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Molecular Dynamics Simulations of Breathing MOFs: Structural Transformations of MIL-53(Cr) upon Thermal Activation and CO_2 Adsorption**

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The elaboration of new porous materials possessing reactive sites and large pores with high surface areas, which are able to capture and release guest molecules, is the subject of intensive research activity.[1] The particular interest in hybrid metal–organic framework (MOF) porous materials stems from their chemical versatility compared with classical porous solids.[1,2] It is possible to tune the pore size, shape, and connectivity by subtle modifications of the inorganic moiety and the organic linker molecules.[1,2] They are currently attracting high fundamental and industrial interest across a wide domain of applications, including gas adsorption, liquid separation, and drug delivery.[1,3]

In addition to this large variety of chemical and structural features, a fascinating property arises with some MOFs, which relates to their dynamic micropores being able to respond to external stimuli such as pressure, temperature, and guest molecules.[4–9] Such dynamic frameworks are topical as they open potential applications for high-performance molecular recognition and high selectivity for guest inclusion and release. This "breathing" phenomenon is currently associated with a structural transition between two states separated by energy barriers higher than the thermal vibration energy.[10] The transformation can reversibly induce an expansion or a contraction of the cell volume corresponding to atomic displacements of up to 10 Å. Such solids include $Cu_2(pzdc)_2(dpyg)$ (pzdc = pyrazine-2,3-dicarboxylate, dpyg = 1,2-di(4-pyridyl)glycol) and some of the MIL (Materials of Institute Lavoisier) series, which exhibit a magnitude of breathing from 25 up to 230% in cell volume variation upon adsorption/desorption of various guest molecules.[9–11] However, although experimental techniques can detect the signature of such structural transformations, they are not able to elucidate the microscopic mechanism in play, mainly because of the fast speed at which such transitions take place. Atomistic simulation, such as Monte Carlo or molecular dynamics[12] techniques, thus appears to be a unique tool to define the structural and energetic features that govern such expansion and contraction on the microscopic scale. Apart from knowledge of the charge distribution within the framework, one of the major prerequisites of such simulations is a force field that is able to describe accurately the interactions within the whole system. When the MOF systems behave as classical porous materials such as zeolites, with a tiny rearrangement of the skeleton upon guest molecules,[13–15] the framework can be modeled as being rigid with atoms fixed at positions derived by X-ray powder diffraction (XRPD) analysis for the bare material during the whole adsorption process. This approximation has been validated for several MOF/guest systems, as previously for zeolites, for which only an appropriate guest/framework force field was required to reproduce the experimental data satisfactorily.[16–22] However, the complexity increases when one aims to investigate the properties of flexible MOF systems.[23] For that purpose, an additional force field for describing the framework itself has to be included in the atomistic simulations. A few attempts have been made to model the MOF-5 structure. Greathouse and Allendorf[24] were the first to report a nonbonded force field that was able to predict framework collapse upon water adsorption. More recently, using the same force field, they were able to capture the contraction/expansion of MOF-5 from 0.7 to 1.5% in cell volume for different guests such as hexane and ethanol.[25] A similar force field was employed by Dubbeldam et al.,[26] who successfully reproduced an experimental thermal expansion of the same MOF system of about 1% in cell volume for a range of temperatures (30–293 K). Using the fully bonded MM3 force field,[27] Schmid and co-workers[28] emphasized that taking into account the flexibility of MOF-5 upon benzene adsorption allows one to fit the experimental diffusion coefficient better, although the volume changes are again very small. However, to the best of our knowledge, large modifications in the unit cell volume of a MOF framework upon adsorption of guest molecules have never been addressed by classical bonded and nonbonded force fields. In that way, our strategy consisted of considering a new bonded force field able to describe accurately a large magnitude of flexibility in a typical MOF system.

In this work our main objective was to follow at the microscopic scale the structural changes of the MIL-53(Cr)

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system over the whole range of CO_2 adsorption. The MIL-53(Cr) material is built up from chains of octahedra sharing μ_2-OH vertices linked by terephthalate groups (Figure 1) and exhibits an unusual adsorption isotherm with the existence of steps (Figure S1 in the Supporting Information).[29] This peculiar behavior was attributed by in situ XRPD analysis to reversible structural switching between a narrow- and a large-pore form, which implies large atomic displacements of 3.0 Å in one direction and of 4.7 Å in the other, corresponding to a volume change of the unit cell from 1072 to 1486 Å^3 or 28 % cell variation (Figure 1).[5] This type of behavior is referred to as "breathing", since the magnitude of the alteration of the framework is much higher than a local relaxation of bonds and angles usually labeled as flexibility in zeolites.

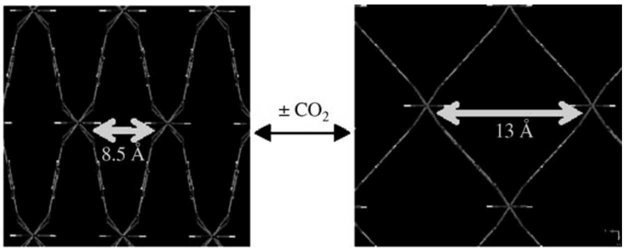

Figure 1. Structural switching of MIL-53(Cr) upon CO_2 adsorption between a narrow- (space group *C2/c* with $\beta = 104.9°$) and a large-pore (space group *Imcm*) form in the *xy* plane. The reported pore diameters are calculated by considering the internuclear distances between two opposing oxygen atoms of the μ_2-OH groups.

Deriving and validating a robust force field for the MIL-53(Cr) framework is thus a crucial step to reveal some insights into the microscopic mechanism of the breathing phenomenon. Such an approach can further predict both the framework behavior and the dimensions of the porosity for a given guest as well as elucidate the adsorption and diffusion processes occurring in flexible MOFs. Some of us recently developed a new force field for the framework itself[30] which, when combined with a host–guest force field, is able to capture substantial degrees of framework flexibility upon adsorption for lattice energy minimizations at 0 K. The energetics of the structural transition between the open and the narrow-pore form of MIL-53(Cr) was thus elucidated. However, this force field based mainly on nonbonded interactions fails to describe the behavior of the MIL-53(Cr) framework when one considers the effect of the temperature, which is crucial to mimic the experimental conditions.

On extending our simulations to encompass molecular dynamics, modifications were required to the previous force field; partial charges and bonded interactions within the metal coordination sphere were included (Tables S1–S4 in the Supporting Information). This strategy differs from the nonbonded approach previously reported.[24–26] This modified force field is still able to reproduce the structural features of both the large- and narrow-pore forms by energy minimizations at 0 K and also leads to simulated vibrational frequencies for the MIL-53(Cr) framework in good agreement with infrared data[31] (Table S5). The organic moiety was thus treated with the widely used cvff force fields including intramolecular and nonbonded Lennard–Jones (LJ) interactions.[32] The inorganic node was described by a Cr–O bonded intramolecular term and nonbonded LJ interactions, instead of Buckingham terms as considered in the previous force field,[30] whose parameters were fitted by ourselves. An additional torsion term was also included for interactions between the inorganic and organic parts. All the parameters of our force field are listed in the Supporting Information (Tables S1–S4).

The next step consisted of validating this new force field by using NσT molecular dynamics simulations, in which we take into account the effect of the temperature and thus match the experimental conditions.[33,34] In contrast to the MD simulations conducted in a NPT ensemble, in this case both the shape and dimensions of the unit cell can vary. These calculations were mainly performed at 300 K by using the Nose–Hoover thermostat for both the large- and narrow-pore structures in the absence of any adsorbate. The simulation box consisted of 32 unit cells containing 2432 atoms, and each run was realized for 5×10^5 steps with a time step of 1 fs (i.e. 0.5 ns). The configurations were then stored every 200 time steps. The Ewald summation was used for calculating electrostatic interactions, and the short range interactions were computed with a cut-off distance of 12 Å.[35] The resulting evolutions of the unit cell volumes for both empty large- and narrow-pore forms of MIL-53(Cr) are reported in Figure S3 in the Supporting Information. It is shown that the simulated structures exhibit cell volumes very similar to the experimental ones, and both of them correspond to an energy minimum at this temperature. This observation is also in agreement with energy minimizations showing that both large- and narrow-pore forms converge towards well defined energy minima, which suggests bistable behavior, as already reported for some hybrid systems.[10] A rather small energy difference of 5 kJ mol^{-1} per formula unit between the two structures is obtained in favor of the large-pore structure, emphasizing the metastability of the narrow-pore form. Such findings are consistent with experimental results, which show that at room temperature the narrow-pore form is observable even without solvent inside the pore.[5] A transition from the narrow- to the large-pore structure can then be thermally activated at a temperature above 600 K, as shown in Figure S3. This observation means that temperature can be seen as an external stimulus that is able to induce the structural switching in the same way as the introduction of guest molecules. This result suggests that the breathing of the MIL-53(Cr) structure involves small energy barriers and was recently confirmed by our joint microcalorimetry–modeling approach, which showed that a minimum adsorption enthalpy of 20 kJ mol^{-1} in the large-pore form is required for inducing the structural switching.[36]

This force field was then transferred to the study of the CO_2 adsorption in the same MIL-53(Cr) system. For this study, it was combined with parameters reported by Yung and Harris[37] to model the CO_2 molecule. NσT MD simulations were then run starting with the large-pore structure, which was loaded with a given number of CO_2 molecules to span the whole pressure range of the adsorption isotherm[6] (Figure S1). The evolution of the unit cell volume for each CO_2 loading is plotted as a function of the MD simulation time in the Supporting Information in Figure S4. We observe that for 1 CO_2/u.c. (u.c. = unit cell), the structure remains in its initial large-pore form with a cell volume of 1508 Å^3, which is very close to that experimentally observed for similar loading.[5] By contrast, a drop in the cell volume occurs for a loading of 2.2 CO_2/u.c., attaining a value of 1092 Å^3, which is in good agreement with that experimentally determined for the narrow-pore structure in presence of CO_2 molecules (1072 Å^3).[5] This first structural switching occurs for a loading that is within the same range as that obtained from previous combined in situ XRPD and manometry experiments (ca. 2 CO_2/u.c).[5] It is also noticeable that this structural transition is very fast, as illustrated in Figure S4, where typically less than 100 ps is required to pass from one form to the other. For 3 CO_2/u.c., corresponding to the adsorbed amount on the first plateau of the isotherm, the structure is still in its narrow-pore version. Further, from 4 CO_2/u.c., an increase in the loading induces a progressive expansion of the unit cell volume. The structure then returns to the large-pore form for 8 CO_2/u.c., which has a simulated volume almost the same as that observed experimentally (1516 Å^3 vs. 1515 Å^3) by in situ XRPD measurements.[5]

Figure 2 summarizes the simulated unit cell volume for MIL-53(Cr) as a function of loading. Our calculations predict the predominance of the large-pore form at very low loading and above 5.2 CO_2/u.c., whereas the narrow-pore version is present in the intermediate domain of loading. Further, the simulated cell parameters reported in Figure S5 in the Supporting Information are in excellent agreement with those extracted by in situ XRPD analysis for both structures, which highlights that the force field is able to reproduce accurately the dynamic behavior of the MIL-53(Cr) framework over the whole range of loading. A further step consisted of probing the spatial distribution of the CO_2 molecules within the channels of the narrow-pore material for a loading of 3 CO_2/u.c. Figure S6a (in the Supporting Information) shows that the CO_2 molecules are aligned along the direction of the tunnel, parallel to each other, leading to a double interaction [O_{CO_2}–H(μ_2-OH) and C_{CO_2}–O(μ_2-OH)] with the μ_2-OH groups present at the pore wall. These geometries are in very good agreement with those previously obtained by our DFT calculations[38] (Figure S6b) and in situ XRPD analysis.[5] This result shows that our force field is also able to predict accurately the arrangements of the adsorbate molecules within the pores.

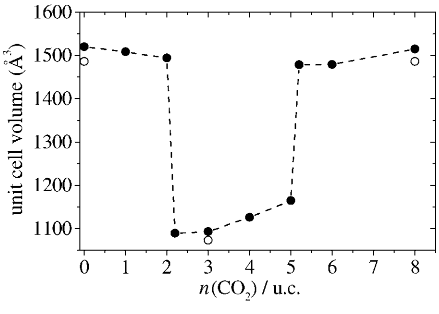

Figure 2. Evolution of the unit cell volume of MIL-53(Cr) as a function of the CO_2 loading calculated at 300 K. ●: simulated data, ○: experimental data.

Further, as shown in Figure 1, the structural transition from the narrow- to the large-pore form is associated with a change in the pore diameter. Figure 3 reports the pore size distributions calculated from averages over the recorded MD frames. We observe first that the pore sizes simulated for the structures loaded with 3 CO_2/u.c. and 8 CO_2/u.c. are centered at 8.3 and 13.0 Å, respectively, which reproduce very well the data obtained experimentally for the narrow- and large-pore forms. Furthermore, for CO_2 loadings within the domain where the structural transition occurs (Figure S1), for example, typically for 4 CO_2/u.c., one observes the presence of two distinct pore sizes that are close to those calculated for the narrow- and large-pore forms. This observation emphasizes the coexistence of the two phases in this domain of loading; the fraction of the large-pore form increases as the number of CO_2 molecules increases. These simulations corroborate the previous experimental findings obtained by in situ XRPD and IR measurements.[5]

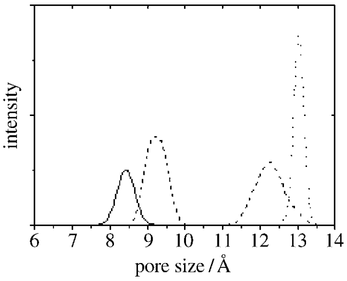

Figure 3. Pore size distributions of MIL-53(Cr) simulated for loadings of three (——), four (----), and eight (•••••) CO_2 molecules per unit cell at 300 K.

As our force field was validated by the very good agreement between the simulated and experimental structural behavior of MIL-53(Cr) over the whole range of CO_2 loading, we then explored the microscopic mechanism of the structural switching upon CO_2 adsorption, a process that is not experimentally accessible. We first explored the structural and energetic features that are significantly modified during the breathing of the material. It was thus possible to show by careful analysis of the MD frames that both the average O–Cr–O valence angles (Figure 4a) and the Cr–(o_c)–(c_c)–(cg2) (see Figure S2 for atom labeling) dihedral angles (Figure 4b) exhibit significant fluctuations during the transition from the large- to the narrow-pore form. The most significant changes are attributed to the (o_h)-Cr-(o_h) valence angle because of the higher degree of freedom of the OH group in our force field.

These structural modifications are associated with a sudden drop of the corresponding intramolecular energy terms (Figure S7 in the Supporting Information). We can also observe much larger free rotation of the phenyl rings during the breathing (Figure S8 in the Supporting Information). The combination of these three contributions are the key features

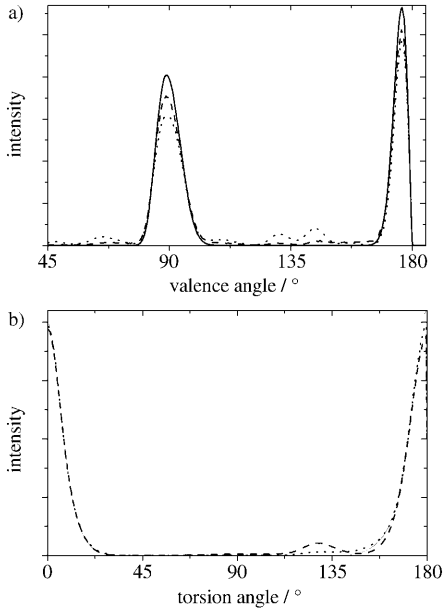

Figure 4. Distributions of the characteristic O—Cr—O valence angles (averages of o_c—Cr—o_c, o_c—Cr—o_h, and o_h—Cr—o_h angles) (a) and dihedral angles Cr—o_c—c_c—cg2 (b; see Supporting Information for atom labeling) for the large-pore form (——), for the narrow-pore form (-----), and during the structural transition occurring for 4 CO_2/u.c. (•••••).

that drive the breathing. However, we have noticed that the structural switching is predominantly governed by a change of the dihedral angle.

In summary, MD simulations were used to study the unusually complex case of guest-induced structural transformations of MIL-53. They successfully capture the two-step structural switching, as induced by CO_2 adsorption in the Cr-containing framework at finite temperatures. It was found that the empty large- and narrow-pore structures are very well reproduced, and moreover the large magnitude of the breathing in presence of CO_2 was reproduced. This study illustrates the potential of force-field-based simulation methods in elucidating the energetics and structural response of flexible framework materials under conditions of thermal activation and guest adsorption. We have shown that the consideration of a bonded force field is crucial to reproduce such large breathing. Indeed, our main philosophy has been to develop a force field as simple as possible so as to allow its direct transferability for a large variety of guest molecules, for which simple force fields are available. This approach is of general interest for the community working on hybrid systems, as the reported force field would require only a minimum adjustment to be exported to other MOF systems. It will allow for example determination of the maximum amplitude of the breathing with various solvents and accurate prediction of their adsorption performance, which is almost impossible when using a rigid framework in the simulation.

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[1] G. Férey, *Chem. Soc. Rev.* **2008**, ***37***, 191–214.
[2] S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109–119.
[3] P. Horacajada, C. Serre, G. Maurin, N. Ramsahye, F. Balas, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Férey, *J. Am. Chem. Soc.* **2008**, *130*, 6774–6780.
[4] K. S. Walton, A. R. Millward, D. Dubbeldam, H. Frost, J. J. Low, O. M. Yaghi, R. Q. Snurr, *J. Am. Chem. Soc.* **2008**, *130*, 406–407.
[5] C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, *Adv. Mater.* **2007**, *19*, 2246–2251.
[6] S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 13519–13521.
[7] K. Sebi, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1968–1971.
[8] K. Uemura, S. Kitagawa, K. Fukui, K. Saito, *J. Am. Chem. Soc.* **2004**, *126*, 3817–3828.
[9] R. Kitaura, K. Fujimoto, S-I. Noro, M. Kondo, S. Kitagawa, *Angew. Chem.* **2002**, *114*, 141–143; *Angew. Chem. Int. Ed.* **2002**, *41*, 133–135.
[10] J-P. Zhang, X-M. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 6010–6017.
[11] C. Mellot-Draznieks, C. Serre, S. Surblé, N. Audebrand, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 16273–16278; C. Serre, C. Mellot-Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk, G. Férey, *Science* **2007**, *315*, 1828–1831.
[12] T. Ziegler, *Chem. Rev.* **1991**, *91*, 651–667.
[13] K. Barthelet, J. Marrot, D. Riou, G. Férey, *Chem. Commun.* **2004**, 520–521.
[14] D. Dubbeldam, H. Frost, K. S. Walton, R. Q. Snurr, *Fluid Phase Equilibria* **2007**, *261*, 152–161.
[15] Q. Y. Yang, C. L. Zhong, *J. Phys. Chem. B* **2006**, *110*, 17776–17783.
[16] N. Rosenbach, Jr., H. Jobic, A. Ghoufi, F. Salles, G. Maurin, S. Bourrelly, P. L. Llewellyn, T. Devic, C. Serre, G. Férey, *Angew. Chem.* **2008**, *120*, 6713–6717; *Angew. Chem. Int. Ed.* **2008**, *47*, 6611–6615.
[17] F. Salles, H. Jobic, G. Maurin, M. M. Koza, P. L. Llewellyn, T. Devic, C. Serre, G. Férey, *Phys. Rev. Lett.* **2008**, *100*, 245901.
[18] A. I. Skoulidas, D. S. Sholl, *J. Phys. Chem. B* **2005**, *109*, 15760–15768.
[19] Q. Yang, C. Zhong, *J. Phys. Chem. B* **2005**, *109*, 11862–11864.
[20] N. Ramsahye, G. Maurin, S. Bourrelly, P. Llewellyn, T. Loiseau, G. Férey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1059–1063.
[21] H. Frost, T. Düren, R. Q. Snurr, *J. Phys. Chem. B* **2006**, *110*, 9565–9570.
[22] D. S. Coombes, R. G. Bell, C. Mellot-Draznieks, N. A. Ramsahye, G. Maurin, *Stud. Surf. Sci. Catal.* **2007**, *170*, 918–925.
[23] N. A. Ramsahye, G. Maurin, S. Bourrelly, P. L. Llewellyn, T. Loiseau, C. Serre, G. Férey, *Chem. Commun.* **2007**, 3261–3263.
[24] J. A. Greathouse, M. D. Allendorf, *J. Am. Chem. Soc.* **2006**, *128*, 10678–10679.
[25] J. A. Greathouse, M. D. Allendorf, *J. Phys. Chem. C* **2008**, *112*, 5795–5802.
[26] D. Dubbeldam, K. S. Walton, D. E. Ellis, R. Q. Snurr, *Angew. Chem.* **2007**, *119*, 4580–4583; *Angew. Chem. Int. Ed.* **2007**, *46*, 4496–4499.
[27] M. Tafipolsky, S. Amirjalayer, R. Schmid, *J. Comput. Chem.* **2007**, *28*, 1169–1176.
[28] S. Amirjalayer, M. Tafipolsky, R. Schmid, *Angew. Chem.* **2007**, *119*, 467–470; *Angew. Chem. Int. Ed.* **2007**, *46*, 463–466.
[29] C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Férey, *J. Am. Chem. Soc.* **2002**, *124*, 13519–13526.
[30] D. S. Coombes, R. G. Bell, S. Bourrelly, P. L. Llewellyn, C. Mellot-Draznieks, submitted.

[31] A. Vimont, A. Travert, P. Bazin, J. C. Lavalley, M. Daturi, C. Serre, G. Férey, S. Bourelly, P. L. Llewellyn, *Chem. Commun.* **2007**, 3291 – 3293.
[32] P. Dauber-Osguthorpe, V. A Roberts, D. J. Osguthorpe, J. Wolff, M. Genets, A. T. Hagler, *Proteins Struct. Funct. Genet.* **1988**, *4*, 31 – 47.
[33] M. Parrinello, A. Rahman, *Phys. Rev. Lett.* **1980**, *45*, 1196 – 1199.
[34] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* **1984**, *81*, 3684 – 3689.
[35] D. Frenkel, B. Schmit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, New York, **2002** (Computational Science Series Vol. 1).
[36] P. L. Llewellyn, G. Maurin, T. Devic, S. Loera-Serna, C. Serre, S. Bourrelly, P. Horcajada, Y. Filinchuk, G. Férey, *J. Am. Chem. Soc.* **2008**, *130*, 12808 – 12814.
[37] J. G. Harris, K. H. Yung, *J. Phys. Chem.* **1995**, *99*, 12021 – 12024.
[38] N. A. Ramsahye, G. Maurin, S. Bourrelly, P. L. Llewellyn, C. Serre, T. Loiseau, T. Devic, G. Férey, *J. Phys. Chem. C* **2008**, *112*, 514 – 520.