A multidisciplary approach to understanding sorption induced breathing in the metal organic framework MIL53(Cr)

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ABSTRACT

A combination of methods (microcalorimetry, FTIR, Synchrotron XRD and molecular modelling) have been used to understand the sorption induced breathing with in the chromium metal organic framework MIL53. Strongly polar probes such as CO_2 and H_2O induce such breathing whereas non-polar molecules such as CH_4 do not. In this system the breathing is strongly related to specific interactions between surface hydroxyls and the probe gas/vapour.

1. INTRODUCTION

One of the technological problems that face society today is the environmentally friendly and economically favourable separation and recovery of gases. Examples of current interest include the recovery of greenhouse gases (CO_2, CH_4) and the purification of hydrogen produced from biomass. Parts of these processes include an adsorption step in which microporous adsorbents such as activated carbon and zeolites are used. In such cases, it is the thermal regeneration step that is most costly in terms of energy.

Recent interest has focused on "Metal Organic Frameworks" (MOF) which are formed of metallic centres linked to each other through organic chains. Several of these organic-inorganic hybrid porous solids have the interesting feature, during adsorption, of being selectively flexible (breathing) as a function of the nature of the adsorptive fluid. A consequence of this particular property is the possibility to develop novel selective separation and storage processes with a favourable energetic cost with respect to already existing processes.

The aim of the present work is to understand the adsorption induced breathing process in the particular case of Chromium MIL53 via a coupling of several methods : microcalorimetry, FTIR, Synchrotron XRD and molecular modelling.

2. EXPERIMENTAL

The structural topology of MIL-53(Cr) [1-3] corresponds to a 4^4 net (Fig.1). It consists of tilted chains of $Cr^{III}O_4(OH)_2$ octahedra sharing trans hydroxyl groups. These chains are linked via carboxylate groups of the terephthalate ions (1,4-benzene dicarboxylate or BTC) forming a 3-D framework.

The resulting pore system is one-dimensional of free diameter close to 0.85 nm. The chemical formula of the metal-benzenedicarboxylate is $Cr(OH)(O_2C–C_6H_4–CO_2)$. The sample was synthesised by the group in Versailles following a previously published protocol [3].
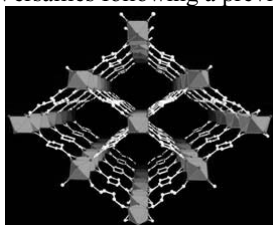

Fig. 1. Schematic diagram of the pore system of MIL53.

In situ sorption measurements were carried out using specially adapted apparatus able to work at ambient temperatures and under pressures up to 30 bars. The microcalorimetry was carried out in Madirel (Marseille) [4] and the FTIR data were collected in LCS (Caen). The *in situ* synchrotron powder diffraction experiments were carried out at the Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility. The molecular modelling was carried out in LPMC (Montpellier).

3. RESULTS AND DISCUSSION

The isotherms below show the adsorption of CO_2 and CH_4 on MIL53(Cr) at 303K (Fig. 2). On the left, the samples were outgassed until free of residual water. It can be seen that the behaviour of CH_4 is much like the adsorption on a zeolite sample. However the adsorption of CO_2 shows a distinct step [5]. The latter proceeds in two stages after a very fast uptake at low pressure (~2-3 mmol.g^{-1}), the isotherm reaches first a plateau between 1 and 4 bars, followed by an adsorption of more than a double amount of CO_2 at higher pressures. Interestingly, desorption occurs with a hysteresis loop with the desorption branch returning to the adsorption one at *ca*. 2 bar. Note that this phenomenon is not related to capillary condensation.

The differential enthalpies of adsorption obtained with the dehydrated sample are shown in Fig. 3. It can be seen that the initial adsorption occurs with an enthalpy of around -30 kJ mol^{-1}. The enthalpy then increases sharply to around -50 kJ mol^{-1} at the end of the first adsorption step. The second adsorption step is accompanied by a large decrease in the enthalpies to around the enthalpy of liquefaction -17.5 kJ mol^{-1}. At the end of this second step, the enthalpies increase again to around -25 kJ mol^{-1}.
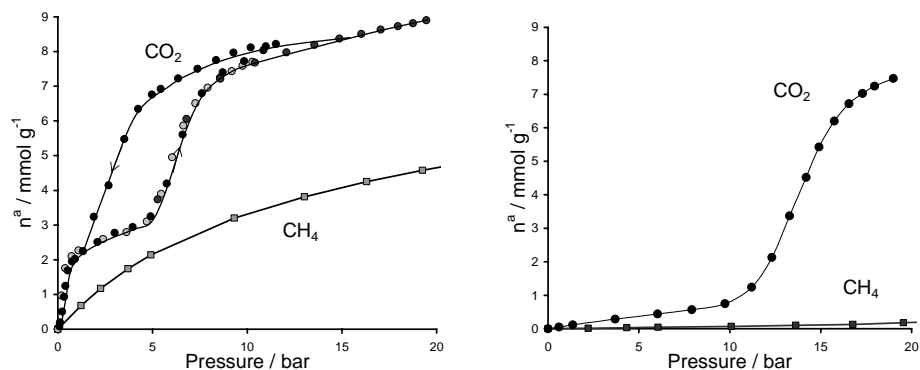
Fig. 2. CO_2 and CH_4 adsorption isotherms obtained at 303 K on the dehydrated (left) and hydrated (right) forms of MIL53(Cr).
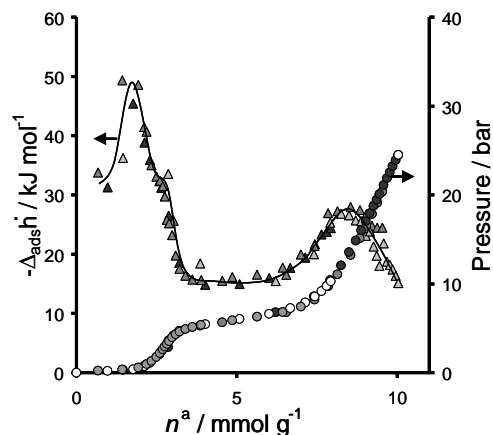

Fig. 3. Enthalpies and isotherm obtained for CO_2 adsorption at 303 K on dehydrated MIL53(Cr).

The evolution of the adsorption enthalpies are quite surprising. Such variations could be due to an initial adsorption on localised sites followed by the filling of the remaining porosity. A second hypothesis is that the adsorption phenomena are due to a change in the structure of the porous phase. This hypothesis emanates from the fact that this structure undergoes a contraction on contact with residual water vapour [6].

To follow the structure of the solid phase, experiments were carried out on an adsorption system adapted for *in situ* X-ray diffraction experiments. The results obtained for the dehydrated system are shown in Fig. 4. The diffractograms show that the dehydrated sample is in the open form. The initial dose of carbon dioxide closes the structure. This closed structure remains to a pressure of around 6-7 bars at which point the opening of the structure is observed. This corresponds to the second step in the isotherm. On desorption, the open structure is maintained to a pressure of around 2 bars at which the structure closes once again. Interestingly, the pore contraction, which occurs in MIL-53 upon adsorption of CO_2 at 1 bar is slightly lower than that in the case of hydration: the unit cell shrinks to 1072 $Å^3$ in the case of

the closed MIL53 (Cr) structure with CO_2 compared to ~1012 $Å^3$ for the hydrated structure. This would be consistent with the larger size of CO_2 compared to H_2O molecule.
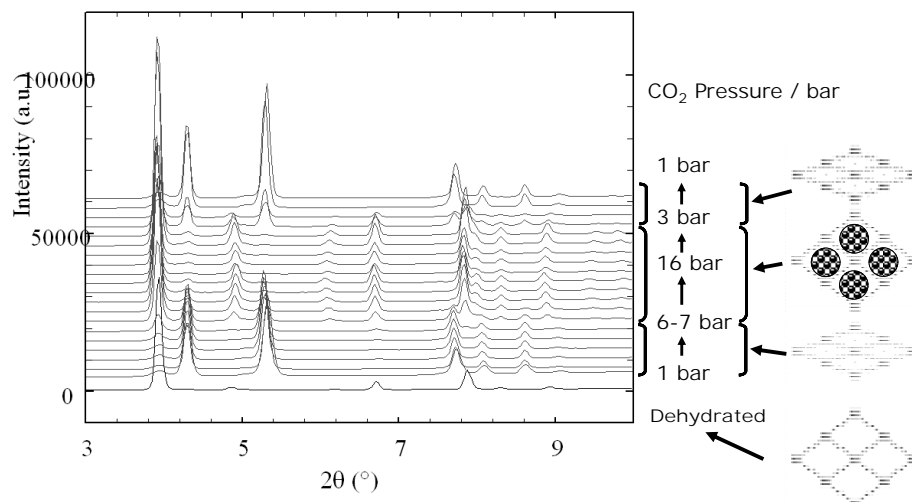

Fig. 4. X-ray diffraction spectra obtained on adsorption and desorption of CO_2 on the dehydrated MIL-53(Cr) sample.

To further understand the adsorption phenomena, Infrared spectroscopic experiments were performed in conditions similar to those used in the *in situ* diffraction studies (figures not shown). CO_2 gas was introduced step by step from 1 to 10 bar to the activated sample, and then progressively evacuated. An amount of the adsorbed CO_2 can be estimated from an integrated intensity of the ν_2 CO_2 bands between 645 cm^{-1} and 665 cm^{-1}. A profile of the adsorption-desorption curves can be deduced from the evolution of the intensities of these peaks versus pressure which is quite similar to the isotherm in Fig. 1. Spectra recorded during an adsorption-desorption cycle provide an evidence that the ν_{18a} ring mode [7] of the terephthalate entities situated at 1022 cm^{-1} for the dehydrated sample shifts to 1017 cm^{-1} under 1 bar of CO_2 and progressively comes back to its initial position when the pressure increases from 6 to 10 bar. This shift can be directly attributed to the changes in the MIL-53 structure: the bands at 1022 and 1017 cm^{-1} correspond to its open and close forms, respectively. This shift enables to evaluate the proportion of the open and close structures upon CO_2 adsorption. The adsorption mode of CO_2 can be deduced from the shape of the ν_2 CO_2 band. This band is split into two components at 653 and 662 cm^{-1} under 1 bar CO_2 due to the symmetry lowering of the adsorbed CO_2 molecule. This reveals that the main interaction involves the formation of electron donor-acceptor (EDA) complexes between the C atom of the CO_2 molecule and an electron-donor centre of the framework [8,9]. Moreover the significant perturbations of both $\nu(OH)$ and $\delta(OH)$ bands of hydroxy groups upon CO_2 adsorption ($\Delta\nu(OH) = 22$ cm^{-1} and $\Delta\delta(OH)= 30$ cm^{-1}) are similar to those observed in the case of CO_2-alcohol EDA complexes [10] and allow us to identify the electron-donor centre as the O-atom of the framework hydroxy groups. For higher CO_2 pressures (from 5 to 10 bar), a new ν_2 band appears at 659 cm^{-1}. This indicates that the opening of the structure gives rise to another form of CO_2 adsorption which still perturbs the OH groups ($\Delta\nu(OH) = 13$ cm^{-1} and

$\Delta\delta(OH)= 15$ cm^{-1}) but to a less extent than that at the low pressure. This second form persists during the desorption process down to 2-3 bars of CO_2, the pressure corresponding to the closing of the structure at the end of the hysteresis loop.
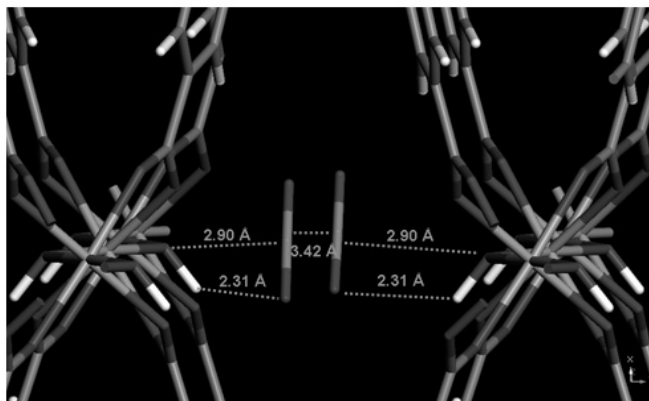

Fig. 5. View of the straight-on and direct interactions between CO_2 and the hydroxyl group in the DFT optimised closed MIL-53 structure (red circles: oxygen, gray circles: carbon, white circle : hydrogen, blue circle : chromium).
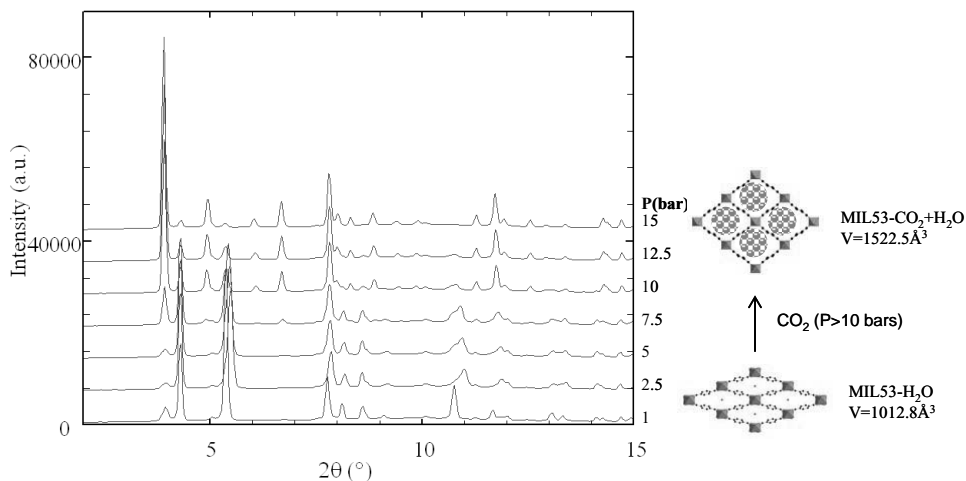

Fig. 6. X-ray diffractogram obtained on adsorption of CO_2 on the hydrated MIL-53 (Cr).

In parallel, as a confirmatory technique, the geometry optimisation of the closed structure of MIL-53 containing 2 CO_2/u.c. was then performed using periodic Density Functional Theory calculation with the PW91 functional, and the DNP basis set, as implemented in the DMol^3 code. The resulting arrangement of the CO_2 molecules (Fig. 5), confirms the presence of the main interaction, i.e. between the carbon of the CO_2 and the oxygen of the hydroxyl group (d$_{C...O}$ = 2.9 Å), which validate the results obtained by IR. The adsorbate molecules,

lying in the same pore, are almost parallel to each other and the characteristic distance between two consecutive CO_2 molecules is $d_{C...C}$= 3.4 Å. In addition, the orientation of the hydroxyl group is slightly modified by interaction with the CO_2, as shown by a comparison of the Cr-O-H angle, which changes by approximately 10% between the optimised CO_2 loaded and unloaded simulation cells. In order to infer the reason for the structural transition between the open and closed forms of MIL-53, we performed complementary DFT calculations on the open structure loaded with the same number of CO_2 molecules. The optimized geometry favors an arrangement where the adsorbates interact with the hydroxyl groups on opposite walls of the same pore, almost parallel to each other, with characteristic distances $d_{C...C}$= 4.4 Å and $d_{O...H}$ = 2.2 Å. Such an interaction would lead to a pulling of the pore walls towards each other, thereby bringing the 2 CO_2 molecules into the positions observed in our DFT calculations on the closed model.

The isotherms shown in Fig. 1 on the right show the adsorption of CO_2 and CH_4 on MIL53(Cr) which has been left in the presence of humidity [11]. It has previously been shown that under such conditions the MIL53 is in a closed form [6] and thus virtually no CH_4 is adsorbed. However, there is an adsorption of CO_2 above 12 bars. The in situ X-ray diffraction (Fig. 5) again allows an insight into the adsorption phenomena. As expected, the hydrated form of the MIL53(Cr) is contracted. The opening of the structure occurs in the region from 7.5 to 10 bars. With decreasing pressures (not shown), the desorption branch in the isotherm corresponds to a contraction of the MIL53 structure. Interestingly, the closed structure after desorption has the same cell volume as that observed during the initial adsorption of CO_2 on the dehydrated sample. Note also that the desorption branch on the hydrated sample does not rejoin the adsorprtion branch and that the final point corresponds to around 2 mmol g^{-1} which is a similar value to that observed with the dehydrated sample. These facts point to a replacement of the water in the hydrated sample by carbon dioxide.

Such results are of major significance for future applications in gas separation and storage. It can be appreciated that the important feature of the above results is that the apparent selectivity is drastically increased for the hydrated sample. That is to say that the relative amount of CO_2 adsorbed with respect to CH_4 is increased 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 has previously been shown that the present sample is stable to higher humidity and thus a process where a significant amount of water is present may not harm the adsorption of carbon dioxide. Thus the need for a preadsorber in a PSA type process would not be required thus leading to simpler process design. Further work on the adsorption of carbon dioxide in the presence of increasing partial pressures of water is planned.

4. CONCLUSIONS

This work highlights the difference in adsorption behaviour between a polar and non-polar probe. To make a generalisation, it will be of importance to follow other molecules of varying polarity. Nevertheless, the above 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 highly flexible MOFs for the separation of other mixtures of polar and non-polar gases. Initially, it will be of interest to study the feasibility to recover CO_2 in natural gas feeds in which the water content is significant.

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