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Gas Sorption

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Controlled Reducibility of a Metal–Organic Framework with Coordinatively Unsaturated Sites for Preferential Gas Sorption**

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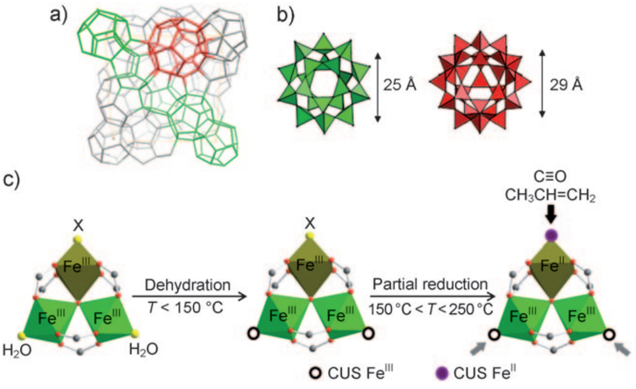
The current interest in porous crystalline metal–organic frameworks (MOFs)[1] is largely due to their wide range of compositions and structure types with low framework densities, their tunability, and the possibility of accessible, coordinatively unsaturated metal sites (CUS). The existence of CUS can strongly modify interactions with gases[2] or liquid adsorbates,[3] and is thus of particular importance gas storage and separations.

The redox properties of transition-metal-substituted zeolites and mesoporous materials have been extensively studied and used for selective catalysis in liquid-phase oxidation,[4] removal of nitrogen oxides,[5] and photocatalytic reactions.[6] These features are very rare for MOFs containing 3d metals, in particular with respect to the reducibility of the framework metal ions.[7] For this reason, we examine herein both the conditions of generation of iron CUS with mixed valence Fe^{II}/Fe^{III} by activation in the iron-containing MOF MIL-100(Fe),[8] $[\{Fe_3O(H_2O)_2F_{0.81}(OH)_{0.19}\}\{C_6H_3(CO_2)_3\}_2]\cdot n\,H_2O$ ($n \approx 14.5$), and its consequences for the selectivity of gas sorption used for potential environmental applications.

MIL-100(Fe), a crystalline three-dimensional iron(III) trimesate (Scheme 1), is based on μ_3-oxo-centered trimers of Fe^{III} octahedra. It has two sets of mesoporous cages (cage diameters: 25 and 29 Å) that are accessible through microporous windows (5 and 9 Å) and corresponding large BET surface areas ($>2000\,m^2\,g^{-1}$) and pore volumes ($>1.0\,cm^3\,g^{-1}$).[8a] In the as-synthesized form (Scheme 1c), the terminal molecules on two of the three iron octahedra are two H_2O molecules, and depending on the synthesis conditions, either F^- or OH^- anions on the third. As shown from an IR spectroscopic study on MIL-100(Cr),[9] these terminal water molecules are removable from the framework by heating above 100 °C under vacuum or a gas stream, leading initially to a large number of Fe^{III} CUS acting as Lewis acid sites in the pore. The structural characteristics of MIL-100(Fe) indeed make it a good candidate for inducing reducibility on the framework iron sites and corresponding improvements in preferential sorption properties on selected gas molecules.

The standard activation processes of porous solids mainly involve high temperatures to remove species present in the



Scheme 1. Representations of MIL-100(Fe): a) one unit cell, b) two types of mesoporous cages shown as polyhedra, c) formation of Fe^{III} CUS and Fe^{II} CUS in an octahedral iron trimer of MIL-100(Fe) by dehydration and partial reduction from the departure of anionic ligands ($X^- = F^-$ or OH^-).

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pores. When reduction in the framework is concerned, a more careful study of the activation is needed. Several points must be examined: 1) the invariance of the framework structure, 2) the efficiency of evacuation from adsorption isotherms, and 3) the influence of temperature, time, and pressure on the coordination and the nature of the metallic species. Owing to the large dimensions of the cell of MIL-100(Fe) (ca. 390000 Å^3), the last point cannot be directly analyzed by X-ray powder diffraction methods. Only in situ spectroscopic studies (IR, Mössbauer) can provide useful information (see the Experimental Section).

MIL-100(Fe) was hydrothermally synthesized at 160 °C for 8 h and then purified by two-step treatments (see the Experimental Section). The shape of the N_2 adsorption isotherms, BET surface areas ((2300 ± 50) m^2 g^{-1}), and pore volume (1.2 cm^3 g^{-1}) (Supporting Information, Figure S1) are not strongly affected upon increasing the activation temperature from 100 to 250 °C (12 h). In situ IR (see below) shows the appearance of Fe^{II} CUS above 150 °C, but this temperature in a stream of helium is not sufficient to provide efficient activation and iron reduction; it must be coupled with secondary vacuum over 12 h to enhance the phenomenon (Figure 1 b).

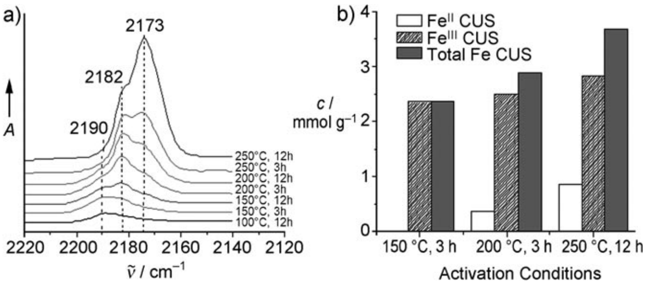

Figure 1. a) IR spectra of MIL-100 under a stream of 10% CO at 25 °C after activation under a helium flux at various temperatures over 3 or 12 h. b) Amount of Fe^{III} CUS and Fe^{II} CUS detected by IR analysis upon CO adsorption at −173 °C on MIL-100(Fe) activated under high vacuum at different temperatures.

The evolution of the oxidation state of iron with activation temperature of the as-synthesized MIL-100(Fe) was examined by both IR and Mössbauer spectroscopic methods. In-situ IR spectroscopic analysis using CO as a probe allowed both the oxidation states of iron and the amount of CUS to be quantified, either after treatment under high vacuum or in a helium stream (operando study; Figure 1). At room temperature, CO does not interact strongly with Fe^{3+} sites (weak band at 2190 cm^{-1}, Figure 1 a).[10] An increase in the activation temperature leads to the appearance of two new bands at 2182 and 2173 cm^{-1} (that are still observed after desorption under vacuum), which were assigned to CO adsorbed on Fe^{II} CUS.[11] The intensity of these bands increases with the activation temperature and the length of the treatment. To determine the number of CUS, CO adsorption experiments at −173 °C were performed on the sample activated under vacuum at 150 °C and 250 °C. The amount of Fe^{III} CUS, using a value of 2.7 cm μmol^{-1} for the molar absorption coefficient for the ν(CO), increases with the activation temperature (Figure 1 b). The CUS might be created not only through the removal of water but also to a much lesser extent from the departure of other molecules, such as trimesic acid coordinated on terminal sites of Fe^{III}. The final number of Fe^{II} CUS (ε(CO) = 4.8 cm μmol^{-1}) reaches 0.85 mmol g^{-1}, which is about 23 mol% of the total number of iron CUS after activation under vacuum at 250 °C for 12 h. These results clearly indicate that the creation of Fe^{II} CUS is not due to the direct reduction of Fe^{III} CUS but rather to the departure of anionic ligands (F$^-$ and OH$^-$), as confirmed by elemental analysis, as a decrease in the molar ratio of F/Fe trimer occurs upon reduction of MIL-100(Fe) (the content of F/Fe trimer before and after the activation treatment is 0.81 and 0.58, respectively). X-ray thermodiffractometry confirms the integrity of the framework after activation at 250 °C (Supporting Information, Figure S2). This important feature points out that significant amounts of Fe^{III} CUS and Fe^{II} CUS can be achieved by thermal activation in an inert gas flow or under vacuum whilst keeping the structure intact. Furthermore, high-vacuum conditions were effective to increase the amount of Fe^{II} CUS as compared with the gas flow one (0.85 mmol g^{-1} under vacuum and 0.24 mmol g^{-1} in helium at 250 °C for 12 h) (Supporting Information, Figure S3).

^{57}Fe Mössbauer analysis of the as-synthesized MIL-100(Fe) according to activation temperature confirms the change in the oxidation state of iron and also quantifies the proportions of Fe^{III} and Fe^{II} (Supporting Information, Figure S4). At $T < 150$ °C under high vacuum ($< 10^{-5}$ Torr), only Fe^{III} sites are present, but a component with a lower isomer shift is observed, clearly attributing to the progressive appearance of an iron site with lower coordination, that is, from six into five, owing to the departure of coordinated water molecules. IR spectroscopy confirms that stretching vibration bands of coordinated water molecules (ν(H_2O) at 3700–3680 and 3610–3600 cm^{-1})[9] were eliminated at $T <$ 150 °C. Above 150 °C, increasing amounts of Fe^{II} are observed by Mössbauer spectroscopy at higher temperatures. The Fe^{II} CUS content, which is negligible after degassing at 150 °C, reaches 14 mol% Fe^{II} with respect to total amount of iron (theoretically, 5.02 mmol g^{-1}) after degassing at 260 °C for 90 h (Supporting Information, Figure S5). At 260 °C, the presence of Fe^{II} suggests unambiguously that it originates from the reduction of Fe^{III}-X into Fe^{II}-□ (X = F$^-$ or OH$^-$, □: ligand vacancy). The 14 mol% contribution corresponds to more than 40% of the total number of Fe-X sites, which confirms only the partial reduction in the present case. Above 260 °C, X-ray thermodiffractometry shows that the framework begins to collapse (Supporting Information, Figure S2), indicating that MIL-100(Fe) are not able to withstand larger amounts of Fe^{II} in the framework. Therefore, we adopted 250 °C/12 h as a standard activation condition to perform secure sorption experiments without any collapse of structure. From the above results, we could show unambiguously that the Fe^{III} CUS are those on which water molecules were initially fixed and that the creation of Fe^{II} CUS originates from the loss of the X ligand according to $Fe^{3+}{-}X^- \rightarrow Fe^{2+}{-}\square$ rather than the direct reduction of Fe^{III} CUS.

Direct microcalorimetric experiments provide energetics of interactions between iron sites and gas probes, such as CO and CO_2, during gravimetric measurements of adsorption (Supporting Information, Figure S6). The heat of adsorption of CO (-28 to -39 kJ mol^{-1} when only Fe^{III} CUS are present) increases up to -51 kJ mol^{-1} for the partially reduced sample activated at 250 °C under vacuum. This higher value confirms the stronger interaction of Fe^{II} CUS with CO than that of Fe^{III} CUS, which was already observed by IR. In contrast, the heat of adsorption of CO_2 remains almost unchanged even after the reduction of iron in the range -25 and -35 kJ mol^{-1}. For MIL-100(Fe) activated at 250 °C, sorption uptakes of CO are higher than those of CO_2 up to 6.5 kPa. These results suggest that MIL-100(Fe) with Fe^{II} CUS could be used for the removal of CO impurity to protect the deactivation of Pt electrodes in low temperature fuel cells[12] or the removal of CO from CO_2-rich mixtures issued from, for example, the production of hydrogen from biomass.[13]

The use of mixed-valent MIL-100(Fe) may be also considered for further applications involving the selective separation or purification of olefins and acetylenes from hydrocarbon mixtures. Indeed, energy-efficient adsorptive separation and purification of these molecules are necessary for the petrochemical industry.[14] We focus herein on the adsorption and separation properties of the propane/propylene system. Figure 2 shows the adsorption isotherms and isosteric heats of adsorption of propane and propylene at 30 °C up to 6.5 kPa over MIL-100(Fe) activated at 250 °C under vacuum. Propane uptakes increase linearly with the sorption pressure, but they are noticeably lower than those for propylene. Remarkably, the sorption affinity for propylene over propane increases at low pressure; microcalorimetry confirmed this fact. In the presence of only pure Fe^{III} sites (activated at 100 °C under vacuum), similar values of the isosteric heats of adsorption (close to -30 kJ mol^{-1}) are observed for propane and propylene (Supporting Information, Figure S7). Using mixed-valent MIL-100(Fe), the introduction of Fe^{II} sites (250 °C under vacuum) dramatically changes the situation. The heat of adsorption of propylene increases up to -70 kJ mol^{-1} at low coverage, whilst that of propane remains the same. From these results, sorption profiles of propylene after activation at 250 °C directly correspond to the sorption in Fe^{II} CUS at lower partial pressure (< 0.25 kPa). At higher partial pressure (> 2.5 kPa), sorption profile mainly depends on Fe^{III} CUS (Figure 2).

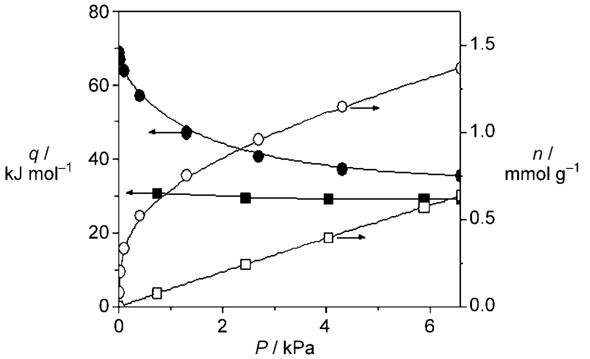

Figure 2. Isosteric heats of adsorption (q, filled symbols) and adsorption isotherms (amount adsorbed n, open symbols) for propane (■, □) and propylene (●, ○) at 30 °C over MIL-100(Fe) activated at 250 °C for 12 h under vacuum.

To evaluate the separation efficiency for propane/propylene mixtures, breakthrough tests of the binary mixtures were performed using a fixed-bed column packed with pellets of MIL-100(Fe). The sample was activated in a helium flux at 150 °C for 3 h and 250 °C for 12 h to determine the relative contribution of Fe^{II} CUS and Fe^{III} CUS in the separation. In the breakthrough curves at 40 °C and 0.25 kPa of C_3 hydrocarbons (Figure 3 a), the sample activated at 250 °C adsorbs propane up to only 7 min in the continuous flow of the mixture. However, the complete adsorption of propylene occurs until 175 minutes. Furthermore, the propane uptakes are almost the same regardless of activation temperature, whilst the propylene uptakes greatly increase with increasing the activation temperature. From the curves, the separation factors α for propylene over propane are estimated to be 28.9 for the sample activated at 250 °C and 5.1 for that treated at 150 °C. This result unambiguously shows that separation of C_3 hydrocarbons at low pressure greatly increases in the presence of Fe^{II} CUS although a few of Fe^{III} CUS are also associated with propylene adsorption. For the former sample, their separation factors markedly decrease by 10.8 at 5 kPa and 5.3 at 20 kPa with increasing partial pressures of gas mixtures (Figure 3 b). However, it is noteworthy that even the separation factor at 5 kPa is at least three times higher than that in the complex $[Cu_3(btc)_2]$ ($\alpha = 2$–3.3 at 40 °C and 5 kPa), which has been tested for the separation of propane and propylene.[15] This value means that Fe^{III} CUS is also effective in the adsorption of propylene, although the sorption affinity to propylene is weaker than those of Fe^{II} CUS. Furthermore, a curve shape for the separation factor over MIL-100(Fe) activated at 250 °C is very similar to that of the heat of propylene adsorption with increasing the sorption pressure of propylene (Figure 2 and Figure 3 b).

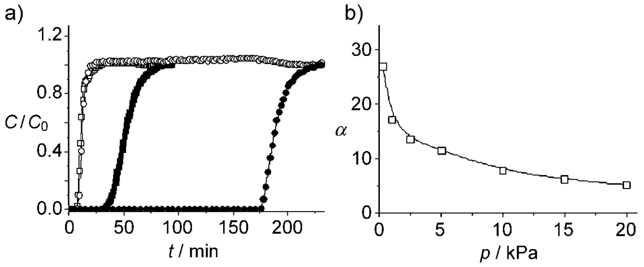

Figure 3. a) Breakthrough curves of an equimolar binary mixture ($p = 0.25$ kPa) of propane (open symbols) and propylene (filled symbols) in MIL-100(Fe) activated in helium at 150 °C for 3 h (■,□; $\alpha = 5.1$) and 250 °C for 12 h (●,○; $\alpha = 28.9$). b) Separation factor $\alpha = C_{propylene}/C_{propane}$ obtained from breakthrough curves of MIL-100(Fe) at partial pressure p. $T = 40$ °C for (a) and (b).

The preferential adsorption affinity of MIL-100(Fe) towards unsaturated gas molecules must be ascribed to the role of unsaturated iron sites that are formed upon activation at 250 °C. Fe^{III} CUS plays a role as a Lewis acid site to induce moderate interactions with these molecules (an electron donor); for example, donation of electrons from the filled π orbital or an electron lone-pair orbital of the unsaturated molecules into an empty d orbital of iron(III) according to the Dewar–Chatt–Duncanson model.[16] In contrast, Fe^{II} CUS offers strong interactions with them through π backbonding,[17] although the content that arises is not so high. The formation of Fe^{II} CUS decreases the Lewis acidity of the iron sites, but the presence of an additional d electron in iron(II) orbitals allows another type of interaction (π back-donation)[17] through delocalization of an additional d electron from partially occupied d orbitals of the iron(II) to the π* antibonding orbitals of the unsaturated gas molecule (π bond). This strengthens the π bonding with the olefin (or CO) and therefore increases the stability of the metal–adsorbate complex.

In conclusion, this work clearly demonstrates that a controlled reduction of a large-pore iron(III) trimesate with unsaturated iron sites, MIL-100(Fe), strongly increases the strength of interaction with unsaturated gas molecules, such as propylene and CO, that have either a double or triple bond. Therefore, this property leads to a dramatic improvement of not only preferential gas sorption but also separation performance for the investigated hybrid compound. The reducibility of MIL-100(Fe) to form Fe^{II} CUS has been unambiguously shown to be essential for selective gas purification or selective removal of unsaturated gas impurities. Therefore, the present results pave the way for the design and use of environmentally friendly gas adsorbents with preferential gas sorption properties.

Experimental Section

MIL-100(Fe) was prepared from a hydrothermal reaction of trimesic acid with metallic iron, HF, nitric acid, and H_2O at 160 °C for 8 h (see the Supporting Information for further details). IR studies were performed in an infrared operando cell using a self-supported wafer of MIL-100(Fe) (17 mg, 2 cm^2). Operando IR spectroscopic analyses were performed in a helium gas stream or under high vacuum after adsorption of CO as a probe gas for the identification of the oxidation states of iron and the quantification of CUS (Supporting Information). ^{57}Fe Mössbauer spectra were recorded in transmission geometry using a conventional constant acceleration spectrometer equipped with a $^{57}Co(Rh)$ source. The powdered sample was located under vacuum in a homemade cryofurnace, and the spectra were recorded in situ at −196 °C after high-temperature activation. A Tian–Calvet microcalorimeter was used to measure the adsorption enthalpies of propane, propylene, CO, and CO_2.[18] Sorption experiments using propane and propylene were performed in a static vacuum volumetric apparatus (Micromeritics Tristar 3000). The gas separation properties of MIL-100(Fe) were tested by breakthrough experiments using gas mixtures of C_3H_8/C_3H_6 with equimolar compositions in helium as a carrier gas at a flow rate of 30 mL min^{-1} (Supporting Information).

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[1] a) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191, and references therein; b) thematic issue: Metal–Organic Frameworks, *Chem. Soc. Rev.* **2009**, *38*, pp. 1201–1508.

[2] S. Ma, J. Eckert, P. M. Forster, J. W. Yoon, Y. K. Hwang, J.-S. Chang, C. D. Collier, J. B. Parise, H.-C. Zhou, *J. Am. Chem. Soc.* **2008**, *130*, 15899.

[3] a) S. S.-Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Prpen, I. D. Williams, *Science* **1999**, *283*, 1148; b) Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem.* **2008**, *120*, 4212; *Angew. Chem. Int. Ed.* **2008**, *47*, 4144; c) A. Demessence, D. M. D'Alessandro, M. L. Foo, J. R. Long, *J. Am. Chem. Soc.* **2009**, *131*, 8784.

[4] J. M. Thomas, R. Raja, G. Sankar, R. G. Bell, *Nature* **1999**, *398*, 227.

[5] M. Schwidder, S. Heikens, A. De Toni, S. Geisler, M. Berndt, A. Bruckner, W. Grunert, *J. Catal.* **2008**, *259*, 96.

[6] K. Ikeue, H. Yamashita, M. Anpo, T. Takewaki, *J. Phys. Chem. B* **2001**, *105*, 8350.

[7] G. Férey, F. Millange, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche, J.-M. Tarascon, *Angew. Chem.* **2007**, *119*, 3323; *Angew. Chem. Int. Ed.* **2007**, *46*, 3259.

[8] a) P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki, G. Férey, *Chem. Commun.* **2007**, 2820; b) J.-S. Chang, Y. K. Hwang, S. H. Jhung, D.-Y. Hong, Y. K. Seo, C. Serre, G. Férey, Patent WO 08/066293A1, **2008**.

[9] A. Vimont, J.-M. Goupil, J.-C. Lavalley, M. Daturi, S. Surblé, C. Serre, F. Millange, G. Férey, N. Audebrand, *J. Am. Chem. Soc.* **2006**, *128*, 3218.

[10] G. Magnacca, G. Cerrato, C. Morterra, M. Signoretto, F. Somma, F. Pinna, *Chem. Mater.* **2003**, *15*, 675.

[11] G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisicaro, A. Zecchina, I. Rossetti, E. Selli, L. Forni, E. Giamello, C. Lamberti, *J. Catal.* **2002**, *208*, 64.

[12] E. D. Park, D. Lee, H. C. Lee, *Catal. Today* **2009**, *139*, 280.

[13] A. Tanksale, J. N. Beltramini, G. Q. Max Lu, *Renewable Sustainable Energy Rev.* **2010**, *14*, 166.

[14] D. M. Ruthven, S. C. Reyes, *Microporous Mesoporous Mater.* **2007**, *104*, 59.

[15] a) N. Lamia, M. Jorge, M. A. Granato, F. A. Almeida Paz, H. Chevreau, A. E. Rodrigues, *Chem. Eng. Sci.* **2009**, *64*, 3246; b) A. Wagener, M. Schindler, F. Rudolphi, S. Ernst, *Chem. Ing. Tech.* **2007**, *79*, 851; c) J. W. Yoon, I. T. Jang, K.-Y. Lee, Y. K. Hwang, J.-S. Chang, *Bull. Korean Chem. Soc.* **2010**, *31*, 220.

[16] a) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939; b) J. Chatt, L. A. Duncanson, L. M. Venanzi, *J. Chem. Soc.* **1955**, 4456.

[17] G. L. Miessler, D. A. Tarr, *Inorganic Chemistry*, Pearson Education, Inc. Pearson Prentice Hall, Upper Saddle River, NJ, **2004**.

[18] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. D. Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jhung, G. Férey, *Langmuir* **2008**, *24*, 7245.