

On The Breathing Effect of a Metal Organic Framework upon CO₂ Adsorption: A Monte Carlo Investigation compared to Microcalorimetry Experiments

Deleted: the Aluminum
Terephthalate MIL-53

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Supporting information

1. Atomic partial charges calculations

The CO₂ 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, G.; Llewellyn, P.L.; Bell, R.G. *J. Phys. Chem. B* **2005**, 109, 16084). The partial charges for the hybrid porous MIL-53 (Al) material were extracted using Density Functional Theory (DFT) calculations. The Accelrys DMol³ (Dmol3, v. 4.0; Accelrys, Inc.: San Diego, **2005**) code was used for these calculations, which were performed using the PW91 GGA density functional (Perdew, J.P.; Wang, Y. *Phys. Rev. B*, **1986**, 33, 8822), and the double numerical basis set containing polarisation functions on hydrogen atoms (DNP) (Hehre, W.J.; Ditchfield, J.H.; Pople, J.A. *J. Chem. Phys.*, **1972**, 56, 2257). A periodic model of both the MIL-53_p (Al) and MIL-53_{np} (Al) material were

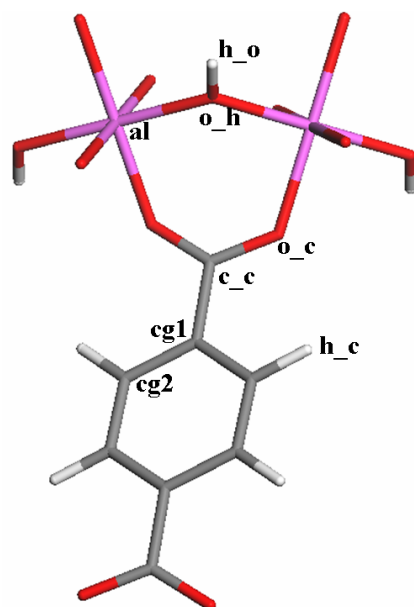
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geometry optimised, using the crystallographic coordinates of the atoms as starting configurations (Loiseau, T. et al *Chem. Eur. J.* **2004**, 10, 1373). The partial charges for the atoms in both models were first extracted using the Mulliken charge partitioning method (Mulliken, R. S. *J. Chem. Phys.*, **1955**, 23, 1833). These calculated results are reported in Table S1.

Table S1: Partial charges (in electron units) extracted for the atoms constituting the MIL-53 (Al) framework using both the Mulliken charge partitioning scheme. The labels of the atoms are detailed in Figure S1.

Atoms	h_c	cg1	cg2	cc	o_c	h_o	al	o_h
Charges	0.145	-0.082	-0.089	0.584	-0.564	0.301	1.420	-0.729

Figure S1: Labels of the atoms for the organic and inorganic sections of the MIL-53 (Al) material corresponding to the forcefield atom types, to allow the reading of the Tables of the potential parameters and charges.



2. Interatomic potential parameters

The adsorbate-adsorbate interactions were modelled by using a repulsion-dispersion 12-6 Lennard Jones (LJ) potential and a Coulombic contribution (equation S1):

$$e_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (\text{S1})$$

where the $(\epsilon_{ij}, \sigma_{ij})$ corresponds to the 12-6 LJ parameter sets for each interacting pairs (c_co_2/c_co_2 , o_co_2/o_co_2 , o_co_2/c_co_2) which previously allowed us to reproduce the solid CO_2 structure realistically (Maurin, G.; Llewellyn, P.L.; Bell, R.G. *J. Phys. Chem. B* **2005**, 109, 16084). The Coulombic part between the point charges q_i , q_j separated by a distance r_{ij} is calculated from the charges assigned to the CO_2 model.

The interaction between the adsorbate and the organic ligand of the MIL-53 (Al) framework was treated in a similar way, using 12-6 LJ parameters derived by Shen *et al* (Shen, I.W. *et al*, *Fluid Phase Equilibria*, **1995**, 104, 375). The interactions between the CO_2 molecules and the inorganic part (Al(OH)) was modelled as follows; the polarisability of the aluminium atoms,

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. The 12-6 LJ parameters for modelling the interactions between CO₂ and the oxygen atoms were extracted from our previous studies which successfully reproduced the CO₂ adsorption properties in aluminosilicate materials (Maurin, G.; Llewellyn, P.L.; Bell, R.G. *J. Phys. Chem. B* **2005**, 109, 16084). 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 (equation S2) whose parameters were recently derived from *ab initio* calculations (Deroche, I. *et al*, *J. Phys. Chem. B*, submitted).

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$$e_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}} + \frac{q_i q_j}{r_{ij}} \quad (\text{S2})$$

where A_{ij} , ρ_{ij} and C_{ij} correspond to the parameter sets for the interacting pairs (o_{co2}/h_o and c_{co2}/h_o).

The whole repulsion-dispersion potential parameters are listed in Table S2, where the atoms are labelled as reported in Figure 1.

Table S2 : Interatomic potential parameters for for both CO₂/CO₂ and CO₂/hybrid porous framework used in the GCMC simulations.

Nonbonded Lennard-Jones Potentials

Atom pairs	σ (Å)	ϵ (kcal.mol ⁻¹)
c_co2 c_co2	3.83	0.925300E-01
o_co2 o_co2	3.36	0.151800E+00
o_co2 c_co2	3.31	0.365000E-01
o_co2 o_c	3.48	0.115000E+00
c_co2 o_c	3.90	0.836500E-01
o_co2 o_h	3.48	0.115000E+00
c_co2 o_h	3.90	0.836500E-01
c_co2 cgl	5.98	0.231866E-04
o_co2 cgl	3.02	0.154593E+00

c_co2	cg2	5.98	0.231866E-04
o_co2	cg2	3.02	0.154593E+00
c_co2	cc	5.98	0.231866E-04
o_co2	cc	3.02	0.154593E+00
o_co2	h_c	2.33	0.146890E+00

Buckingham Potentials

Atom pairs	ρ (Å)	A (kcal.mol ⁻¹)	C (kcal.mol ⁻¹)
c_co2 h_o	2.500000	1860.509038	0.000000
o_co2 h_o	4.680000	29500.000000	382.1320

3. Grand Canonical Monte Carlo (GCMC) simulations

Absolute adsorption isotherms were then computed using a Grand Canonical Monte Carlo algorithm which allows displacements (translations and rotations), creations and destructions of the CO₂ molecules. This code is implemented in the *Sorption* module of the Cerius2 software suite (v. 4.0; Accelrys, Inc.: San Diego, 2005). In the Grand Canonical ensemble, the chemical potential, μ , the cell volume, V and the number of particles, N, are kept constant during the simulations. 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 300 K using one unit cell of MIL-53 np (Al) and MIL-53 lp (Al) with typically $3 \cdot 10^6$ Monte Carlo (MC) steps, the frameworks of both MIL-53 (Al) structures being considered rigid, with atoms at the positions derived by X-ray Diffraction. Crystal data for MIL-53 lp (Al) are as follows : orthorhombic system, Pnma, a= 6.608 Å, b= 16.675 Å, c = 12.813 Å (Loiseau, T. et al *Chem. Eur. J.* **2004**, 10, 1373); for MIL-53 np , monoclinic system, C2/c, a = 19.501 Å, 8.301 Å, c = 6.599 Å, β = 105.59° (Serre, C.; Bourrelly, S.; Vimont, A.; Ramsahye, N.A.; Maurin, G.; Llewellyn, P.L.; Daturi, M.; Filinchuk, Y.; Leynaud, O.; Barnes, P.; Férey, G., *Adv. Mater.*, in press). The Ewald summation was used for calculating the long range electrostatic interactions and the short range non-bonded interactions were calculated with a cut-off distance of 12 Å (Frenkel,

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D.; Smit B. “*Understanding Molecular Simulation: From Algorithms to Applications*”; Academic Press, San Diego, CA, **2002**). The calculation of the differential enthalpies of adsorption at 300 K for both MIL-53 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 and switching off the adsorbate-adsorbate interactions (equation S3) (Nicholson, D.; Parsonage, N.G. “*Computer simulation and the statistical mechanics of adsorption*” Academic Press, London, **1982**).

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$$\Delta_{\text{ads}} \dot{h} = RT - \frac{\langle U.N \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (\text{S3})$$