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Low temperature activation and reactivity of CO₂ over a Cr^{III}-based heterogeneous catalyst: a spectroscopic study

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5 A new heterogeneous catalyst for CO₂ activation was identified in the Cr^{III}/SiO₂ Phillips catalyst, one of the most important catalyst used industrially for olefin polymerization. Interestingly, it was found that Cr^{III}/SiO₂ strongly activates CO₂ already at room temperature, making it available for chemicals synthesis. A preliminary attempt in this direction was done by following the reaction of CO₂ with ethylene oxide at room temperature by means of FT-IR spectroscopy, which showed the formation of ethylene carbonate.
10 Besides non-reductive CO₂ activation, Cr^{III}/SiO₂ showed good performances in catalytic reduction of CO₂ to CO, when heated in mild conditions or irradiated with UV-Vis light. Both, in situ FT-IR and UV-Vis spectroscopy were applied to highlight the red-ox process occurring at the Cr centres. These results open interesting perspectives to be developed in the field of CO₂ chemical fixation.

1. Introduction

15 The use of carbon dioxide as raw chemical is a central research field on the environmental and economic point of view. In fact, the duty to decrease the anthropogenic CO₂ emissions in the atmosphere would cause in the next years a considerable raise of the CO₂ amounts coming from sequestration and capture plants, increasing its availability on the market with a consequent lowering of the price. Because of the enormous quantity of CO₂ to be handled,¹ the most promising sequestration technology proposed so far is the geological sequestration that, however, is not completely lacking of disadvantages.² On the other side, the possibility to use CO₂ as a versatile feedstock in many chemical reactions is an appealing vision³ that has activated the research in many fields, which consider its use not only as reagent^{1, 4-6} but also as medium for chemical reactions.⁷ CO₂ conversion in only one type of chemical is not a reasonable solution, because it would bring necessarily to the saturation of the market;⁸ it is then mandatory to spread as much as possible the number of syntheses involving CO₂ as reagent. Among the envisaged products obtainable, the main interest is addressed to polymers,^{1, 9-13} fine chemicals^{1, 4} and liquid fuels.^{1, 4, 14}
35 Reactions of interest for carbon dioxide use can be essentially classified into two types: reductive and non reductive reactions, both of them requiring the C=O double bond activation. In both cases, two problems should be faced: i) the large thermodynamic stability¹⁵ and ii) the appreciable kinetic barrier to CO₂ activation.¹⁶ The industrial, large-volume conversion of CO₂ into added value chemicals is now well-established.³ However, in order to determine an increase of the CO₂ industrial consumption comparable with the huge anthropogenic CO₂ production, it is essential to couple the above mentioned reactions with the use of renewable energy sources and, more critically, to design new and more efficient catalysts for CO₂ activation.

Among non reductive reactions, carboxylation reactions are of particular interest because they allow the incorporation of the whole CO₂ moiety. This is the case, for example, of CO₂ copolymerization with ethylene oxide^{9, 13, 17} or propylene oxide,^{9, 13, 18-24} that offers the double value advantage, on the environmental point of view, to chemically fix CO₂ in a

biodegradable plastic. Homogeneous complexes are by far the most employed catalysts for this reaction, among which various Lewis acidic metal halides, carboxylate or alk/aryloxide complexes, mono- and dinuclear well-defined Zn-complexes, Cr- and Co-salen complexes.¹³ In contrast, examples of heterogeneous catalysts applied for the copolymerisation of PO and CO₂ are more rare: supported zinc glutarate is the most widely applied. In this respect, the ability of the catalyst support to produce carbonates has been demonstrated to favour CO₂ incorporation in the growing chain.²⁵ In most of the cases, mild temperatures but high CO₂ pressures (> 10 bar) and long reaction times are required.¹³

65 Reductive reactions involving CO₂ are more challenging because they require energy (thermal, electrochemical or photochemical processes) to generate reduced forms of CO₂, such as formates, oxalates, hydrocarbons and CO.⁶ In particular, production of CO from CO₂ is considered an important objective in the context of production of renewable carbon feedstock chemicals.¹⁶ However, the CO₂ → CO + ½ O₂ reaction is characterized by a ΔG⁰ of 257 kJ/mol, and therefore for a full CO₂ conversion it would be carried out at very high temperature.⁶ As a matter of fact, CO₂ splitting into CO and O₂ was recently carried out at temperatures in excess of 1000 K in solar reactors, in presence of oxygen-defective materials (e.g. ferrites and ceria)^{6, 26} as heterogeneous catalysts. A few (and quite exotic) homogeneous catalysts have been reported to be able to reduce CO₂ to CO already at room temperature, although the resulting metal-oxygen bonds are necessarily strong and catalytic turnover is rare,²⁷ but only a few of them involve early- and early-middle transition metals.^{16, 28-32} Among them, the homogeneous W^{II}Cl₂(PMePh₂)₄ complex showed excellent performances and a high specificity for CO production in mild conditions (room temperature, CO₂ pressure of 1 bar, induction time of 10 min).^{16, 33}

Herein, we report for the first time on the almost unique ability of a diluted chromia-silica catalyst (Cr^{III}/SiO₂) to activate CO₂ in a highly versatile way. Diluted chromia-silica (also known as Phillips catalyst) is better known for its ability in polymerizing ethylene in mild conditions.^{34, 35} The industrial relevance of this catalyst, which accounts for more than one-third of all the

polyethylene supply,^{34, 35} explains the numerous efforts devoted along more than 60 years in the investigation of the surface properties of the active Cr sites. Direct spectroscopic methods have played the major role in this direction.³⁶⁻⁴⁰ Currently, there is broad agreement that Cr^{II}/SiO₂ contains a large variety of active sites, unless both the preparation and activation procedures have been carefully designed and controlled.^{34, 36} Nevertheless, by following appropriate methods, Cr^{II}/SiO₂ catalysts having rather homogeneous active sites endowed with high coordinative unsaturation can be prepared.³⁷ Grafted Cr^{II} sites are known to display outstanding ability to form polycarbonyl, polynitrosyl and mixed carbonyl-nitrosyl Cr^{II} coordination complexes.³⁷⁻³⁹ Very recently, some of us demonstrated that, by exploiting the combination of high coordinative unsaturation and redox capacity characteristic of single Cr^{II} sites on chromia-silica, it is possible to reduce nitrogen oxides by CO, giving carbon dioxide and dinitrogen as reaction products.⁴¹

On the basis of these results and of experience accumulated by our research group over several decades on the chemistry and reactivity of Cr^{II} sites, in this work we explored the possibility to employ the highly unsaturated Cr^{II} sites for: i) CO₂ activation at room temperature; ii) use of the activated CO₂ for chemicals production (in particular, the reactivity of CO₂ with ethylene oxide was chosen as a reaction test); and finally iii) CO₂ thermal- or photo-reduction to CO. In all the three cases, CO₂ activation and reactivity on Cr^{II}/SiO₂ were investigated by means of in situ FT-IR spectroscopy. As a matter of fact, among all of the spectroscopic techniques, FT-IR spectroscopy is the most versatile and has enough sensitivity to identify the intermediates of a reaction, being able to directly discern between the vibrational manifestations of different species even under operando conditions and in presence of very diluted systems.^{37, 42-44} These preliminary spectroscopic results demonstrate that divalent chromium-based heterogeneous catalysts are able to activate CO₂ and to transform it into valuable chemicals. Although CO₂ chemistry with homogeneous Cr-based catalysts has been already reported in literature,^{13, 18, 20, 23, 24, 45} at the best of our knowledge, this is the first example where an heterogeneous chromium-system is employed. Moreover, in this case a divalent oxidation state is involved whereas the large majority of homogeneous complexes are trivalent chromium systems.

Experimental

Materials

Two chromia-silica catalysts were prepared by wet impregnation of SiO₂ (aerosil, surface area *ca.* 400 m²g⁻¹) with an aqueous solution of CrO₃ having the right concentration to give a Cr:SiO₂ ratio of 1.0 wt% and 0.5 wt%, respectively. The former was used for FT-IR spectroscopy, and the latter for UV-Vis spectroscopy. In both cases, the low Cr:SiO₂ ratio was chosen in order to avoid segregation of a Cr(III) oxide phase during subsequent thermal treatments, and to favour formation of single-cation surface sites. From this parent material, the Cr^{II}/SiO₂ sample used for CO₂ activation was obtained by heating at 923 K under a dynamic vacuum, followed by heating in O₂ at 923 K and reduction by heating in CO at 623 K. Further details can be found in Ref. ³⁷

Ethylene oxide (3.0 grade, Union Carbide), ethylene carbonate

(99+% ACROS organics) and carbon dioxide (4.6 grade, Praxair) were dosed from the gas phase and used as received without further purification.

Methods

Transmission FT-IR spectra were collected (at 2 cm⁻¹ resolution) on a Vertex70 Bruker instrument. The self-supported sample wafer was placed inside a home-made quartz cell that allowed thermal activation, in-situ gas dosage and thermal treatments in a controlled atmosphere to be performed. Reflectance UV-Vis spectra were recorded on a Varian Cary5000 instrument using in this case the 0.5 wt.% Cr/SiO₂ sample in the form of a thick self-supported pellet (surface density *ca.* 60 mg cm⁻²). The sample was placed inside a home-made quartz cell equipped with a cuvette in optical quartz, allowing treatments and measurements in controlled atmosphere.

For photo-reduction experiments, the irradiation was carried out using a SOL2/500S lamp (Hönle UV technology, Munchen, Germany) simulating solar light. The SOL-bulb and the H₂ filter together yield a spectrum very similar to the natural sunlight, ranging from ultraviolet to infrared radiation (approx 295-3000 nm). The sample temperature was kept constant at 308 K by using a ventilation system.

3. Results and Discussion

3.1 CO₂ activation at room temperature and potential application in chemicals synthesis

A typical FT-IR spectrum of CO₂ (equilibrium pressure P_{CO₂} = 100 mbar) adsorbed at room temperature on the reduced Cr^{II}/SiO₂ sample is shown in Figure 1a (bold dark grey). A very intense (and out of scale) IR absorption band appears around 2349 cm⁻¹, along with a sharp band at 1368 cm⁻¹; simultaneously, a complex series of IR absorption bands appear immediately in the 1800 – 1400 cm⁻¹. The relevant changes undergone by the FT-IR spectrum of Cr^{II}/SiO₂ in presence of CO₂, suggest that CO₂ molecules are not only adsorbed, but also activated, on the catalyst surface.

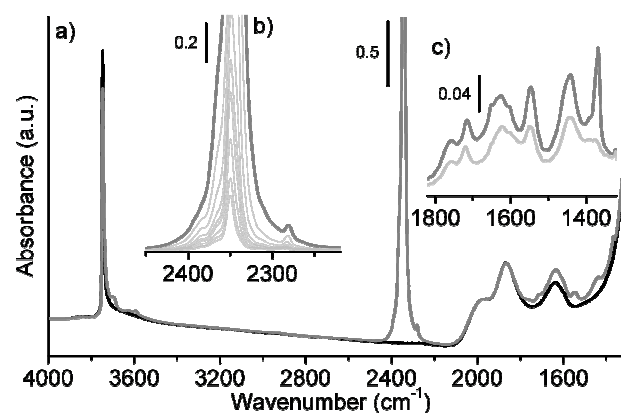


Figure 1. Part a): FT-IR spectra of Cr^{II}/SiO₂ catalyst before (bold black) and after (bold dark grey) dosage of CO₂ (equilibrium pressure 100 mbar). Part b): Magnification of the spectra in the $\nu(\text{CO}_2)$ region as a function of the CO₂ coverage (from dark to light bold grey), after subtraction of the background. Part c): Magnification of the background subtracted FT-IR spectra in the region where carbonates or carboxylates give their contribution.

Going in more details, the intense IR absorption band centred at 2349 cm^{-1} , which does not appear upon dosing CO_2 on pure silica pre-activated at the same temperature (see Figure S1), is easily assigned to the ν_3 vibrational mode (asymmetric stretching) of linear CO_2 adsorbed on the surface Cr^{II} sites. This IR absorption band decreases in intensity upon outgassing at room temperature, as shown in Figure 1b (subtracted spectra). The much weaker IR absorption band observed at 2281 cm^{-1} (i.e. on the low frequency side of the main absorption band) is assigned to the Cr^{II} adducts formed in presence of the naturally abundant $^{13}\text{CO}_2$. The sharp band at 1368 cm^{-1} is assigned to the Raman

active ν_1 vibrational mode (symmetric stretching), which is activated by the slight asymmetry caused by molecule adsorption on the surface. Finally, the two weak IR absorption bands centred around 3715 and 3610 cm^{-1} (showing the typical roto-vibrational profile of gaseous CO_2) are due to the combination of ν_1 and ν_3 modes of CO_2 in the gas phase. The reason for the presence of a doublet is a strong Fermi resonance effect among the first overtone of the ν_2 vibrational mode (degenerate deformation, at 667 cm^{-1} for gaseous CO_2) and the ν_1 mode, which induces a band splitting in two components 100 cm^{-1} apart.^{46, 47}

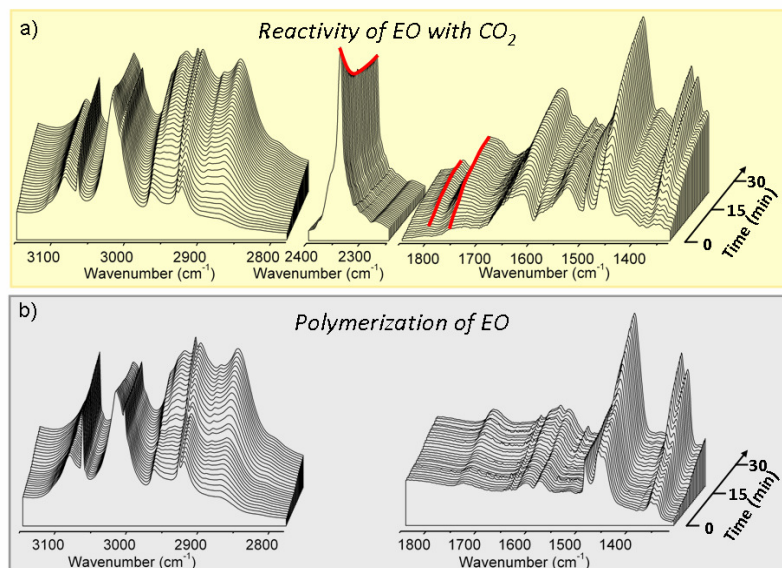


Figure 2. Part a): Time-resolved FT-IR spectra collected within the first 30 minutes of reaction of a 1:1 CO_2 :EO mixture over $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst. Left, middle and right parts show the $\nu(\text{C-H})$, $\nu(\text{CO}_2)$, and $\delta(\text{C-H})$ regions, respectively. Red lines evidence the consumption of the IR absorption band due to CO_2 and the attendant formation of new IR absorption bands associated to ethylene carbonate. Part b): FT-IR spectra collected during an experiment analogous to that shown in part a), but in presence of EO only.

The above discussed results provide an evidence that weakly bounded 1:1 end-on CO_2 adducts are formed on the surface Cr^{II} sites, as already reported in literature.⁴⁸ However, beside CO_2 adsorption on the highly uncoordinated Cr^{II} sites, a fast reactivity is also observed, as testified by the appearance in the FT-IR spectrum of multiple bands in the $1800 - 1400\text{ cm}^{-1}$ region (Figure 1c, subtracted spectra), and by the small decrease of the IR absorption band at 3747 cm^{-1} due to the free hydroxyl groups. The newly formed IR absorption bands decrease only partially in intensity upon outgassing, suggesting that the associated surface species are quite stable. A detailed assignment of all the IR absorption bands in this frequency range is complicate, for many reasons: i) several species (such as carbonates or carboxylates) are characterized by IR absorption in this wavenumber region;⁴⁹ ii) lower wavenumber regions, where additional characteristic IR vibrational modes can give a contribution, are not available due to the strong absorption of the silica support; iii) it is difficult to discriminate between species in interaction with silica or with Cr^{II} sites. Nevertheless, it should be noticed that CO_2 does not react with pure silica pre-activated at the same temperature (not shown): therefore, it must be concluded that the highly uncoordinated Cr^{II} sites at the silica surface catalyze the

activation of the adsorbed CO_2 molecules, with the attendant formation of highly activated species that can be potentially exploited for chemicals synthesis.

In order to evaluate the potential of $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst in fostering the use of CO_2 for chemicals production, we have investigated the reactivity of CO_2 with ethylene oxide (EO) at room temperature. A 1:1 CO_2 :EO mixture was dosed on the pre-activated $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst, followed by collection of FT-IR spectra at a time resolution of 1 min. Figure 2a displays the sequence of FT-IR spectra collected within the first 30 minutes of reaction in the $\nu(\text{C-H})$, $\nu(\text{CO}_2)$, and $\delta(\text{C-H})$ regions (left, middle, and right, respectively). The evolution of the FT-IR spectra provides an evidence that three time-dependent processes occur simultaneously: i) EO polymerization; ii) CO_2 consumption and iii) ethylene carbonate formation. The occurrence of the first process is demonstrated by the evolution of the FT-IR spectra in the $\nu(\text{C-H})$ and $\delta(\text{C-H})$ regions, where the progressive growth of complex IR absorption bands centred around 2945 , 2880 and 1355 cm^{-1} can be easily associated to the formation of $(\text{CH}_2-\text{CH}_2-\text{O})_n$ oligomeric/polymeric chains. A similar spectral evolution is observed in presence of EO only (Figure 2b), as already reported in the past.⁴⁴

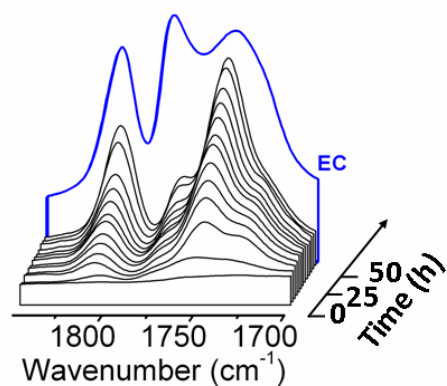


Figure 3. Evolution of the FT-IR spectra during 48 hours of reaction of a 1:1 CO_2 :EO mixture over $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst. Only the $\nu(\text{C}=\text{O})$ vibrational region is displayed. Also the spectrum of ethylene carbonate adsorbed on $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst is shown for comparison (blue spectrum, vertically translated for clarity).

However, EO polymerization is not the only phenomenon observed in presence of CO_2 :EO mixture, as testified by the decrease in intensity of the IR absorption band due to adsorbed CO_2 (Figure 2a, middle) and by the concomitant appearance of additional IR absorption bands in the $1850 - 1700 \text{ cm}^{-1}$ region (red curves in Figure 2a, right). These bands, that further increase in intensity in the successive 48 hours of reaction at room temperature (as shown in Figure 3), are assigned to ethylene carbonate (EC) adsorbed on both silica surface and Cr^{II} sites. As a matter of fact, the same IR absorption bands are observed when EC is directly dosed on $\text{Cr}^{\text{II}}/\text{SiO}_2$, as shown in Figure 3. The two IR absorption bands at higher wavenumber values (1807 and 1780 cm^{-1}) are easily assigned to physisorbed EC (see Figure S1).⁵⁰ The doubling of this band has been explained as a Fermi resonance effect: the $\text{C}=\text{O}$ stretching vibration interacts with the first overtone of the skeletal breathing vibration (2ν around 1780 cm^{-1}).⁵⁰ On the contrary, assignment of the IR absorption band centred around 1750 cm^{-1} is less straightforward, since it has been found that EC itself not only is strongly adsorbed to the Cr^{II} sites but also slowly reacts on $\text{Cr}^{\text{II}}/\text{SiO}_2$ at room temperature, likely through a ring opening polymerization mechanism. Usually, organic carbonates are characterized by specific vibrational modes in the large $1850\text{-}1700 \text{ cm}^{-1}$ range, that becomes even wider when interaction of the carbonate moiety with cationic sites is considered (see calculated spectra in Figure S1).

Although further measurements should be performed in order to clarify the reaction mechanism and the nature of all the products formed during the reaction, the set of experiments shown in Figures 2 and 3 demonstrate that the $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst is able to catalyse a reaction between epoxides and CO_2 . Current efforts are underway to optimize the reaction conditions in order to increase the selectivity towards EC formation vs. EO and EC polymerization. A similar chemistry has been reported to occur on several chromium-based homogeneous catalysts in presence of high pressures of CO_2 (usually $> 10 \text{ bar}$).^{13, 18, 20, 23, 24, 45} nevertheless, this is the first evidence that an heterogeneous chromium-system is able to activate CO_2 and to incorporate it into organic compounds working at low pressure conditions ($< 1 \text{ bar}$). It is also noteworthy that at difference of the homogeneous complexes reported in literature, which exhibit a trivalent

oxidation state, herein a divalent oxidation state is involved.

3.2 Thermo- and photo- catalytic reduction of CO_2 to CO

As discussed in the previous section, CO_2 is easily activated at room temperature over $\text{Cr}^{\text{II}}/\text{SiO}_2$ in the form of carbonate-carboxylate species. A further reactivity is observed upon giving energy to the system, either by heating at 350°C in presence of CO_2 or (even more interesting) by irradiating it with UV-Vis light at room temperature. Figure 4a shows the FT-IR spectrum of CO_2 adsorbed on $\text{Cr}^{\text{II}}/\text{SiO}_2$ before (black) and after irradiation with UV-Vis light for increasing time up to 1 h (light grey). In this experiment the CO_2 equilibrium pressure was intentionally maintained small in order to appreciate any change in the intensity of the corresponding IR absorption band. Similar results were obtained by heating $\text{Cr}^{\text{II}}/\text{SiO}_2$ at 350°C (spectra not shown).

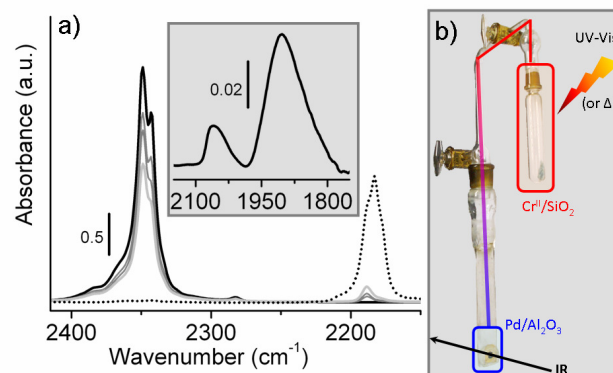
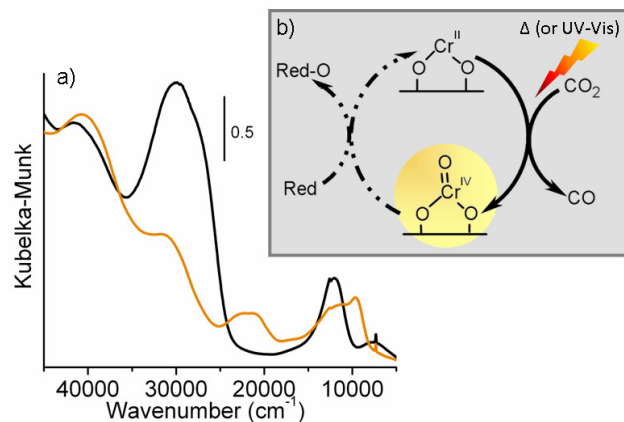


Figure 4. Part a): FT-IR spectra of CO_2 adsorbed on $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst before (black spectrum) and after irradiation with UV-Vis light for increasing time (up to 1 h, light grey spectrum). Also the FT-IR spectrum of CO adsorbed on a pellet of $\text{Cr}^{\text{II}}/\text{SiO}_2$ having the same thickness is shown for comparison (dotted). The inset displays the background subtracted IR spectrum collected on a commercial $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst contacted with the reaction mixture obtained after irradiation of $\text{Cr}^{\text{II}}/\text{SiO}_2$ in presence of CO_2 with UV-Vis light, according to the experimental set-up shown in part b).

Upon progressive irradiation under UV-Vis light, the IR absorption band due to CO_2 adsorbed on the surface Cr^{II} sites gradually decreases in intensity (up to about half of the initial intensity), along with the appearance of a weak IR absorption band at around 2180 cm^{-1} . This band is easily assigned to CO adsorbed on a small fraction of Cr^{II} sites.^{37, 40} For comparison, also the FT-IR spectrum of CO adsorbed on a $\text{Cr}^{\text{II}}/\text{SiO}_2$ pellet of the same thickness (dotted spectrum) is shown. The results shown in Figure 4 clearly suggest that $\text{Cr}^{\text{II}}/\text{SiO}_2$ is able to catalyze CO_2 reduction to CO at a relatively mild temperature. However, the detection of the formed CO is made difficult by the presence in the reaction cell of a large amount of CO_2 , acting as poison for the Cr^{II} sites, as well as by oxidation of the Cr^{II} sites involved in the reaction (vide infra) that are no more able to coordinate CO.

In order to better detect the CO produced during the catalytic photo-reduction of CO_2 , a second in situ FT-IR experiment was performed by using the experimental set-up displayed in Figure 4b. A properly activated $\text{Cr}^{\text{II}}/\text{SiO}_2$ catalyst, placed in a quartz tube, was irradiated with UV-Vis light in presence of CO_2 for 30 minutes, in communication with an IR cell containing a pellet of

a commercial Pd/Al₂O₃ catalyst, that is able to selectively adsorb CO. In this way, the CO evolved from the photo-reduction of CO₂ over Cr^{II}/SiO₂ is adsorbed on Pd/Al₂O₃, acting as CO trap. The FT-IR spectrum of the so contacted Pd/Al₂O₃ (inset of Figure 5a), shows the IR absorption bands characteristic of linear and bridged carbonyls on Pd nanoparticles.^{43, 51-55} Therefore, this experiment is a further proof that Cr^{II}/SiO₂ catalyses the reduction of CO₂ to CO under UV-Vis light irradiation.



10 Figure 5. Part a): Diffuse Reflectance UV-Vis spectra of Cr^{II}/SiO₂ catalyst before (black) and after heating in presence of 100 mbar of CO₂ at 350°C for 1 hour (orange). Part b): Proposed red-ox process occurring at the Cr centres, where Red = reducing agent, Red-O = oxidised form of the reducing agent.

15 Likely, the driving force for CO₂ reduction over Cr^{II}/SiO₂ catalyst is a red-ox process occurring at the Cr centres. In order to identify the final oxidation state of the metal sites after the CO₂ conversion, an UV-Vis experiment was performed. After thermal treatment in CO₂ at 350°C (or prolonged irradiation with UV-Vis light up to 1 hour, not shown) the optical spectrum of standard Cr^{II}/SiO₂ drastically changes in both the d-d and the charge-transfer (CT) region (Figure 5a). In particular, the two d-d bands around 12000 and 7000 cm⁻¹ and the intense CT band centred at 30000 cm⁻¹, all characteristic of highly unsaturated Cr^{II} sites (black spectrum),³⁷ strongly decrease in intensity (although they do not disappear completely), along with the appearance of two new absorption bands in the d-d region, at around 10000 and 22000 cm⁻¹ (orange spectrum). Similar absorption bands have been recently observed in the UV-Vis spectrum of Cr^{IV}-oxo species formed upon controlled oxidation of Cr^{II}/SiO₂ in presence of N₂O.⁴¹ Therefore, it can be concluded that CO₂ reduction to CO over Cr^{II}/SiO₂ catalyst proceeds through a partial oxidation of Cr^{II} to Cr^{IV}-oxo species, according to the reaction scheme shown in Figure 5b and similarly to what has been reported for homogeneous complexes.^{16, 28-32}

35 CO₂ reduction doesn't proceed up to the complete oxidation of the surface Cr^{II} sites to Cr^{VI}, also after prolonged reaction times; likely, this is a consequence of the inability of the Cr^{IV}=O species to coordinate CO₂, besides their lower reductive potential with respect to Cr^{II}. It is highlighted here that the Cr^{IV}-oxo species resulting from oxidative addition of CO₂ are amenable to be easily reduced in mild conditions, as recently demonstrated in presence of ethylene at room temperature.⁵⁶ Although ethylene cannot be considered as the election reducing agent to close the

45 redox cycle shown in Figure 5b (because it easily polymerizes), nevertheless its fast reactivity towards Cr^{IV}-oxo species indicates that reductive removal of the oxo-ligand from the Cr sites could be feasible in mild conditions. The potentiality of other reducing agents (such as non polymerising alkenes) able to convert Cr^{IV}=O back into Cr^{II} would be explored in an incoming work: when this step would be successfully achieved this catalyst would represent an improvement with respect to the homogeneous systems proposed so far in literature. In fact, up to now, the redox cycle has been closed only at very high temperature.^{6, 26}

55 Conclusions

The versatile ability of Cr^{II}/SiO₂ catalyst in CO₂ activation was explored by in situ FT-IR and UV-Vis spectroscopy. It was found that CO₂ is adsorbed and strongly activated already at room temperature, with the attendant formation of carbonate or 60 carboxylate-like surface species. As a preliminary test in this direction, it was demonstrated that activated CO₂ reacts with ethylene oxide at low pressure (< 1 bar) to give ethylene carbonate, along with some polymerization by-products. Current efforts are underway to optimize both, the reaction conditions and 65 the catalyst design in order to increase the selectivity towards ethylene carbonate formation, taking inspiration from the literature on catalysts for CO₂/epoxide polymerization^{13, 25} and on modification of the Phillips catalyst,^{35, 56} respectively. In this regard, substitution of silica with alumina support could facilitate the incorporation of CO₂ in chemicals of interest, because of the significantly larger ability of alumina to form surface carbonate species.²⁵

Besides non-reductive CO₂ activation, Cr^{II}/SiO₂ catalyst showed good performances in reduction of CO₂ to CO in 75 conditions significantly milder than for other heterogeneous catalysts proposed so far in literature,^{6, 26} i.e. upon heating at 350°C or, even more interesting, upon irradiation with UV-Vis light. In situ UV-Vis spectroscopy revealed the occurrence of a red-ox process converting Cr^{II} into Cr^{IV}-oxo species. Although a sustainable step to close the catalytic cycle by reducing Cr^{IV}-oxo species back to Cr^{II} is still missing, the fast reactivity of ethylene towards Cr^{IV}-oxo species suggests that reductive removal of the oxo-ligand from the Cr sites could be feasible in mild conditions. Further quantitative measurements are necessary before 85 proposing the Cr^{II}/SiO₂ catalyst for industrial application in CO₂ conversion. However, the spectroscopic results discussed herein provide a first evidence that this catalyst offers promising perspectives in this field.

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References

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† Electronic Supplementary Information (ESI) available: FTIR spectra of carbon dioxide and ethylenoxide adsorbed on silica, theoretical IR spectra of ethylene oxide (EO), ethylene carbonate (EC), EC•••Na⁺ complex,

- polyethylene oxide (PEO), polyethylenecarbonate (PEC) and the PEC•••Na⁺ complex. See DOI: 10.1039/b000000x/
1. M. Mikkelsen, M. Jorgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43-81.
 2. S. J. Freeth and R. L. F. Kay, *Nature*, 1987, **325**, 104-105.
 3. E. A. Quadrelli, G. Centi, J. L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194-1215.
 4. K. M. K. Yu, I. Curcic, J. Gabriel and S. C. E. Tsang, *ChemSusChem*, 2008, **1**, 893-899.
 5. C. A. Tsipis and P. A. Karipidis, *J. Phys. Chem. A*, 2005, **109**, 8560-8567.
 6. S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, *ACS Nano*, 2010, **4**, 1259-1278.
 7. W. Leitner, *Acc. Chem. Res.*, 2002, **35**, 746-756.
 8. D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem.-Int. Edit.*, 2010, **49**, 6058-6082.
 9. D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388-2410.
 10. H. Sugimoto and S. Inoue, *Pure Appl. Chem.*, 2006, **78**, 1823-1834.
 11. Y. Niu, W. Zhang, H. Li, X. Chen, J. Sun, X. Zhuang and X. Jing, *Polymer*, 2009, **50**, 441-446.
 12. S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287.
 13. M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141-163.
 14. N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645-1669.
 15. H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults and W. Tumas, *Chem. Rev.*, 2001, **101**, 953-996.
 16. U. Jayarathne, P. Chandrasekaran, H. Jacobsen, J. T. Mague and J. P. Donahue, *Dalton Trans.*, 2010, **39**, 9662-9671.
 17. M. Acemoglu, F. Nimmerfall, S. Bantle and G. H. Stoll, *J. Control. Release*, 1997, **49**, 263-276.
 18. D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers and A. L. Phelps, *Inorg. Chem.*, 2004, **43**, 1831-1833.
 19. W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725-727.
 20. D. J. Darensbourg, J. L. Rodgers and C. C. Fang, *Inorg. Chem.*, 2003, **42**, 4498-4500.
 21. D. J. Darensbourg and J. C. Yarbrough, *J. Am. Chem. Soc.*, 2002, **124**, 6335-6342.
 22. D. J. Darensbourg, J. C. Yarbrough, C. Ortiz and C. C. Fang, *J. Am. Chem. Soc.*, 2003, **125**, 7586-7591.
 23. R. Eberhardt, M. Allmendinger and B. Rieger, *Macromol. Rapid Commun.*, 2003, **24**, 194-196.
 24. R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498-11499.
 25. Y. Qin, X. Wang and F. Wang, *Progr. Chem.*, 2011, **23**, 613-622.
 26. P. Furler, J. R. Scheffe and A. Steinfeld, *Energy Environ. Sci.*, 2011.
 27. D. S. Laitar, P. Muller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2005, **127**, 17196-17197.
 28. G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 1979, **101**, 1767-1775.
 29. J. C. Bryan, S. J. Geib, A. L. Rheingold and J. M. Mayer, *J. Am. Chem. Soc.*, 1987, **109**, 2826-2828.
 30. F. M. Su, J. C. Bryan, S. Jang and J. M. Mayer, *Polyhedron*, 1989, **8**, 1261-1277.
 31. K. A. Hall and J. M. Mayer, *J. Am. Chem. Soc.*, 1992, **114**, 10402-10411.
 32. I. Castro-Rodriguez and K. Meyer, *J. Am. Chem. Soc.*, 2005, **127**, 11242-11243.
 33. T. J. Crevier and J. M. Mayer, *J. Am. Chem. Soc.*, 1997, **119**, 8485-8491.
 34. M. P. McDaniel, *Adv. Catal.*, 1985, **33**, 47-98.
 35. M. P. McDaniel, *Adv. Catal.*, 2010, **53**, 123-606.
 36. B. M. Weckhuysen, I. E. Wachs and R. A. Shoonheydt, *Chem. Rev.*, 1996, **96**, 3327-3349.
 37. E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, *Chem. Rev.*, 2005, **105**, 115-183.
 38. E. Groppo, A. Damin, F. Bonino, A. Zecchina, S. Bordiga and C. Lamberti, *Chem. Mater.*, 2005, **17**, 2019-2027.
 39. A. Damin, F. Bonino, S. Bordiga, E. Groppo, C. Lamberti and A. Zecchina, *ChemPhysChem*, 2006, **7**, 342-344.
 40. D. Gianolio, E. Groppo, J. G. Vitillo, A. Damin, S. Bordiga, A. Zecchina and C. Lamberti, *Chem. Commun.*, 2010, **46**, 976-978.
 41. A. Zecchina, C. O. Arean and E. Groppo, *ChemCatChem*, 2010, **2**, 259-262.
 42. C. Lamberti, E. Groppo, G. Spoto, S. Bordiga and A. Zecchina, *Adv. Catal.*, 2007, **51**, 1-74.
 43. C. Lamberti, A. Zecchina, E. Groppo and S. Bordiga, *Chem. Soc. Rev.*, 2010, **39**, 4951-5001.
 44. E. Groppo, J. Estephane, C. Lamberti, G. Spoto and A. Zecchina, *Catal. Today*, 2007, **126**, 228-234.
 45. J. E. Earley and W. Alexander, *J. Am. Chem. Soc.*, 1970, **92**, 2294-2297.
 46. S. Bordiga, F. Bonino, A. Damin and C. Lamberti, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4854-4878.
 47. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules (Molecular Spectra and Molecular Structure, Volume 2)*, D. Van Nostrand Company, 1945.
 48. E. Garrone, S. Abello, E. Borello, G. Ghiotti and A. Zecchina, *Mater. Chem. Phys.*, 1991, **29**, 369-378.
 49. G. Busca and V. Lorenzelli, *Mater. Chem.*, 1982, **7**, 89-126.
 50. C. L. Angell, *Trans. Faraday Soc.*, 1956, **52**, 1178-1183.
 51. E. Groppo, S. Bertarione, F. Rotunno, G. Agostini, D. Scarano, R. Pellegrini, G. Leofanti, A. Zecchina and C. Lamberti, *J. Phys. Chem. C*, 2007, **111**, 7021-7028.
 52. E. Groppo, W. Liu, O. Zavorotynska, G. Agostini, G. Spoto, S. Bordiga, C. Lamberti and A. Zecchina, *Chem. Mater.*, 2010, **22**, 2297-2308.
 53. T. Lear, R. Marshall, J. A. Lopez-Sanchez, S. D. Jackson, T. M. Klapotke, M. Baumer, G. Rupprechter, H. J. Freund and D. Lennon, *J. Chem. Phys.*, 2005, **123**, Art. No. 174706.
 54. T. Lear, R. Marshall, E. K. Gibson, T. Schutt, T. M. Klapotke, G. Rupprechter, H. J. Freund, J. M. Winfield and D. Lennon, *Phys. Chem. Chem. Phys.*, 2005, **7**, 565-567.

-
55. A. Zecchina, D. Scarano, S. Bordiga, G. Spoto and C. Lamberti, *Adv. Catal.*, 2001, **46**, 265-397.
56. E. Groppo, A. Damin, C. Otero Areán and A. Zecchina, *Chem. Eur. J.*, 2011, **17**, 11110 – 11114.