

DOI: 10.1002/anie.200602278

How Hydration Drastically Improves Adsorption Selectivity for CO₂ over CH₄ in the Flexible Chromium Terephthalate MIL-53***Philip L. Llewellyn,* Sandrine Bourrelly,
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One of the technological problems that face society today is the environmentally friendly and economically feasible separation, recovery, and recovery/reuse of vapors and gases. Several examples are currently of interest: the selective recovery of solvents, the recovery of greenhouse gases, and the purification of hydrogen. Many processes include an adsorption step in which microporous adsorbents, such as activated carbon and zeolites, are used. Recently a new class of porous materials have found interest: these metal organic frameworks (MOFs)^[1,2] or metal coordination polymers^[3] are built up from inorganic subnetworks and organic complexing molecules (phosphonates, carboxylates, sulfonates). These subnetworks often contain divalent or trivalent cations connected by organic groups such as carboxylates. Such structures possess tunnels or cavities with pore sizes between 3 and 35 Å. Several of these organic–inorganic hybrid porous solids^[4–11] have the interesting feature of being selectively flexible during the adsorption process by means of a breathing^[12] or gate-opening process,^[9] which depends on the nature of the adsorptive. Examples discovered by Férey and co-workers include flexible porous carboxylates formed by chains of metallic centers (MIL-53, -69)^[13,14] and with metal-center trimers (MIL-88A),^[15] These solids have shown to “breathe” with unprecedented increases in volume between 50 and 85% depending on the nature of the fluid. A consequence of this particular property is the possibility to develop novel selective separation and storage processes that could be less expensive than existing processes.

In many adsorption processes since the presence of water is detrimental, it is often removed using a precolumn. In the

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[**] The authors thank Alexandre Vimont for discussions concerning initial IR results. This work was supported by EU funding through the FP6-Specific Targeted Research Project “DeSANNS” (SES6-020133).

case of zeolites, this detrimental effect can be explained by the shielding of the specific cation sites by the water molecules.^[16] In some cases, however, a small amount of water can be beneficial, for example, for the separation of xylenes over $\text{BaX}^{[17]}$ where the water frees up the barium cation making it more available to interact with the xylene molecules.

Prior studies have dealt with the interaction of water with MOF systems, for example, MIL-53 (chemical formula $\text{M}(\text{OH})(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2)$).^[18] The structure of MIL-53 is built up from infinite chains of corner-sharing $\text{MO}_4(\text{OH})_2$ octahedra ($\text{M} = \text{Cr}^{3+}, \text{Al}^{3+}, \text{Fe}^{3+}$) interconnected by benzenedicarboxylate units.^[13] This results in a 3D metal-organic framework containing 1D diamond-shaped channels with pores of free diameter close to 8.5 Å.

In the presence of water, the MIL-53 ($\text{Cr}^{3+}, \text{Al}^{3+}$) solids exhibit an original breathing phenomenon upon hydration-dehydration which involves ca. 5-Å atomic movements (Figure 1).^[18] In the hydrated form (Figure 1, left) the pores

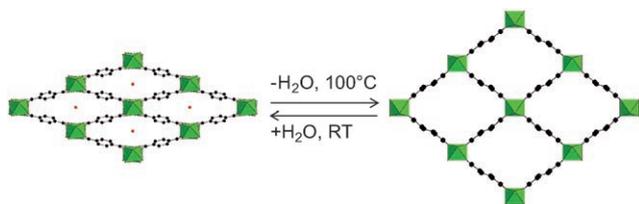


Figure 1. Hydration and dehydration process occurring in MIL-53(Cr, Al). Left: MIL-53LT (hydrated); right: MIL-53HT (dehydrated).

are slightly deformed owing to hydrogen-bond interactions between the hydrogen atoms of the water molecule and the oxygens of the carboxylate and the μ_2 -hydroxo group. The water is rapidly removed upon heating to give a structure with the more open porosity (Figure 1, right).

The adsorption of carbon dioxide in these solids is also accompanied by unusual structural phenomena.^[12] The dehydrated solid shows a marked two-step adsorption process, which has been interpreted as the initial closing of the structure before it reopens at higher pressures. This isotherm shape with carbon dioxide is in contrast to that with other molecules such as methane. Indeed, it is interesting to compare the adsorption of these greenhouse gases from basic principles. Whilst CO_2 has a significant quadrupole moment ($-1.4 \times 10^{-35} \text{ C m}$) that induces specific interactions with adsorbents (molecular orientation, hydrogen bonding...), CH_4 has no specific moment. It would thus seem that polar molecules have a distinct effect on the framework flexibility. With this in mind we studied the adsorption of carbon dioxide and methane on the hydrated form of MIL-53(Cr), in particular, in the presence of a second polar molecule (water). The thermodynamic and structural behavior of the hydrated form of the chromium form of MIL-53(Cr) was followed in adsorption and X-ray synchrotron measurements. The results indicate that the hydrated form is better suited than the dehydrated form for potential applications for the recovery of carbon dioxide from methane.

The gas adsorption isotherms (CO_2 , CH_4) of the hydrated and dried MIL-53(Cr) solids are shown in Figure 2. First, the

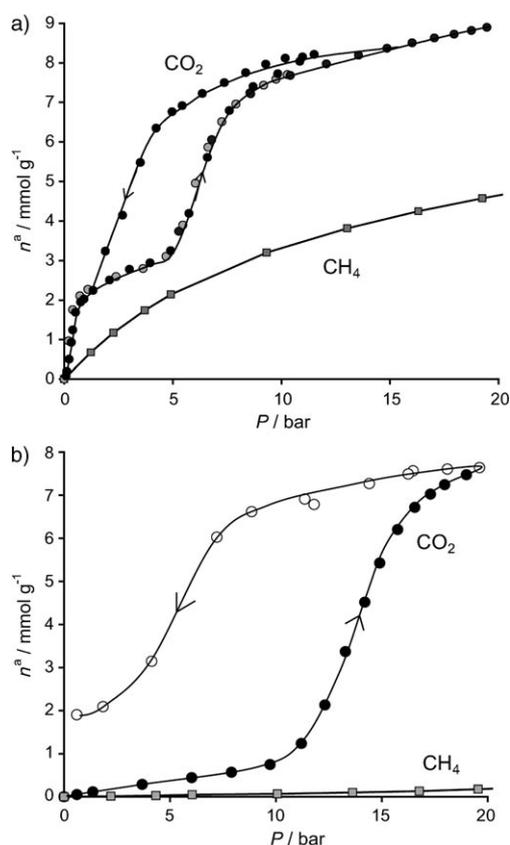


Figure 2. Comparison of the adsorption isotherms of carbon dioxide and methane at 304 K on a) dehydrated and b) hydrated forms of MIL-53(Cr). Grey- and black-filled circles represent two different experiments. n^a = amount adsorbed.

adsorption of carbon dioxide on the dehydrated MIL-53(Cr) sample occurs in a distinct two-step process with an initial plateau at around 3 mmol g^{-1} and a step in the 5–8-bar region of pressure with an uptake at the end of the step of around 8.5 mmol g^{-1} . Second, the adsorption of carbon dioxide on the hydrated sample shows very little uptake at pressures up to 10 bar, while a single and distinct uptake of ca. 7.7 mmol g^{-1} occurs in the 12–18-bar pressure range.

Previously, we suggested that a breathing process occurs for the adsorption of carbon dioxide^[12] in dehydrated MIL-53(Cr). To observe the structural evolution of the hydrated sample MIL-53(Cr) under CO_2 atmosphere, we performed in situ X-ray diffraction experiments under various pressures of carbon dioxide using an adequate gas system and synchrotron radiation (Figure 3). Prior to gas introduction, the sample is hydrated and exists in the closed form, as reported previously.^[18] This closed form is maintained for pressures up to 5 bar, although a small variation in cell parameters can be observed in this pressure region. In the region from 5 to 15 bar the open and closed structures coexist, while the amount of the former decreases as the proportion of the latter form increases. At 15 bar the open structure phase is almost pure. The cell parameters of this phase were determined by DicvolGV^[19] and refined using Fullprof^[20] as $a = 16.479(1)$, $b = 13.503(1)$, $c = 6.842(1) \text{ Å}$; $V = 1522.5 \text{ Å}^3$ space group *Imcm* (no. 74). This is rather close to the cell parameters of

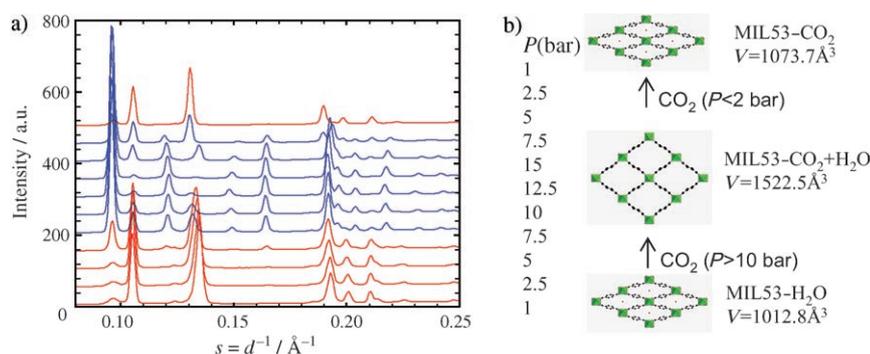


Figure 3. a) Evolution of X-ray diffraction patterns ($\lambda = 0.71118 \text{ \AA}$) with increasing pressure of carbon dioxide for the hydrated MIL-53(Cr) solid. b) Schematic view of the resulting breathing phenomenon for MIL-53(Cr).

the MIL-53_{HT} solid, that is, the “open” dehydrated phase: $a = 16.733(1)$, $b = 13.038(1)$, $c = 6.812(1) \text{ \AA}$; $V = 1486.5 \text{ \AA}^3$, despite a slightly higher cell volume for the phase in the presence of CO₂ at 15 bar.

The closed structure allows the adsorption of only a small amount of carbon dioxide with around 0.8 mmol g^{-1} adsorbed before the step at 11 bar. This is in contrast with the dried sample, which has an uptake $2\text{--}3 \text{ mmol g}^{-1}$ of CO₂ at 2 bar. Thus it would seem that the carbon dioxide is not able to enter this closed structure either because of steric hindrance or unfavorable interactions in the presence of water.

The adsorption of CO₂ above 11 bar leads to a total opening of the structure. Not only is the pressure associated with this step higher but also the pressure region of the adsorption step is much broader (11–18 bar) for the hydrated sample than for the dehydrated one (5–8 bar). The X-ray patterns suggest the coexistence of open and closed forms during this step and over a fairly large pressure domain. This may be a result of a particular particle size distribution where the smaller particles may undergo the opening process before the larger ones. A second explanation is the progressive diffusion of CO₂ into the core of the particle with increasing pressure. This process may occur over a large range of pressure as it may be accompanied by a displacement of the water. This point raises the question of the nature of the species adsorbed at high pressure (15 bar). Does CO₂ displace water, and is there a coexistence of the two species? Preliminary studies by IR spectroscopy suggest a replacement of the hydrogen-bonded water with CO₂ molecules.

The desorption isotherm obtained with the dried sample occurs in the 2–4-bar pressure region. This isotherm rejoins the adsorption branch at around 2 bar. The desorption isotherm obtained with the hydrated sample occurs below 6 bar. It is of interest that 1.9 mmol g^{-1} of gas is still adsorbed at the final point obtained here at 0.6 bar. This value is similar to that obtained with the dried sample and would suggest that CO₂ is present in majority in the pores and thus that the sample has more affinity for CO₂ than H₂O on desorption.

The adsorption of methane on dehydrated MIL-53(Cr) occurs with a gradual uptake for pressures up to 40 bar with an adsorbed amount close to 4.6 mmol g^{-1} at 20 bar. Adsorption of CH₄ on the hydrated samples shows almost no

methane uptake (0.2 mmol g^{-1}) at 20 bar. This is probably a result of the repulsive effect of the free water present in the pores that block or induce highly unfavorable conditions for the introduction of the nonpolar methane molecules.

The important feature of these results is that the apparent selectivity is drastically increased for the hydrated sample; in other words, the relative amount of CO₂ adsorbed with respect to CH₄ is greater for the hydrated material. This is not the case for other carbon dioxide adsorbents such as zeolites where often the water blocks specific sites. It was shown previously that the present sample is stable to

higher humidity, and thus a process in which a significant amount of water is present may not diminish the adsorption of carbon dioxide. Thus a preadsorber would not be required in a pressure-swing-adsorption-type process and process design could be simplified. Further work on the adsorption of carbon dioxide in the presence of increasing partial pressures of water is planned.

This work highlights the difference in adsorption behavior between a polar and nonpolar probe. In general, it will be important to examine other molecules of varying polarity. Nevertheless, these results are particularly interesting when one considers the recovery of carbon dioxide in mixed-gas streams or the use of such materials in sensor-type applications. As it would initially seem that the structural flexibility of these materials is related to the polar nature of the probe gas molecule, such results could pave the way for the use of highly flexible MOFs for the separation of other mixtures of polar and nonpolar gases. Initially, it will be of interest to study the feasibility to recover CO₂ in natural-gas feeds in which the water content is significant.

Experimental Section

The adsorption of CO₂ and CH₄ was carried out at 304 K and up to 20 and 40 bar, respectively. The isotherms were obtained using an adsorption manometry device using a point-by-point introduction of gas to the sample. The CH₄ and CO₂ were obtained from Air Liquide (Alphagaz, France) and are of 99.9999% purity. Each experiment was repeated several times, and each curve in the figures includes points from at least two experiments.

The in situ synchrotron powder diffraction experiments were carried out at the Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility. The data were collected on 0.7-mm quartz capillaries filled with the sample and attached to a gas manifold, using an MAR345 imaging plate at a sample-to-detector distance of 250 mm, $\lambda = 0.71110 \text{ \AA}$. The data were integrated using Fit2D program (Dr. A. Hammersley, ESRF) and a calibration measurement of a NIST LaB6 standard sample. CO₂ (Alphagaz, France, 99.9999% purity) was introduced to each pressure point. The response of the system to the pressure increase was immediate, as evident from in situ powder diffraction. Equilibrium was assumed

when two repeatedly measured diffraction patterns had become identical.

Received: June 7, 2006

Published online: October 20, 2006

Keywords: adsorption · carbon dioxide · microporous materials · organic–inorganic hybrid composites · X-ray diffraction

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