Adsorption (2007) 13: 461–467
DOI 10.1007/s10450-007-9025-5

Adsorption of CO_2 in metal organic frameworks of different metal centres: Grand Canonical Monte Carlo simulations compared to experiments

**Naseem A. Ramsahye · Guillaume Maurin ·
Sandrine Bourrelly · Philip L. Llewellyn ·
Thomas Devic · Christian Serre · Thierry Loiseau ·
Gerard Ferey**

Received: 30 April 2007 / Revised: 10 July 2007 / Accepted: 13 July 2007 / Published online: 29 September 2007

Abstract A Grand Canonical Monte Carlo study has been performed in order to compare the different CO_2 adsorption mechanisms between two members of the MIL-n family of hybrid metal-organic framework materials. The MIL-53 (Al) and MIL-47 (V) systems were considered. The results obtained confirm that there is a structural interchange between a large pore and narrow pore forms of MIL-53 (Al), not seen with the MIL-47 (V) material, which is a consequence of the presence of μ_2-OH groups. The interactions between the CO_2 molecules and these μ_2 OH groups mainly govern the adsorption mechanism in this MIL-53 (Al) material. The subsequent breaking of these adsorption geometries after the adsorbate loading increases past the point where no more preferred adsorption sites are available, are proposed as key features of the breathing phenomenon. After this, any new adsorbates introduced into the MIL-53 (Al) large pore structure experience a homogeneous adsorption environment with no preferential adsorption sites in a similar way to what occurs in MIL-47 (V).

Keywords CO_2, adsorption · Metal-organic frameworks · Grand Canonical Monte Carlo · Microcalorimetry · Isotherm · Differential adsorption enthalpy, adsorption mechanism, breathing effect

1 Introduction

Carbon dioxide is a necessary intermediate in existing hydrogen production processes, and a greenhouse gas implicated in the current opinion of global warming (Kikkinides et al. 1993). In addition, recent commitments to the Kyoto Agreement means that efforts must be concentrated to reduce CO_2 emissions, opening up the need for materials to efficiently capture and store this gas. Promising candidates for this application include the nanoporous "Metal-Organic Framework" materials (Férey et al. 2005; Yaghi et al. 2003), which are built up from metal-oxygen polyhedra containing either divalent (Zn^{2+}, Cu^{2+}) or trivalent (Al^{3+}, Cr^{3+}) cations interconnected by variable organic groups such as carboxylates or phosphonates. 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 (Bourrelly et al. 2005) or a gate opening process (Zhao et al. 2004), during the adsorption of different gases. Some experimental data previously published have revealed this class of materials as possible hosts for CH_4 (Sudik et al. 2005), and CO_2 (Sudik et al. 2005) storage. The MIL (Materials of the Institut Lavoisier) series of hybrid porous materials synthesised by the group of Férey, are promising candidates, for the purpose of H_2 (Férey et al. 2003; Latroche et al. 2006; Surble et al. 2006), CH_4 and CO_2 adsorption (Bourrelly et al. 2005). The structure of the MIL-53 material, is made up of chains of corner-sharing $MO_4(OH)_2$ octahedra ($M = Cr^{3+}$, Al^{3+}, Ga^{3+}, Fe^{3+}) interconnected by dicarboxylate groups (Serre et al. 2002;

N.A. Ramsahye · G. Maurin (✉)
Institut Charles Gerhardt Montpellier, UMR CNRS 5253, UM2, ENSCM, Université Montpellier 2, 34095 Montpellier cedex 05, France
e-mail: gmaurin@lpmc.univ-montp2.fr

S. Bourrelly · P.L. Llewellyn
Laboratoire MADIREL UMR CNRS 6121, Université de Provence, 13397 Marseille cedex 20, France

T. Devic · C. Serre · T. Loiseau · G. Ferey
Institut Lavoisier, UMR CNRS 8637, Université de Versailles Saint-Quentin-en-Yvelines, 78035 Versailles cedex, France

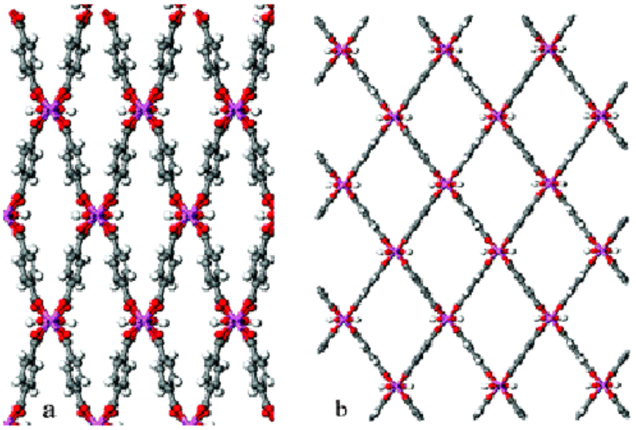


Fig. 1 Views of the 3-D structure of the narrow and large pore MIL-53np (Al) **(a)** and MIL-53lp (Al) **(b)** structures, contrasting the small pores of the MIL-53np (Al) form, and the more open channel of the MIL-53lp (Al) version. The MIL-47 (V) material is isostructural to the large pore form of MIL-53 (Al)

Loiseau et al. 2004). 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 vanadium analogue MIL-47 (V) (Barthelet et al. 2002), in which the μ_2-OH groups are absent. It has been previously reported 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* (Al) (narrow pore) version, in which the pores are slightly deformed due to the hydrogen bonding, and the MIL-53*lp* (Al) (large pore) form, characterised by a more open porosity. The MIL-47 (V) material is isostructural to the MIL-53*lp* (Al) framework (Barthelet et al. 2002). The MIL-53 (Al) narrow and large pore structures are shown in Figs. 1a and 1b respectively.

Some of us (Bourrelly et al. 2005) recently reported an unusual microscopic type of behaviour of CO_2 in the MIL-53 (Al, Cr) structures, concluded from our Microcalorimetry data. The adsorption isotherm obtained from this data 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 similar way to that already observed upon water adsorption (Loiseau et al. 2004). This phenomenon is not featured in the isotherm reported for adsorption of CO_2 on MIL-47 (V) (Bourrelly et al. 2005).

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. Computational methods can thus play a useful role in order to deepen our understanding of the whole CO_2 adsorption mechanism at the atomic level, consistent with available experimental data (Maurin et al. 2005). Several molecular simulation studies on H_2 and CH_4 adsorption in MOFs, using mainly quantum and Monte Carlo calculations (Roswell and Yaghi 2006; Frost et al. 2006; Yang and Zhong 2006a; Duren et al. 2004) are available in the literature. However, few studies report the simulation of CO_2 adsorption in such materials (Yang and Zhong 2006b). This paper reports a comprehensive theoretical study comparing the CO_2 adsorption in the MIL-53 (Al) and MIL-47 (V) hybrid porous materials, using Grand Canonical Monte Carlo (GCMC) simulations based on atomistic potential parameters and a partial charge model. The calculated adsorption isotherms and enthalpies are then compared to microcalorimetry data. Finally the adsorption mechanism is provided in both systems, consistent with the evolution of the differential adsorption enthalpy as a function of loading.

2 Computational details

2.1 Atomic partial charges calculations

The CO_2 molecule was modelled by an atomic point charge model in which the charges (in electron units) assigned to the carbon C (+0.72) and the oxygen O (−0.36) atoms were previously derived by *ab initio* calculations (Maurin et al. 2005). A periodic model of both the MIL-53*lp* (Al), MIL-53*np* (Al) and the MIL-47 (V) materials were first geometry optimised, using the crystallographic coordinates of the atoms as starting configurations (Loiseau et al. 2004; Barthelet et al. 2002). The partial charges for the hybrid porous MIL-53 (Al) and MIL-47 (V) materials were then extracted using Density Functional Theory (DFT) calculations. The Accelrys DMol^3 code (DMol^3 2005) was used for these calculations, which were performed using the PW91 GGA density functional (Perdew and Wang 1992), and the double numerical basis set containing polarisation functions on hydrogen atoms (DNP) (Hehre et al. 1972). The partial charges for the atoms in both models were first extracted using the Mulliken charge partitioning method (Mulliken 1955) as previously reported in our recent article (Ramsahye et al. 2007a). These calculated results are reported in Table 1, and the location of each atom type on the hybrid framework is described in Fig. 2.

2.2 Interatomic potentials

The interaction between the adsorbate and the organic ligand of both the MIL-53 (Al) and MIL-47 (V) frameworks

Table 1 Partial charges (in electron units) extracted for the atoms constituting the MIL-n frameworks of both MIL-53(Al) and MIL-47(V), using the Mulliken charge partitioning scheme. The labels of the atoms are detailed in Fig. 2

Atoms	h_c	cg1	cg2	c_c	o_c	h_o	M	o_h
Charges (Al)	0.145	−0.082	−0.089	0.584	−0.564	0.301	1.420	−0.729
Charges (V)	0.146	−0.071	−0.068	0.604	−0.496		1.207	−0.596

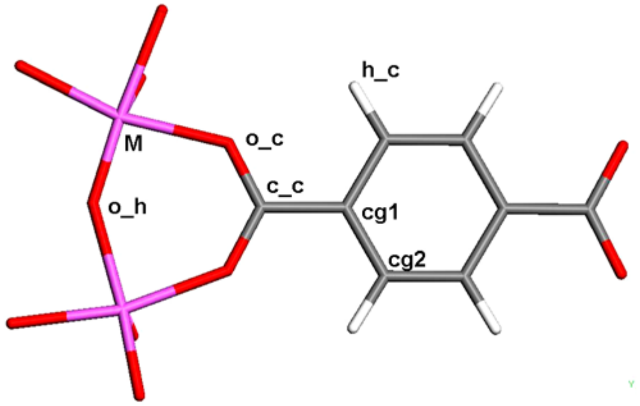


Fig. 2 Labels of the atoms for the organic and inorganic sections of the MIL-53 (Al) and MIL-47 (V) materials corresponding to the forcefield atom types, to allow the easy reading of Table 1

was treated in a similar way, using 12-6 Lennard-Jones parameters derived by Shen et al. (1995). The interactions between the CO_2 molecules and the inorganic part (Al(OH) and V(O)) were modelled as follows; the polarisability of the metal centers, which is much lower than those of the oxygen atoms, suggests that the repulsion-dispersion contribution of the inorganic part can be assigned only to the oxygens as well as the protons of the μ_2-OH groups in the case of the MIL-53 (Al) material. The 12-6 Lennard-Jones parameters for modelling the interactions between CO_2 and the oxygen atoms were extracted from our previous studies where we successfully reproduced the CO_2 adsorption properties in aluminosilicate materials (Maurin et al. 2005). In addition, the interaction between the protons and the carbon dioxide was represented by the sum of a Coulombic term and a Buckingham dispersion-repulsion potential whose parameters were recently derived from *ab initio* calculations (Déroche et al. 2007 submitted). All the potential parameters have been already reported in our previous publication (Ramsahye et al. 2007c).

2.3 Grand Canonical Monte Carlo (GCMC) simulations

Absolute adsorption isotherms were then computed using a Grand Canonical Monte Carlo algorithm that allows displacements (translations and rotations), creations and destructions of the CO_2 molecules. These simulations consisted of evaluating the average number of adsorbate molecules whose chemical potential equals those of the bulk phase for given pressure and temperature. All calculations were performed at 303 K using simulation boxes composed of 16 unit cells for both MIL-53*lp* (Al) and MIL-47 (V) and 32 unit cells for MIL-53*np* (Al) with typically $3{\cdot}10^6$ Monte Carlo (MC) steps, the frameworks of both pore forms of the hybrid structures being considered rigid, with atoms at the positions derived by X-ray Diffraction (Serre et al. 2007). The Ewald summation was used for calculating the long range electrostatic interactions and the short range nonbonded contributions were calculated with a cut-off distance of 12 Å (Frenkel and Smit 2002). The calculation of the differential adsorption enthalpies at 303 K for both hybrid structures was performed through the fluctuations over the number of particles in the system and from fluctuations of the internal energy U by considering very low pressure (1) (Nicholson and Parsonage 1982).

$$\Delta_{\mathrm{ads}}\dot{\mathrm{h}} = \mathrm{RT} - \frac{\langle \mathrm{U.N}\rangle - \langle \mathrm{U}\rangle\langle \mathrm{N}\rangle}{\langle \mathrm{N}^2\rangle - \langle \mathrm{N}\rangle^2}. \qquad (1)$$

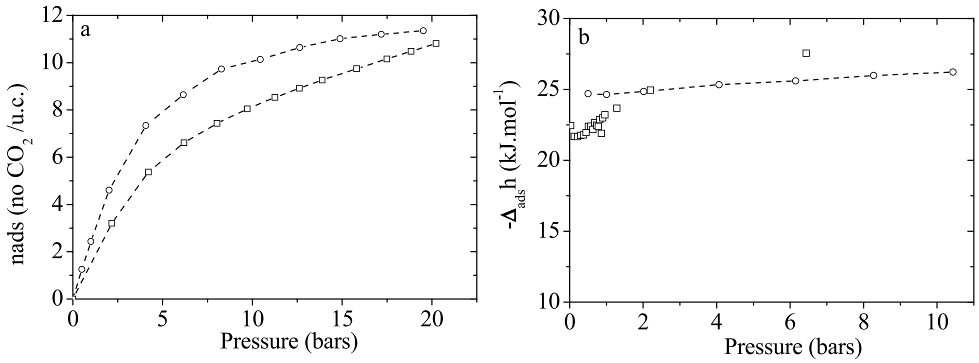
3 Results and discussion

3.1 Adsorption in the MIL-47 material

Recent microcalorimetry measurements performed by some of us (Bourrelly et al. 2005) for CO_2 adsorption on the MIL-47 material, yields a type I isotherm as shown in Fig. 3a. This is as one would expect for molecular adsorption in a nanoporous material, signifying steady, continuous adsorption. The shape of the experimental isoterm is reproduced by our simulation, although we overestimate the adsorbed amount most probably due to only a partial removal of organic molecules within the pores of the sample, during calcination (Fig. 3a).

Furthermore, this system has a flat enthalpy profile at the initial stage of loading with a significant increase at higher pressures as shown in Fig. 3b. Similar profiles have already been obtained for other systems such as siliceous zeolite where no preferential adsorption sites exist (Maurin et al. 2005). Indeed, carbon dioxide probes MIL-47 (V) as a homogeneous energetic surface with no preferential adsorption sites within the pore due to the absence of μ_2-OH groups. It gives rise to an almost constant CO_2/adsorbent interaction energy combined with a CO_2/CO_2 contribution increasing

Fig. 3 **(a)** The absolute adsorption isotherms and **(b)** evolutions of the differential adsorption enthalpy as a function of the pressure for carbon dioxide adsorbed in the MIL-47 (V): simulation (O) and experiment (☐)



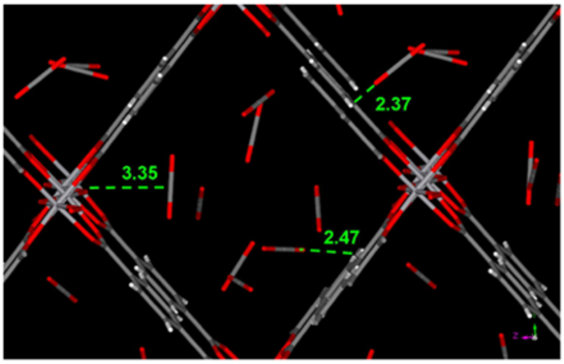


Fig. 4 A typical illustration of the CO_2 arrangement in the MIL-47 (V) structure at high loading corresponding to 8 molecules per unit cell. The reported distances are in Å. Although some molecules interact with the framework, there are no preferential adsorption sites

at higher loading, thus leading to an increase of the differential adsorption enthalpy with coverage as reported in Fig. 3b. Both simulated values and evolution of the enthalpies are in agreement with the experimental data, although our simulation does not reproduce the magnitude of the increase of the adsorption enthalpy so well.

The predicted CO_2 adsorption geometries relate well to the general conclusions previously drawn from the differential enthalpy plots (Fig. 3b). The CO_2 configurations calculated by our GCMC simulations show that there are no preferential adsorption sites within the pore although some association with the framework may be seen at high loadings. For instance, the adsorbate molecules can be located near the μ_2 oxygen atoms and interact with the framework by its C atom, although the interaction distances $O\ _{\mu 2}$–C_{CO2} are generally over 3.5 Å. An O_{Carboxyl}–C_{CO2} interaction is also possible, with similar O_{Carboxyl}–C_{CO2} distances to the $O_{\mu 2}$–C_{CO2} ones being predicted by the simulations. This observation is consistent with those previously obtained by our DFT calculations (Ramsahye et al. 2007b). A typical illustration of this CO_2 arrangement observed at high loading is provided in Fig. 4. These simulated findings are in very good agreement with our recent in situ X-Ray Diffraction data collected upon CO_2 adsorption (Ramsahye et al. 2007d).

3.2 Adsorption in the MIL-53 (Al) material

For each of the MIL-53 (Al) narrow and large pore structures, the simulated adsorption isotherms for CO_2 shows a similar shape to those obtained for MIL-47 (V), as shown in Fig. 5a. These calculated isotherms are what one would expect to obtain if the proposed interconversion between the large and narrow pore structures did not occur during the CO_2 loading process, and thus if one could measure the experimental isotherm for each structure type individually. The maximum amounts of CO_2 measured are around 2 molecules/u.c. for the narrow pore structure and 9 molecules/u.c. for the large pore form, which is slightly less than the saturation capacity measured for the isostructural MIL-47 (V) structure (Fig. 3a). This observation may be a result of changing the nature of metal and the resulting distribution of charges within the framework as well as that the CO_2 molecules can pack more efficiently in MIL-47 (V) because they do not have the "imposed" orientation of some of them given by the hydroxyl groups in MIL-53 (Al). As suggested by previous experimental evidence in this material (Bourrelly et al. 2005), one can assign the isotherm calculated for the narrow pore material to the region of the experimental isotherm between 1 and 6 bars, whereas that of the large pore corresponds to the maximum amount as a whole, and therefore could be assumed to be the resident structure for the isotherm above 6 bars. Thus, the "absolute" calculated isotherms from each version of MIL-53 (Al) may be combined in order to obtain a "composite" isotherm, to reproduce that measured by microcalorimetry. The "composite" adsorption isotherms for MIL-53 (Al) are shown in Fig. 6a.

For MIL-53*np* (Al), an almost smooth enthalpy profile is obtained from our simulations, with an average adsorption enthalpy of $-37\ \text{kJ}\cdot\text{mol}^{-1}$, as shown in Fig. 5b, which is in agreement with the range of experimental values $[-34\ \text{kJ}\cdot\text{mol}^{-1}, -40\ \text{kJ}\cdot\text{mol}^{-1}]$ measured by microcalorimetry for pressures between 0 and 6 bars (Fig. 6b). Our calculation indicated one main adsorption configuration

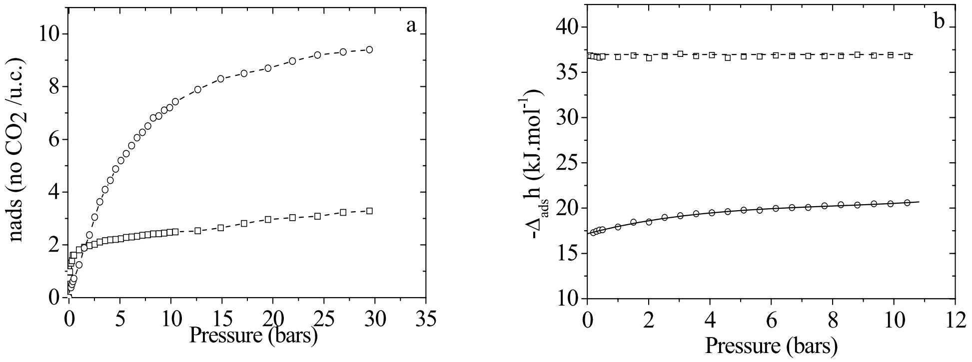


Fig. 5 Simulated absolute adsorption isotherms **(a)** and evolutions of the differential adsorption enthalpy as a function of the pressure **(b)** for carbon dioxide in both MIL-53np (Al) (□), MIL-53lp (Al) (O) forms

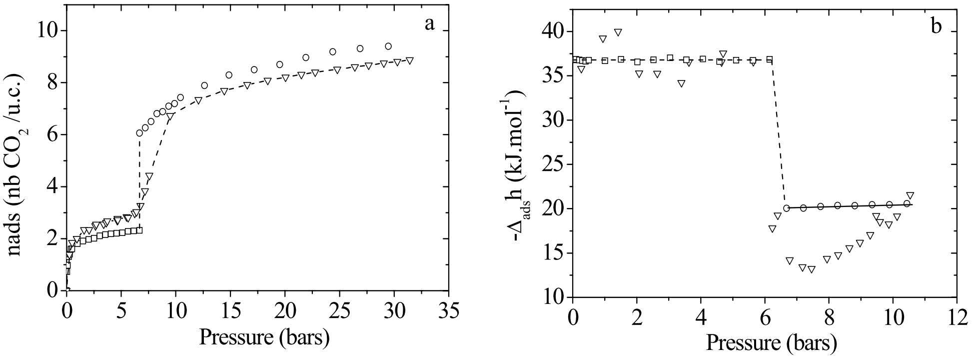


Fig. 6 "Composite" absolute isotherm **(a)** and differential enthalpy of adsorption for carbon dioxide in MIL-53 (Al) at 303 K. The simulations (O, □) are compared with the experimental data (∇) collected by microcalorimetry

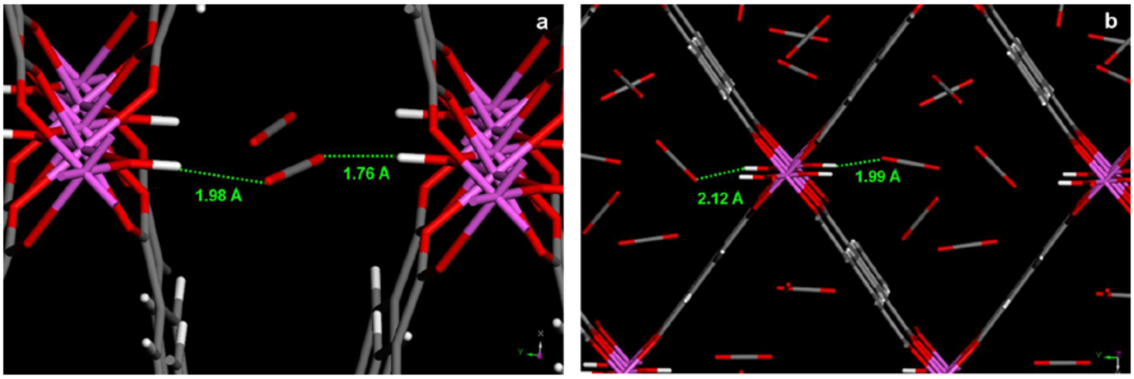


Fig. 7 **(a)** The double interaction, the most prevalent for the Al-containing structure, and **(b)** two examples of the interaction of one CO_2 molecule with a μ_2-OH group in MIL-53lp (Al). The characteristic distances are also reported. These snapshots have been obtained for a loading of 2 and 7 CO_2 molecules per unit cell for Figs. 7a and 7b respectively

of the CO_2 molecule inside this structure, involving the μ_2 OH group. This geometry is predicted to be a double interaction, where two μ_2-OH groups situated on opposing sides of the pore wall are involved, with a CO_2 molecule 'bridging' between them. An illustration of this is shown in Fig. 7a with typical O_{CO2}–$H_{\mu 2\text{-OH}}$ distances of 1.98 Å and 1.76 Å. This pore-bridging double interaction is only possible in this MIL-53*np* (Al) material, because of (a) the presence of the μ_2-OH group, and (b) the fact that the pore width is only 8.30 Å. As one increases the CO_2 loading, the preferential adsorption sites (i.e. the μ_2-OH groups) that could allow this most stable (favourable) geometry are more and more "solvated" by the adsorbate molecules. Indeed, the CO_2/MIL-53*np* (Al) interaction energy slightly decreases due to the solvation process whereas the energy part of the CO_2/CO_2 interactions increases. The combination of these two contributions leads to the relative constant value of the differential adsorption enthalpy when the loading increases. This simulated behaviour is consistent with what can be observed by microcalorimetry below 6 bars (Fig. 6b).

As shown by further GCMC simulations, when one reaches the saturation capacity of this MIL-53*np* (Al) form, the increase of the intermolecular interactions between CO_2 molecules, tends to break these favourable interactions leading to geometries with weaker adsorbate-adsorbent interactions. This is likely to ultimately be responsible for a transition from the narrow pore structure to the large pore version, occurring at around 6 bars.

For the MIL-53*lp* (Al) material, the experimental enthalpy profile features a steady increase in enthalpy with increasing pressure, above 6 bars. In this domain of pressure, all of the preferred μ_2-OH adsorption sites are already saturated by the adsorbate molecules as depicted by our simulated arrangement of CO_2 in this material, reported in Fig. 7b. It has to be noticed that in this large form, the pore width of 13.8 Å prohibits the double interaction seen in the narrow pore version. Therefore any adsorbates introduced after this stage of adsorption would experience a relatively homogeneous adsorption environment and the evolution of the adsorption enthalpy would be thus mainly governed by the increase of the intermolecular interactions between the CO_2 molecules. This behaviour is consistent with what we found by our simulations as reported in Fig. 6b, the increase of the enthalpy values being less pronounced than those observed by experiments.

Finally, in a similar fashion to the adsorption isotherms, the composite adsorption enthalpy can then be deduced from the plots of the data calculated for MIL-53*np* (Al) and MIL-53*lp* (Al) in the range of loading [0,6] bars and above 6 bars respectively (Fig. 6b). We observe a good agreement between this simulation and the experiments. The result of this exercise then provides further evidence for the structural switching around 6 bars of pressure. Since this phenomenon is not observed for the MIL-47 (V) material, one can infer that the presence of the μ_2-OH groups in the MIL-53 (Al) structure plays a major role in the structural switching process.

4 Conclusions

Using Grand Canonical Monte Carlo simulations, combined with our calculated partial charges and interatomic potentials, we have reproduced the experimental isotherms for CO_2 adsorption in MIL-47 (V) and MIL-53 (Al) hybrid metal-organic framework materials. We have also shown that the experimental isotherm of MIL-53 (Al) is made up of contributions from the large pore and narrow pore forms. Further, we proposed a microscopic mechanism for CO_2 adsorption for each system investigated, which is consistent with the evolution of the differential adsorption enthalpy as a function of the coverage. In both narrow and large pore versions of MIL-53 (Al), the adsorption mechanism is mainly governed by the interactions between CO_2 and the μ_2-OH groups. These preferential interactions in the narrow pore framework are broken as the loading increases past the point where no more preferred adsorption sites are available, and the structure switches to the large pore form. Since most of the favourable interactions in this pore also involve the μ_2-OH group, these sites are already occupied with interactions with adsorbates at this point, and so any new molecules introduced into the pore experience a homogeneous adsorption environment. In MIL-47 (V), there are no preferential adsorption sites, although some weak interactions between the C_{CO2} and the $O_{\mu 2}$ atoms are possible.

Acknowledgements This work was supported by EU funding via FP6-Specific Targeted Research Project "DeSANNS" (SES6-020133).

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