On the breathing effect of a metal–organic framework upon CO_2 adsorption: Monte Carlo compared to microcalorimetry experiments†

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Grand Canonical Monte Carlo simulations have explained the breathing of a metal–organic framework upon CO_2 adsorption, first suggested by microcalorimetry.

Carbon dioxide is a necessary intermediate in existing hydrogen production processes, and a greenhouse gas implicated in the current opinion of global warming.[1] Therefore, with a future world economy based on hydrogen fuels on the horizon,[2] coupled with the recent commitments to the Kyoto Agreement whereby efforts must be made to reduce CO_2 emissions, there is a need for materials to efficiently capture and store CO_2. Zeolite materials such as X and Y Faujasite systems hold great promise for this purpose, and in recent years, extensive research using both computational and experimental methods has been performed in order to investigate the possibilities.[3,4] These potential adsorbents have been revealed to be adequate for pressure swing adsorption (PSA) type applications,[5] but are rather difficult to regenerate without significant heating entailing low productivity and high costs. Promising alternative solids for such applications include the nanoporous "Metal–Organic Framework" materials,[6,7] which are generally built up from metal–oxygen polyhedra containing either divalent (*e.g.* Zn^{2+}, Cu^{2+}, Mn^{2+}…) or trivalent (*e.g.* Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}…) cations interconnected by variable organic groups such as carboxylates or phosphonates. As in the case of zeolite systems, the number of different structures of these materials is large and some of these new organic–inorganic hybrid porous solids show the unusual feature of being selectively flexible *via* a breathing[8] or a gate opening process,[9] during the adsorption of different gases. Most recent theoretical and experimental investigations have focused on H_2 adsorption[10–12] in a large number of different MOF materials (*e.g.* Cu-BTC, the IRMOF family, MOF-5…), and only a limited number of experimental reports have revealed this class of materials as possible hosts for CH_4[13] and CO_2[8,13] storage.

The MIL (Matériaux Institut Lavoisier) series of hybrid porous materials synthesised by the group of Férey are promising candidates for the purpose of H_2[10] and CO_2[8] adsorption. Indeed, amongst these new materials, metal-benzenedicarboxylate MIL-53 (Al, Cr) has been found to present a higher adsorption capacity than Faujasite zeolites for gases such as CH_4 and CO_2.[8] The structure of the MIL-53[14,15] material is made up of chains of corner-sharing $MO_4(OH)_2$ octahedra (M = Cr^{3+}, Al^{3+}) interconnected by dicarboxylate groups. This 3D metal–organic framework contains 1D diamond-shaped channels with pores of nanometre dimensions. The chemical formula of the MIL-53 material is $M(OH)(O_2C–C_6H_4–CO_2)$ where M denotes the trivalent chromium or aluminium. One notes that this structure contains hydroxyl groups located at the metal–oxygen–metal links (μ_2 OH groups). This opens up the possibility of additional preferential adsorption sites and consequently a different adsorption mechanism to that of other members of the MIL family, such as its isostructural vanadium analogue MIL-47 (V),[16] in which the hydroxyl groups are absent. It has been previously reported[15] that the MIL-53 (Al) solids exhibit a breathing phenomenon upon H_2O adsorption, with hydrogen bonding between the water molecules and the framework being responsible for the switching between the MIL-53*np* (narrow pore) version, in which the pores are slightly deformed due to the hydrogen bonding, and the MIL-53*lp* (large pore) form, characterised by a more open porosity.

Some of us[8] recently reported an unusual microscopic type of behaviour of CO_2 in the aluminium-containing MIL-53 structure, concluded from our microcalorimetry data. The adsorption isotherm obtained from these data is not characteristic of a typical adsorption process in nanoporous materials, such as zeolites or MOF materials at room temperature. It contains steps, that were attributed to a "breathing" mechanism of the framework, whereby the structure interchanges between the narrow (MIL-53*np* (Al)) and the large (MIL-53*lp* (Al)) pore forms, in a way similar to that already observed upon water adsorption.[15]

The resulting questions on the adsorption mechanism at the molecular level, and the arrangement of the adsorbates within the porosity are still to be answered. In particular, the fact that a breathing mechanism has been proposed means that the experimental isotherm and the evolution of the enthalpy might contain distinct regions corresponding to adsorption either in the narrow or in the large pore form of MIL-53 (Al). However, the assignment of different regions of the isotherm to specific forms of the MIL-53 (Al) material has not yet been confirmed. Computational methods can thus play a useful role in order to deepen our understanding of the CO_2 adsorption mechanism at the atomic level, consistent with the experimental data.[4] Although several molecular simulations have been performed on hydrogen in MOFs using mainly quantum calculations,[11,17,18] this paper focuses on the theoretical

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study of the CO_2 adsorption in hybrid porous materials using Grand Canonical Monte Carlo (GCMC) simulations based on atomistic potential parameters and a partial charge model.[19]

The simulations were performed using the GCMC implementation in Accelrys Cerius2.[20] The CO_2 molecule was modelled as a three site Lennard–Jones model with parameters and charges previously validated for CO_2 adsorption in zeolite systems.[4] The narrow and large pore forms of the MIL-53 (Al) framework were modelled as being rigid with the constituent atoms at the positions reported by crystallography.[15,21] This approach is reasonable, since *in situ* X-ray studies show that there is no change in cell parameters between 0 and 6 bars, and 6 and 30 bars, upon CO_2 loading.[21] The partial charges for the hybrid material were extracted using Density Functional Theory (DFT) calculations, which are described in detail elsewhere.[22] The interatomic potentials used to describe the adsorbate–adsorbent and the adsorbate–adsorbate interactions were a combination of parameters from Shen[23] and our previously derived potentials.[4] The GCMC technique allowed us to calculate first the isotherms and the evolution of the differential enthalpies of adsorption as a function of the pressure for both the narrow and large pore MIL-53*np* (Al) and MIL-53*lp* (Al) forms which are further combined to reproduce the experimental data measured by microcalorimetry.

As stated before, it was assumed that the existence of a step, and then a sharp increase in the amount of CO_2 adsorbed in the experimental isotherm indicates that there are two forms of the MIL-53 (Al) structure resident during the CO_2 adsorption process. At very low pressures (below 0.10 bar), and pressures above 6 bars, the large pore form is present, whereas between 0.25 and 6 bars one would find the narrow pore analogue. The GCMC-derived isotherms, calculated separately for the MIL-53*np* (Al) and MIL-53*lp* (Al), are reported in Fig. 1a. We can observe that the maximum simulated amount of CO_2 is much greater for MIL-53*lp* (Al) than MIL-53*np* (Al). Furthermore, to reproduce the experimental adsorption isotherm from these calculated results, it seems appropriate to follow the MIL-53*np* (Al) curve up to a pressure around 6 bars and then to switch over the MIL-53*lp* (Al) curve. As indicated in Fig. 2a, the simulated "composite" isotherm displays the experimental characteristic step around 6 bars as well as a saturation loading about 9 CO_2 per unit cell, only slightly overestimating the experimental values. The suddenness of the structural transition of the hybrid porous material would dictate the sharpness of the jump observed in the experimental isotherm. From this good agreement between experiment and simulation (Fig. 2a), it can be clearly established that the measured isotherm is actually a combination of two distinct contributions from both the narrow and large pore versions. This unusual behaviour is analogous to that previously observed for the adsorption of *p*-xylene in silicalite whereby a structural switching of two forms of this zeolite material was reported.[24]

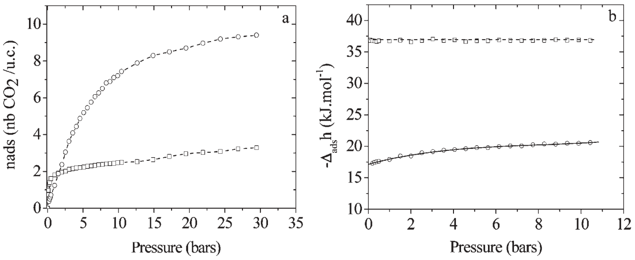

Fig. 1 Simulated absolute isotherms (a) and evolutions of the differential enthalpy of adsorption as a function of the pressure (b) for carbon dioxide in both MIL-53*np* (Al) (□), MIL-53*lp* (Al) (○) forms.

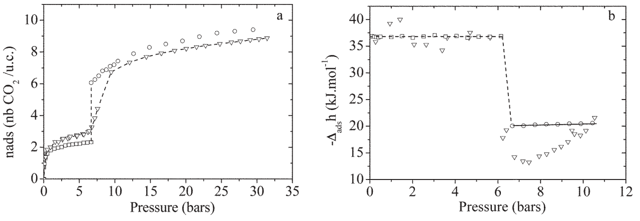

Fig. 2 "Composite" absolute isotherm (a) and evolution of the differential enthalpy of adsorption as a function of the pressure (b) for carbon dioxide in MIL-53 at 300 K obtained by using the MIL-53*np* (Al) (□) predictions up to 6 bars and then switching over to the MIL-53*lp* (Al) (○) simulations. The resulting isotherm and evolution of the differential enthalpy of adsorption are compared with the experimental data collected by microcalorimetry (▽). Lines are to guide the eyes.

A further indication of the transition in structural form comes from the significant modification of the differential enthalpy of adsorption observed by microcalorimetry and our simulations help to explain the reason for this change in the measured enthalpies of adsorption. Beyond 6 bars, there is a sharp decrease in the enthalpies indicating a change in the mode of interaction between the hybrid porous framework and the CO_2 molecule. This drop in enthalpies occurs at the same pressure as the increase in adsorbed amount in the experimental isotherm. The simulated evolutions of the differential enthalpies of adsorption as a function of the pressure are reported in Fig. 1b for the narrow and large pore MIL-53 (Al) forms. An almost flat enthalpy profile is obtained for the MIL-53*np* (Al) form, in the wide range of pressure with value centred around 37.0 kJ mol^{-1} whereas an increase of the enthalpy of adsorption with the pressure is predicted for the MIL-53*lp* (Al) material with values ranging from 20 to 24 kJ mol^{-1} (Fig. 1b). Both value and trend of the "composite" enthalpy plot reported in Fig. 2b compare well with the experimental data collected in the range of pressure [0–6 bars] where the corresponding enthalpy of adsorption is centred around 35.0 kJ mol^{-1} (Fig. 1b). Note, however, that the enthalpies obtained experimentally do not show a completely flat profile in this initial region. Above 6 bars, the simulated enthalpy values are slightly overestimated by our model when one compares them with the experimental ones. The two distinct simulated energetic behaviours thus obtained for the narrow and large pore forms of the hybrid material respectively allow us to confirm the existence of a structural switching during the adsorption process already demonstrated from the analysis of the isotherms. Nevertheless, one should bear in mind that the simulation study only takes into account the adsorption process, and does not take into account the heat effects generated during the actual breathing process of the MOF structure. Experimentally, however, a global measurement is obtained and thus any differences in enthalpies between experiment and simulation at the beginning of the isotherm (for example, the peak at the beginning of the enthalpy profile measured by microcalorimetry) and during the isotherm step can be assigned to the breathing effects. In our GCMC-calculated enthalpy profile, these specific features are not modelled.

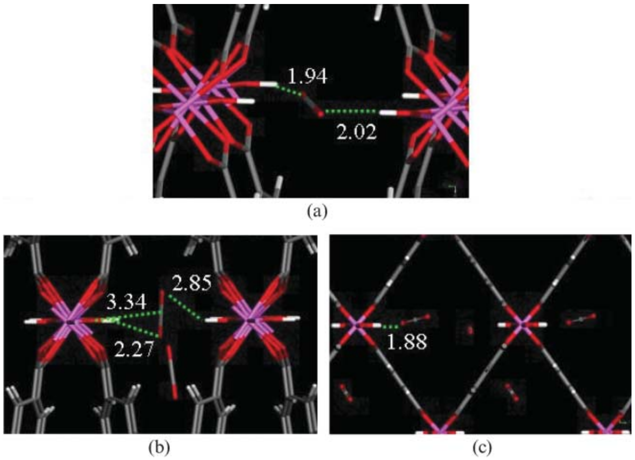

Fig. 3 Typical arrangements of the CO_2 molecule in MIL-53*np* (Al) at the initial stage of loading (a), beyond 2 CO_2/u.c (b) and in MIL-53*lp* (Al) at the initial stage of loading (c). The characteristic distances O_{CO_2}–$H_{\mu2\text{-}OH}$ are reported in Å.

Our simulation showed that the adsorbate molecules mainly interact with the μ_2 hydroxyl groups in both versions of MIL-53 (Al). In the case of MIL-53*np* (Al), at the initial stage of loading, a double interaction between the oxygen atoms of the adsorbate molecule and two hydrogen atoms on μ_2 hydroxyl groups on opposing pore walls is the preferential adsorption arrangement. An illustration of this interaction is provided in Fig. 3a where the interaction between the quadrupolar CO_2 molecule and the μ_2 hydroxyl groups involves characteristic O_{CO_2}–$H_{\mu2\text{-}OH}$ distances (d = 1.94 Å and 2.02 Å) of the same order of magnitude as those of the hydrogen bonds previously observed in the case of the polar water interacting with the carboxylate groups. In this structure, such a strong interaction, possible because of the narrow pore width of 8.5 Å, would be responsible for the contraction of the 1D channel. At 2 CO_2 molecules per unit cell, which corresponds to the loading observed in the experimental and simulated isotherms at around 6 bars (Fig. 2a), all four of the hydroxyl groups present in one unit cell are involved in forming this double interaction. For higher amounts of adsorbate molecules, we observed that such a favourable geometry is broken, due to interaction between the CO_2 molecules. The resulting arrangement corresponds to a less energetic single interaction between the CO_2 adsorbate and both organic linker and μ_2 hydroxyl group (Fig. 3b). Indeed, the removal of such strong interactions would explain the breathing phenomenon leading to a more open porosity for the next step of the adsorption process. Then, the increased pore width in the MIL-53*lp* (Al), to 13 Å rules out such a double interaction in that version of MIL-53, and the most likely CO_2 arrangement is a direct, 'straight on' O_{CO_2}–$H_{\mu2\text{-}OH}$ single geometry, shown in Fig. 3c, with a characteristic distance of 1.88 Å between the two entities. This weaker interaction explains the difference in enthalpy of adsorption obtained both experimentally and computationally for the two MIL-53 (Al) forms. As the pores are further filled, our simulations predict geometries whereby the probe molecule interacts with the hydrogen atoms on the organic groups, as well as the inorganic part.

In summary, our GCMC simulations have provided evidence for a breathing mechanism upon CO_2 adsorption in the MIL-53 (Al) materials as previously suggested by microcalorimetry measurements.[8] The adsorption amounts from the predicted isotherms for each of the forms of the MIL-53 (Al) correspond well to those in the relevant region of the experimental isotherm which can thus be explained as containing a contribution from both forms. This evidence is reinforced by the simulation of the differential enthalpies of adsorption whose values and profile as a function of the pressure match those obtained by microcalorimetry quite well, the values in the region below 6 bars matching well those calculated for the MIL-53*np* (Al) and those above 6 bars being close to those for the high temperature MIL-53*lp* (Al) analogue. Such a nice agreement between experiment and simulation validates both our interatomic potential parameters and the MIL-53 (Al) framework model taken directly from the previous hydration–dehydration study. This observation suggests that the quadrupolar CO_2 molecule induces a breathing effect within the same order of magnitude as that of the polar H_2O molecule and which is confirmed by ongoing *in situ* X-ray synchrotron measurements under various pressures of carbon dioxide.

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