their hierarchically organized molecular structures, MOFs have the potential to mimic the natural ordered nanostructures responsible for photosynthesis in biological systems. Exploiting the enormous structural tunability of MOFs, researchers explored a large numbers of structures in order to obtain photoactive materials, either using luminescent/chromophoric (photoactive) linkers or metal nodes (117,118) or inserting photoactive guest molecules in the MOF pores, using the ordered nanostructure to optimize the exciton migration. (119) Porphyrin-containing (117) MOFs, as well as Ruthenium based framework (118) have been explored for a possible use in hybrid photovoltaics such as Dye-Sensitized Solar Cells, (120) and their role as interfacial active agents at semiconductor interface or in the electrolyte (121,122) has been investigated. Organic photovoltaic cells have been studied as well, focusing on the charge transfer processes. (119)

Until now, power conversion efficiencies in working devices are still very low, especially respect to the state of the art of these systems, but the first results are encouraging and two routes of improvement are now clearly depicted: the introduction of an intrinsic conductivity in the framework (see Section 3.3.3) and the narrowing of the HOMO-LUMO energy gap. A convergent design that will take into account both strategies and exploit the huge synthetic versatility of MOFs

(also from the point of view of thin layers production) will have the chance to obtain highly efficient and stable devices.

3.3.2. Energy storage

The application of MOFs in electrochemical systems (being batteries and supercapacitors the two major technologies in this field) is now an area of emerging interest. (114) In fact efficient and reliable electrical energy storage (EES) devices, capable of both high power and energy density, are highly required, especially in conjunction with renewable energy sources, (i.e. solar and wind) with intermittent nature. Many applications in EES systems have been explored. (123) Cathodes and anodes with new working mechanism have been designed, exploiting the high chemical versatility and broad functionalization possibilities of this class of materials. (124) Thanks to their high surface area and pore volume, MOFs can be used to host electrolytes or as fillers in new formulations. (125) Apart from direct use, MOFs are successfully employed as hard template for obtaining either metal oxides and carbon materials with unprecedented nanostructures. (126) These novel MOF-derived nanostructures represent now the most promising alternative for their successful usage, even if the way to their industrial and commercial employment is still long , being poor stability and low conductivity the two major concerns.

3.3.3. Conductive properties

Solid-state semiconductor materials play a fundamental role in energy-related technology (production, storage and saving), therefore the possibility to have high porous materials (like MOFs), combined with electronic transport properties, will represent a great step forward in the field. Unfortunately MOFs are typically electric insulators (standard organic linkers have a HOMO-LUMO gap of several electron-volts), but, thanks to the impressive versatility of these structures, and to the recent synthetic advances, nowadays there are works that demonstrated the realization of electronically conducting systems, as recently extensively reviewed by Dinca and coworkers. (115)

Typical conducting MOFs can be obtained with an appropriate combination of electroactive linkers and frameworks, especially when linkers are in close proximity, allowing electronic transport perpendicular to the linkers (π -stacks among electroactive molecules), as demonstrated in tetrathiafulvene (TTF) based MOF (127) and, more recently, in related two-dimensional layered structures. (128)

A second winning approach is the use of host molecules in MOFs pores as “dopants” able to impart the electronic transport properties. These guest molecules can be used either as charge transfer systems or as an additional bridge between the metal centers in order to create the transport path. (129) For example, starting from an insulating platform, TCNQ-infiltrated HKUST-1 possesses electrical conductivity approaching conducting organic polymers (8).

3.4. Biomedical applications

Along with other applications reviewed so far, the interesting and particular characteristics of MOFs make them also potentially suitable for biological applications. In fact, their remarkably large surface areas and large pore sizes, their capacity to control and functionalize the nanosized pore volume, their intrinsic biodegradability and versatile multifunctionality, their unconventional physicochemical and thermo-mechanical characteristics have opened up new opportunities for their use and exploitation in nanotechnology, biology and medicine (130).

The biological application of MOFs is still quite new, but research so far has produced promising results. Recently MOFs have been suggested for a range of biomedical applications, such as delivery of therapeutic agents, drug carriers, NO storage, sensing and imaging agents (Figure 10.13). Some excellent reviews have been published in the last few years (10,131,132) and will be summarized in the next paragraphs.

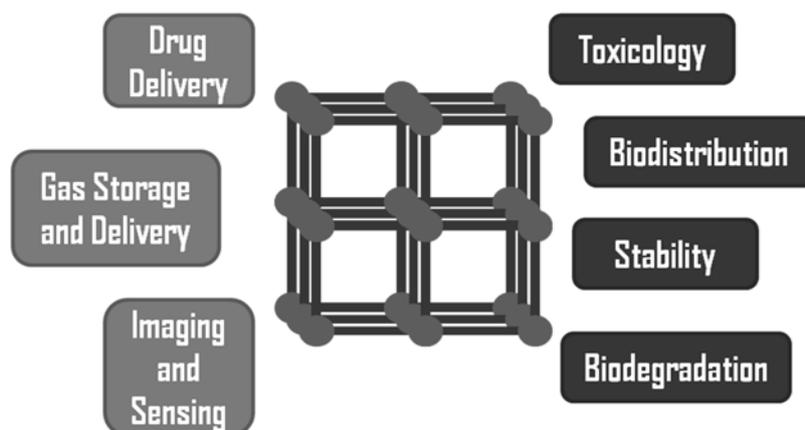


Figure 10.13: Schematic representation of the different use (left) and limitations (right) of MOFs for biomedical applications.

3.4.1. Design & Synthesis

The synthesis of MOFs has been reviewed elsewhere (see for example Ref. (20)) and in this chapter (see Section 2), but few comments on the synthesis of MOFs for biological applications are needed to be reported here.

As already mentioned, the greatest advantage of MOFs over other well-known nanoporous materials such as zeolites and carbon nanotubes is the ability to tune the structure and functionality of MOFs directly during synthesis. Moreover, another huge advantage is the possibility to tune compositions, size, shapes and chemical properties by choosing different building blocks. In principle, due to the wide choice of metal corners and organic linkers, the synthesis could lead to a virtually infinite number of materials with specific and designed physicochemical properties for every specific applications needed.

However, the typically obtained bulk size MOF crystals, ranging from micrometers to millimeters, is not suitable for the majority of biomedical applications. Therefore, MOFs need to be scaled down to the nanoregime to form nanoscale metal-organic frameworks (NMOFs) for use as delivery vehicles for imaging agents and drug molecules. NMOFs exhibit particle dimensions in the tens to

hundreds of nanometers range, maintaining the structural diversity and physicochemical properties as bulk MOFs (133).

The synthesis of nano- and micro-scale MOFs has recently been reviewed (134) and only few general methods can be applied for this synthesis in order to achieve the desired homogeneous, monodispersed and stable NMOFs (133). Along with the selection of the right method, the choice of the solvent is crucial for biomedical applications since the most common used solvents for the synthesis of MOFs (i.e. DMF, pyridine, methanol) are toxic and should be avoided and replaced by other solvents more compatible with physiological conditions.

3.4.2. Issues

Along with the necessity of small-sized crystals which would present enormous advantages from the point of view of their transportation as well as effective cellular uptake, other issues need to be examined (Figure 10.13).

When considering a material for biological applications, particularly for *in vivo* medical uses, considerations on the stability (both chemical and thermal) as well as the toxicology and the biodistribution need to be taken into account. In particular, for a possible future application in clinical trials, the requirements concerning the materials' toxicology, stability, efficacy and their ease and reproducibility of manufacture are even stricter than those for other types of commercial activity (132).

Although the toxicity of most MOFs remains unknown, this aspect has attracted much attention recently (135). The main concern is that every MOF contains transition metal ions, normally not compatible with any *in vivo* biochemical study. Moreover, the toxicity also depends on other components such as ligands, solvents and drugs or molecules used for their surface modification or encapsulation. Therefore, the toxicity that should be taken into account has to consider all these molecules within MOFs' structure.

Another important issue is the biodegradability and stability of MOFs. Because of the nearly infinite number of possible structures, it is difficult to make a general comment. Some MOFs are in fact quite unstable under humid environment while other structures are stable for many days (135). NMOFs should be intrinsically biodegradable due to their labile metal-ligand bonds (136).

Toxicology studies have started recently (135) but more research is needed to get further insight into the use of MOFs in healthcare applications. Moreover, the degradation profile of any MOF should be considered as an essential parameter in their optimization and design for the desired application (imaging, drug delivery, sensing).

3.4.3. Loading of Therapeutic Agents for Optical and MRI Imaging and Drug Delivery

The application of MOFs as drug carriers and imaging agents (32) starts from the insertion or loading of the desired compound that can be achieved in two ways: i) direct incorporation during MOFs synthesis or ii) postsynthetic loading. The first loading method consists in the direct incorporation, within the MOFs structure, of biomedically relevant agents during the synthesis. The advantage of this technique is the loading capacity that can be achieved, being very high and uniform. On the other hand, it is very difficult to be able to control the physicochemical properties and the morphology of the resulting material and the integrity of the therapeutic agent.

In the second loading strategy, the desired compounds are inserted after the synthesis of MOFs by encapsulation, doping or via covalent or non-covalent interactions (Figure 10.14). This method prevents MOF structure deformation or alteration but the loading capacity is lower than by the first method and is strongly dependent by the chemical nature of the drug. Moreover, the drug distribution may not be uniform affecting the release kinetics.

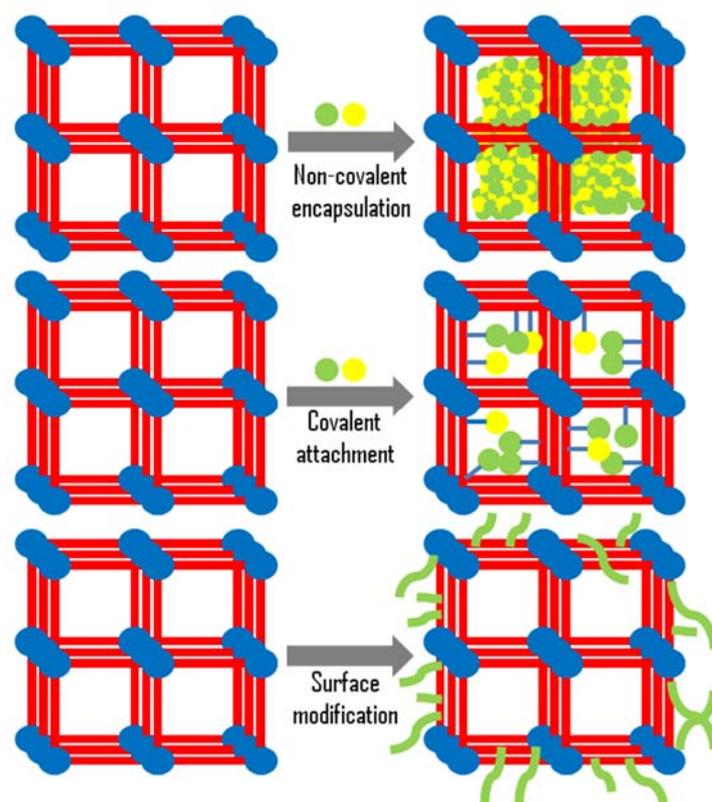


Figure 10.14: Loading of drugs into MOFs via non-covalent encapsulation (top), covalent attachment (middle) and surface functionalization (bottom).

The performances of MOFs can be also improved by surface modification. This is a novelty in the biomedicine domain and few examples are present in the literature (10)(133,136). Surface modification can be achieved with silica, lipid layer, polymer or other biological materials such as oligonucleotides or nucleic acids. Surface modification is important since it can change MOFs properties in physiological conditions improving water dispersity, blood circulation, targeted delivery, stability, and biocompatibility or imparting additional functionalities.

All these methods are excellently reviewed along with some examples of drugs (common anti-inflammatory and analgesic drugs such ibuprofen, antivirals or antitumorals and other chemotherapeutic agents) in different kinds of MOFs and NMOFs (10)(130,131,135,136).

Another important aspect for these applications is the ability of MOFs of releasing the encapsulated or linked drugs. Most of the studied drug release and their kinetics have been undertaken in the past

and, again due to the huge versatility of MOFs structure, it is difficult to draw a complete scenario. For this, interested readers are asked to refer to the literature (10,130,137,138).

3.4.4. Storage and Delivery of Gases

As already mentioned in Section 3.1, MOFs are well known and widely used for their excellent gas capture, storage, separation and delivery capacities. These properties can be exploited for biomedical applications where some gases (above all NO, but also H₂S and CO) are involved in various biological processes as well as for many in vivo antibacterial and antithrombotic applications.

NO diffuses easily through the body with different effects on the body depending on the concentration and location of the gas which can cause or excessive bleeding and inflammation if present at too high concentration or can lead to hypertension or reduced ability to fight bacteria if its concentration is too low. The development of new materials with high storage capacity and good delivery properties of NO into specific sites in the human body is of the utmost importance.

A good NO storage material should exhibit high adsorption affinity for NO, but the interaction between the storage material and gas should not be extremely high to prevent the release of NO when it is needed. Fast kinetics and good thermal/mechanical properties are also required for storage materials so that the release can occur at the desired time and rate for a certain application. This has been excellently reviewed very recently (10,135) where, along with the description of the MOF materials proposed so far for NO adsorption, storage and delivery, the authors report on the very few examples of in vitro experiments designed to test the antithrombosis action, the vasodilatory properties and the antibacterial activity of NO-loaded MOFs. The first proposed MOFs for NO adsorption and delivery were CPO-27 and H-KUST-1 which showed excellent delivery properties. Other nontoxic iron-materials (Fe-MIL-88 (139), Fe-MIL-100 and Fe-MIL-101) were proposed as well as different metal-based M-CPO-27 (M = Mg, Zn, Co, Ni or Mn) but with lower performances.

4. CONCLUSIONS AND PERSPECTIVES

Crystalline nanoporous Metal Organic Frameworks (MOFs), built from metal ions and organic linkers, offer vast potential for the design of porous materials with molecularly selective interfaces, novel physical properties, enormous surface areas and a diverse array of functionalities. Their first reports were focused towards the discovery of unknown structures. More recently, the attention has moved towards MOF applications within many fields such as catalysis, gas storage, separation, energy conversion, energy storage and drug delivery.

The chapter gave some examples showing how MOF rational design and advanced characterization are the first steps towards their application in emerging fields. In particular, advances in the different research areas will be obtained by combining theoretical and experimental results to allow a judicious material design to obtain MOFs to be used, in the near future, in real working device and in biological applications.

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