Communication

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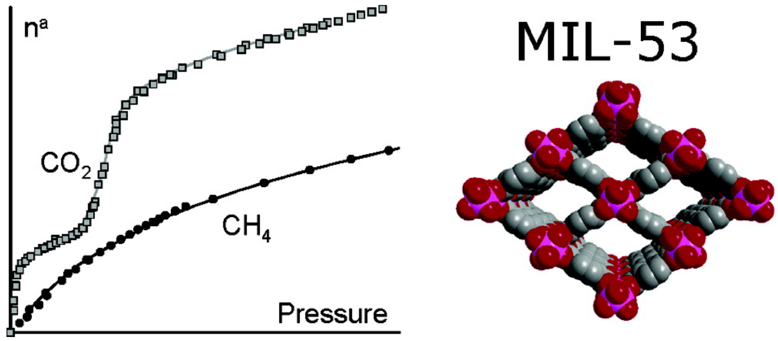

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Different Adsorption Behaviors of Methane and Carbon Dioxide in the Isotypic Nanoporous Metal Terephthalates MIL-53 and MIL-47

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One aspect of the sustainable development of our society concerns the environmentally friendly and economically favorable separation, capture, and storage of small gas molecules, i.e., H_2, CO_2, CH_4, etc. This is particularly the case for CO_2 that will be increasingly important in the future world economy since it is a necessary intermediate product in most of the H_2 production processes. The potential benefits of its storage include also reduced air pollution and thus improvements to human health. In processes such as pressure swing adsorption (PSA) for the capture of CO_2, adsorbents such as zeolites are adequate but difficult to regenerate without significant heating entailing low productivity and high costs. Nanoporous materials such as metal organic frameworks[1,2] are promising alternative solids for these applications. To date, most studies have concentrated on H_2 adsorption[3−5] in these materials, but a few reports have also shown the possibility to adsorb large amounts of CO_2[6−11] and CH_4.[7,12,13]

Several isotypic Cr,[14] Al,[15] and V[16] porous terephthalates, reported previously by the group of Férey, are good candidates for H_2 storage.[3] In this paper, we describe the adsorption of CH_4 and CO_2 at 304 K with direct microcalorimetry measurements carried out on the MIL-53 (M = Cr, Al) solids and its isostructural vanadium(4+) analogue, MIL-47.[16] Adsorption isotherms and energy curves for chromium and aluminum compounds exhibit unexpected adsorption behavior, depending on the probe gas (CH_4 or CO_2), which differs with the CO_2 uptake observed for the vanadium one. The possibility of a breathing effect of the MIL-53 structure upon CO_2 adsorption will be discussed.

The structure of the MIL-53/MIL-47 series is built up from infinite chains of corner-sharing $MO_4(OH)_2$ ($M = Al^{3+}, Cr^{3+}$) or $V^{4+}O_6$ octahedra interconnected by the dicarboxylate groups. This results in a 3D metal organic framework containing 1D diamond-shaped channels with pores of free diameter close to 0.85 nm. The chemical formula of the metal−benzenedicarboxylate MIL-53 is $M(OH)(O_2C{-}C_6H_4{-}CO_2)$ where M denotes the trivalent chromium[14] or aluminum.[15] The corner-sharing $\mu_2{-}OH$ groups of MIL-53 are replaced by μ_2-oxo groups in MIL-47 to give a chemical formula of $V^{IV}O(O_2C{-}C_6H_4{-}CO_2)$ for the latter.[16]

N_2 adsorption characterization at 77 K reveals a type I isotherm with an average surface area (Langmuir) about 1500 $m^2 \cdot g^{-1}$ in both cases.

Previously, the MIL-53 (Al^{3+}, Cr^{3+}) solids have been shown to exhibit an original breathing phenomenon upon hydration−dehydration[15] which is schematized in Figure 1. The structure to the left shows the hydrated form in which the pores are slightly deformed due to hydrogen-bond interactions between the hydrogens of the water molecule and the oxygens of the carboxylate and the μ_2-hydroxo group. This water is rapidly removed upon heating to give a structure schematized in the structure on the right with the more open porosity.

MIL-47 is totally anhydrous at room temperature, ands its structure resembles that of the dehydrated MIL-53.

The direct calorimetric measurements obtained during adsorption give information on the energetic nature of adsorbents which can be of importance to characterize solids in terms of specific adsorption sites and defects. Moreover, such information is of great interest for defining the adsorbent performance in process design. In general, the calorimetric curves highlight three different types of behavior.[17] The interaction of an adsorbate molecule with an energetically homogeneous surface will give rise to a relatively constant gas/adsorbent interaction energy. Adsorbent heretogeneity (pore size, defects, extraframework cations, etc.) will result in a decreasing energy curve with increasing coverage. Initially, the relatively strong interactions between the adsorbing molecules and the “specific surface sites” will gradually give way to lower interactions as these sites are occupied. Finally, in each system, an increase in the amount of gas adsorbed on a sample leads to an increase of the interactions between the adsorbate molecules themselves. Peaks in the calorimetric curve occur in the rare cases where phase transitions occur in the adsorbed phase.[18,19] Thus, each differential enthalpy curve varies and results from both adsorbate/adsorbate and adsorbate/adsorbent contributions.

It is interesting to compare the adsorption isotherms of CO_2 and CH_4 because, while CO_2 has a significant quadrupole moment (-1.4×10^{-35} C·m) that induces specific interactions with adsorbents (molecular orientation, hydrogen bonding, etc.), CH_4 has not. Thus, Figure 2 shows the isotherms (left) and the corresponding pseudo-differential enthalpies[17] (right) obtained for the adsorption of CH_4 and CO_2 on MIL-53 (Cr, Al)[20] at 304 K.

The adsorption isotherms obtained for CH_4 are typical of those obtained with nanoporous materials such as zeolites and activated carbons. It is interesting to note however, that greater amounts are adsorbed on the MIL-53 samples (≥ 6 $mmol \cdot g^{-1}$ at 35 bar) than on zeolites such as Faujasite or HZSM-5.[21] The amount adsorbed at 35 bar is about 155 (Al) and 165 (Cr) cm^3 of CH_4 (STP) per cm^3, which is close to the best results obtained with MOFs to date,[13] but lower than those reported for activated carbons.[22]

The enthalpies of adsorption obtained for the CH_4 adsorption are relatively constant during pore filling at around 17 $kJ \cdot mol^{-1}$, well above the liquefaction enthalpy of CH_4 (8.2 $kJ \cdot mol^{-1}$). This suggests gas interactions with a relatively homogeneous pore system as is the case, for example, during the adsorption of methane on known homogeneous adsorbents such as the purely siliceous zeolite silicalite.[23] The values observed of 17 $kJ \cdot mol^{-1}$ for both MIL-53

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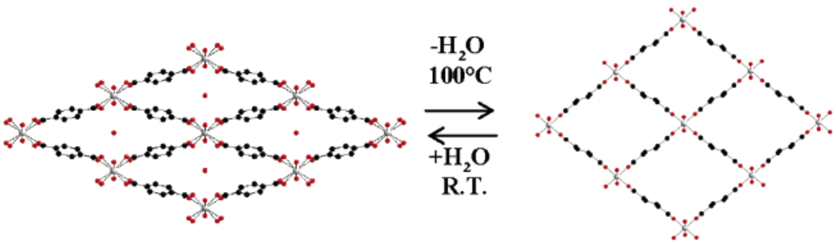

Figure 1. Hydration and dehydration process occurring in MIL-53 (Al, Cr). (Left) MIL-53_{LT} (hydrated). (Right) MIL-53_{HT} (dehydrated).

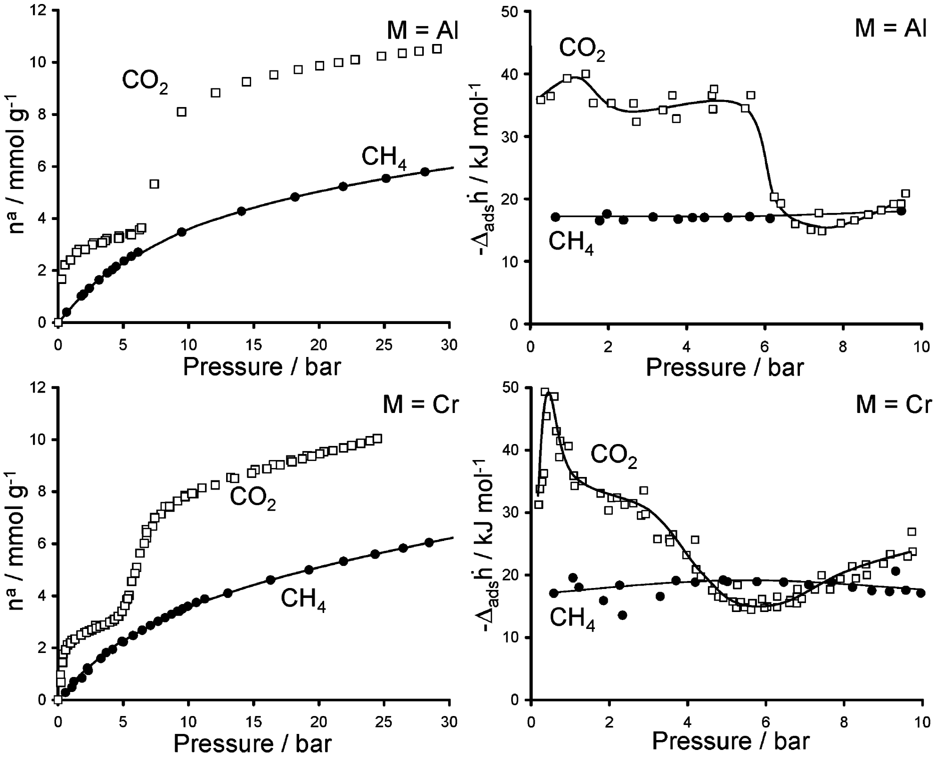

Figure 2. Isotherms (left) and differential enthalpies (right) at 304 K for the adsorption of CH_4 and CO_2 MIL-53 (Al) (top) and MIL-53 (Cr) (bottom). Data represent at least two experiments for each system. Lines are to guide the eye.

samples are similar to the values obtained for the adsorption of methane on NaY zeolite (17−17.8 kJ·mol^{-1}).[21,24]

Turning to CO_2, the striking feature of the adsorption isotherms obtained with both MIL-53 samples is the presence of a step at around 6 bar. The apparatus does not currently permit desorption at the present although such studies will be undertaken shortly. Such a behavior is unusual for the adsorption of CO_2 on other nanoporous materials under similar experimental conditions. The corresponding adsorption enthalpy for CO_2 on MIL-53 (Al) is around 35 kJ·mol^{-1} during the initial adsorption up to 6 bar. When the adsorption step occurs, the adsorption enthalpies sharply decrease to a minimum slightly below the enthalpy of liquefaction (17.2 kJ·mol^{-1}). The adsorption enthalpies of CO_2 on the chromium-containing sample show a distinct peak during initial adsorption before a region at around 32 kJ·mol^{-1}. A similar decrease in the enthalpy curve is observed during the step in the isotherm. The adsorption enthalpies for the two MIL-53 samples are lower with respect to those of aluminosilicate zeolites (50−70 kJ·mol^{-1}).[21,23] This relatively weak interaction with the MIL-53 samples is also confirmed by the possibility of removing the totality of the CO_2 under a 5 mbar vacuum. The total amounts adsorbed (~10 mmol·g^{-1}) at 30 bar are well above those obtained typically with zeolites[21,23−25] and comparable with the microporous carbons[26−28] and close to the best MOFs.[29]

Such a step in the adsorption isotherm during gas storage is uncommon, but some related phenomena have previously been observed for other systems.[8,11,12,30] A first theory used the concept of a molecular gate,[30] while others explain this behavior by a transition from a disordered structure to a more ordered one.[7] The adsorption of CH_4 and CH_3OH on a copper-containing MOF sample,[12] showed such steps in the isotherms which would be caused by the opening of the porosity with increasing pressure. Note that in these previous studies, the initial adsorption prior to the step is almost negligible. In the present case, however, there is significant adsorption below 1 bar, suggesting a different adsorption mechanism. The significant step observed with CO_2 but not for CH_4 highlights the role of the permanent quadrupole moment of the CO_2 in the adsorption process. It is thus possible that this probe molecule initially interacts with specific adsorption sites before completion of pore filling. In the present case, such adsorption sites could be the metallic centers. However, these sites are shielded by the organic ligands in MIL-53. A second possibility would be that the MIL-53 undergoes a structural change on adsorption as has already been observed previously during the adsorption of water.[14,15]

As the MIL-53 samples are outgassed at 100 °C prior to the gas sorption experiments, its open dehydrated form is initially present. Thus, to explain the unusual step in adsorption of CO_2, we assume that this is due to specific interactions between the gas and the

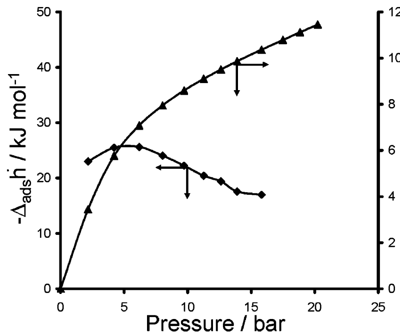

Figure 3. Isotherm (▲) and differential enthalpies of CO_2 adsorption (◆) at 304 K on MIL-47 (V).

framework which would cause a shrinkage of the structure for low uptake values (<6 bar). This would mean that the CO_2 initially sorbs to the hydroxyl groups. The total amount of CO_2 adsorbed before the step in the isotherms correspond to a ratio of 0.75 CO_2 per structural OH group in both MIL-53 samples. A further increase in the adsorption pressure would then lead to a reopening of the total porosity and total pore filling.

While a small peak in the enthalpy curve can be observed for the adsorption of CO_2 on the Al containing MIL-53 sample, this is far more pronounced in the Cr-containing sample. This can be the result of the MIL-53 structure transition. The reopening of the MIL-53 structure would be expected to require energy and thus be an endothermic phenomenon which is balanced by the exothermic adsorption phenomenon. This would explain the relatively low measured enthalpies at this point which is a result of both phenomena. Indeed one would not expect adsorption to occur if the corresponding enthalpy is below that of liquefaction.

It has previously been shown that CO_2 forms hydrogen bonds during adsorption in MOF samples,[10] and others report that a disordered MOF structure can be modified under the influence of probe molecule insertion.[9,11] In our case, the sample is not disorganized, and a molecular gate effect does not occur. To shed some light on this phenomenon, we have undertaken the CO_2 adsorption on the vanadium (IV) MIL-47,[16] which is isostructural to the MIL-53 solids.

As noted above, the corner-sharing μ_2-OH groups of MIL-53 are replaced by μ_2-oxo groups in MIL-47. As a consequence, MIL-47 is totally anhydrous at room temperature and does not breathe like MIL-53.

The CO_2 adsorption isotherm obtained with MIL-47 (Figure 3) does not present a distinct step. Nevertheless the amounts of CO_2 adsorbed above 10 bar are close to those obtained for the adsorption on the MIL-53 samples. The enthalpies of adsorption are lower than those observed for the MIL-53 samples. Indeed, such values of 20−25 kJ mol^{-1} are comparable to those obtained with the purely silicious zeolite, silicalite.[21] This relatively weak enthalpy of adsorption thus suggests no specific adsorption sites are present in the MIL-47 sample for the CO_2 quadrupole to interact with.

This result seems to confirm that the initial adsorption observed during CO_2 sorption on MIL-53 is due to the presence of interactions between the gas molecules and the OH groups.

This paper has highlighted a stepwise isotherm for the adsorption of the polar molecule CO_2 in two nanoporous MIL-53, metal terephthalates containing aluminum or chromium. Such an adsorption behavior is not observed in the case of the nonpolar probe CH_4. A comparison with the adsorption behavior in MIL-47 (with vanadium), strongly suggests that the MIL-53 samples undergo a "breathing type" mechanism. The observation of the step in the CO_2/MIL-53 isotherm would thus seem to be due to an adsorption mechanism different from those involving a molecular gate effect or structural disorganization/organization previously observed. A structural study of the unusual behavior is currently under progress. This variation in sorption behavior could be used in devices such as sensors and could also be used in novel separation/purification applications.

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