Metal–Organic Frameworks

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Using Pressure to Provoke the Structural Transition of Metal–Organic Frameworks**

*Isabelle Beurroies, Mohammed Boulhout, Philip L. Llewellyn, Bogdan Kuchta, Gérard Férey, Christian Serre, and Renaud Denoyel**

Easy and efficient energy storage is one of the problems treated by numerous researchers today. Hydrophobic nanoporous materials can potentially be used as actuators, but also as molecular springs, dampers, or shock absorbers.[1] In this case, the reversible intrusion of a liquid in nonwetting pores at high pressure, a process subject to hysteresis, is used to store or produce mechanical work. Herein, we show the possibility to store mechanical energy using porous metal–organic framework materials (MOFs) in which their flexibility is used instead of nonwetting properties. Indeed, MOFs have found increasing interest over the past few years in potential applications such as gas separation and storage,[2–4] liquid-phase separation,[5] or drug delivery.[6]

One of the unique properties of some of these materials is their high degree of framework flexibility, which has reached 230% in the case of the MIL-88 series (MIL stands for Materials from Institut Lavoisier). In most cases, the flexibility of these materials has been induced by adsorption of guest species,[7] which produce various types of flexibility.[8,9]

One of the most interesting classes of flexible solids are those of the MIL-53 series. These are metal(III) terephthalates built up from chains of corner sharing metal(III) octahedral (M = Al, Cr, Fe, Ga, In, …) and terephthalate groups that delimit one-dimensional microporous pore system.[2] The Al and Cr forms are found in the large pore (LP) form after thermal removal of the guest species, whereas in the presence of various fluids, a narrow pore (NP) form is observed (MIL-53(Cr) NP; space group $C2/c$; $V \approx 1020$ Å^3) before re-expansion to the LP form (MIL-53(Cr) LP; space group $Imcm$; $V \approx 1490$ Å^3; see Figure 1). In the case of MIL-53(Al), this reversible flexible character has also been observed as being dependent on the temperature[10] with hysteresis between the cooling and heating processes. The transition from LP to NP occurs on cooling in the 125–150 K range whereas that from NP to LP occurs on heating in the range 325–375 K. The presence of these different crystalline states opens the possibility for phase diagrams to be established.

[*] Dr. I. Beurroies, M. Boulhout, Dr. P. L. Llewellyn, Prof. B. Kuchta, Dr. R. Denoyel
Laboratoire Chimie Provence (UMR6264)
CNRS-Université Aix-Marseille I,II,III; Marseille (France)
Fax: (+33) 4-9163-7127
E-mail: renaud.denoyel@univ-provence.fr
Prof. G. Férey, Dr. C. Serre
Institut Lavoisier (UMR CNRS 8180), Versailles (France)

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Although previous gas adsorption studies have been carried out under various pressures,[4,5,9] to the best of our knowledge, the response of these materials solely under pressure, without any adsorption effect in pores, has not been reported to date. In the recent study of Moggach et al., ZIF-8 samples were submitted to a high hydrostatic pressure that provokes crystal phase transitions, but with the presence of liquid inside pores.[11] Logically, one would expect that a transition from the LP to the NP phase would occur provided a high enough pressure is applied to the MOF phase in question. One reason for this behavior is that the MIL-53 phases are usually synthesized in the form of micrometer-sized particles and it is not easy to impose a mechanical stress around the particle in a controlled manner. However, the use of mercury porosimetry permits an isostatic pressure around the MIL-53 particles to be created. Indeed, mercury intrusion is often used to characterize the porosity of solids as mercury is most often nonwetting and a significant pressure is required for it to penetrate the pores of a solid. One often assumes a value for the contact angle, usually in the range 130–140°, allowing the pore size and pore volume to be derived from the intrusion curve applying the Laplace–Washburn equation. In the usual intrusion pressure range 0–400 MPa, the screened pore size ranges from around 300 μm to 3 nm. Thus, mercury cannot penetrate micropores such as those usually present in many MOF materials. A problem often encountered with mercury porosimetry is the compressibility of the material or the possible destruction of the pore structure that both lead to an apparent intruded volume that does not correspond to any real porosity. In the case of flexible microporous MOF materials, these technical drawbacks can be an advantage with the possibility to observe a response with pressure for systems which apparently shrink. Finally, is it possible by this technique to show that the LP to NP transition can be observed simply by applying mechanical pressure? In the present case with MIL-53(Cr), the results from mercury porosimetry experiment are given in Figure 1, which shows two intrusion–extrusion cycles.

At a first glance, this result is a classical one that could be observed with mesoporous solids in the form of powder. In the initial pressure range to 1 MPa, the gradual intruded volume corresponds to the compactibility of the particle bed with pressure.[12] Between 1 and 3 MPa, the large increase in volume corresponds to the intrusion of mercury between particles. The second step, which occurs at around 55 MPa, could be at first sight attributed to intrusion into mesopores with a corresponding pore size of around 23 nm, if usual values of the contact angle are applied. However, since such a pore size is not observed from other pore size measurements,

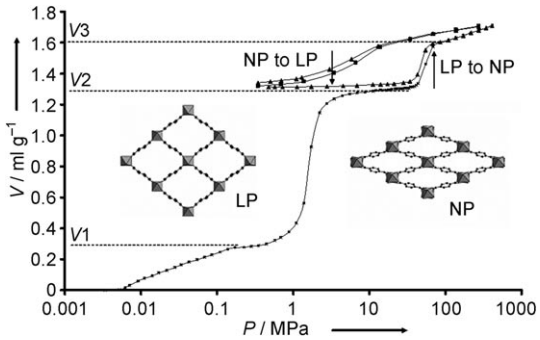

Figure 1. Intrusion–extrusion of mercury in MIL-53 (Cr) sample: cumulative intruded volume versus applied pressure. The arrows show the steps that correspond to the LP to NP transition. Squares: first intrusion–extrusion cycle. Triangles: second intrusion–extrusion cycle.

such as nitrogen adsorption at 77 K,[12] in which a pure type I isotherm is observed, which is characteristic of microporosity (see the Supporting Information in reference [12]). Therefore, this step in the mercury intrusion experiment can be interpreted solely by the transition from the LP phase to the NP phase in which the decrease in cell volume (logically 1490 to 1020 Å^3) leads to the apparent intrusion volume. As shown in Figure 1, this transition is reversible and displays hysteresis, as is also observed in the temperature-induced transition.[13] A second intrusion–extrusion cycle follows the same pathway. This hysteresis shows the presence of an energetic barrier between the two phases.

A simple model may interpret the mechanism of the structural "breathing" transition in MOF MIL-53 and similar structures. Most of the studies published so far focus on structural and energy characterization (by calorimetry, force field based calculations, and DFT) and a general thermodynamic interpretation. However, there is no general analysis of the competing energetic and entropic factors defining the mechanism of the transformation within the MOF structure itself. In the simple model proposed herein, two energetic contributions are considered: one due to the deformation of the bond angles and the other due to the distance between ligands. They both vary during breathing of the structure. The flexibility of the structure is restricted to the connection between the inorganic chain and the carboxylic function of the terephthalate.[14] Its two oxygen atoms are covalently bound to the carbon atoms but are linked to the chromium atoms through ionocovalent bonds. This situation allows possible rotation around the O–O axis of the two planes O-Cr-Cr-O and O-C-O. The dihedral angle between these two planes is around 180° for the open structure (LP) and 140° for the closed one (NP). The corresponding deformation energy constitutes a first energetic factor: the energy of the crystal increases when the bonds are deformed. This energy, which stabilizes the open structure, may be represented here by a deformation of dihedral energy term that depends on an energetic parameter H [Eq. (1)]

$$E_{\mathrm{dih}} = (H/2)^*[1+\cos(180-2\phi)] \quad (1)$$

In Equation (1), $180-2\phi$ represents the dihedral angle between two planes O-Cr-Cr-O and O-C-O. The term has a minimum for $\phi = 0$. All energies are calculated with respect to this state ($E_{\mathrm{dih}} = 0$). This potential flexibility may be activated by the presence of inserted species in the channels by the creation of weak bonds as a result of physisorption between the guest and the skeleton, but it is easy to imagine that it can also be induced by mechanical (pressure) factors. This in turn will activate the second energetic factor, which results from the attractive interaction between the benzene rings: the energy of the crystal decreases when the distance between the rings decreases and thus stabilizes the narrow pore structure. This energy may be represented by a typical Lennard–Jones (6–12) function [Eq. (2)], where ε is the energetic parameter

$$E_{\mathrm{disp}} = 4\varepsilon^*[(\sigma/r)^{12}-(\sigma/r)^6] \quad (2)$$

(depth of the potential well) and σ the size parameter (distance of approach between molecules). The distance r is measured between the centers of the benzene rings. It depends also on the angle ϕ. This angle will thus be used as an order parameter that characterizes the transition. In reality, the distance dependence may be different than the one deduced from the (6-12) function representation. Different combinations (n,m) of the power parameters have been tested, but they do not change the qualitative behavior presented below. This problem will be addressed in future studies in which the transition will be modeled and analyzed using a quantitative approach.

The competition between the two energy terms stabilizes one of the two phases with an energy barrier between them, which leads to hysteresis when one phase is being transformed into the other, as observed experimentally. The energy $E_{\mathrm{dih}} + E_{\mathrm{disp}}$ versus the angle ϕ is plotted in Figure 2. Quantitative estimations have been made using the dihedral parameter from ab initio calculations ($H = 20\ \mathrm{kJ\,mol^{-1}}$).[15] Entropy is not included in our qualitative model. The influence of the different strengths of the dispersive energy have been studied parametrically for different values of the H/ε ratio, leading to two main conclusions: 1) the relative strengths of the energy terms (characterized by $V_{\mathrm{D}}/\varepsilon$) will affect the relative stability of the phases, that is, the pressure or temperature of transition and 2) the barrier between the phases (indicated in Figure 2 as TS; transition state) changes for different values of V/ε and affects the energy required to transform one phase into another. Evidently, the dispersive interactions between the ligands are not high enough relative to the dihedral energy to stabilize the NP phase, but the energy provided by pressure may induce the transition to this less stable state.

During the isostatic compression experiment, the only work (W) provided to the system is mechanical. One can then write the free energy variation (ΔF) of the system during the isothermal transition as $\Delta F = W$ [Eq. (3)], which is the work

$$W = \int_{V2}^{V3} P\,\mathrm{d}V \quad (3)$$

of the pressure forces during the step corresponding to the transition. $V2$ and $V3$ are defined in Figure 1. ($V3-V2$) is the

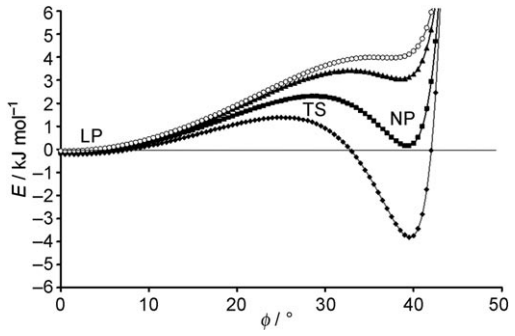

Figure 2. $E = E_{dih} + E_{disp}$ as a function of the dihedral angle ϕ for different H/ε ratios. The minimum at $\phi = 0$ represents the open structure LP, the other minimum represents the NP structure. There is a barrier between the minima indicated as TS (for transition state). ◆ $H/\varepsilon = 1.7$, ■ $H/\varepsilon = 2.5$, ▲ $H/\varepsilon = 4$, ○ $H/\varepsilon = 5$.

variation of volume undergone by the material during the transition from one state to the other. This work is in fact used to overcome the energetic barrier represented in Figure 2. It is larger than that needed to reach the NP form along a reversible path. The excess of energy is dissipated in the form of heat, which is not measured in the present experiment. Consequently the free energy variation between the two phases calculated by applying Equation (3) to the experimental data is an upper estimation. Calculating this variation with present data gives a value of 14 $J\,g^{-1}$. Assuming that the molar mass of dried MIL-53 (Cr) is 233 $g\,mol^{-1}$,[13] a value of 3.5 $kJ\,mol^{-1}$ is obtained for the transition free energy, which is in reasonable agreement with the range of calculated values shown in Figure 2. This result is also in the range of the values (2–6 $kJ\,mol^{-1}$) obtained by Coudert et al.,[16] who proposed a thermodynamic analysis of various host–guest systems which includes the free energy of this transition, whereas a value of 5 $kJ\,mol^{-1}$ was obtained indirectly from DSC measurements of the dehydration energy.[17] This value is slightly smaller than the published value issued from DFT and force-field calculations:[15] 30 kJ per unit cell or 7 $kJ\,mol^{-1}$, as one unit cell contains four Cr atoms.

From mercury porosimetry, the density of the material was also obtained at the end of the intrusion branch; it then corresponds to the apparent density of the narrow pore form. A value of 1.59 $mL\,g^{-1}$ was obtained, which is very close the theoretical value of 1.65 $mL\,g^{-1}$.[13] The variation of volume between LP and NP forms at the transition pressure is around 0.25 $cm^3\,g^{-1}$, which is close to the value deduced from the structural studies. Indeed, 0.3 $cm^3\,g^{-1}$ is derived from the difference between the unit cell volumes of the LP and NP forms.[13] The difference between these two values may arise from an already slightly compressed LP phase at the transition pressure.

From a fundamental point of view, this study shows that the mechanical properties of flexible MOF materials can be studied directly using mercury porosimetry. The modulation of an external pressure can lead to energetic and volumetric information on the flexibility of MOF systems. It also shows that these systems may be potentially used in mechanical energy storage type applications based on a much simpler approach from the one using nonwetting porous materials.[1] Furthermore, the energy absorbed in a cycle of intrusion–extrusion, calculated by integration of Equation (3) along a full cycle, is around 12 $J\,g^{-1}$, which is larger than the storage capacity of mesoporous hydrophobic solids.[18,19] Moreover, the simple model used herein to explain the observed behavior opens the prospects that by varying the nature of metal centers and ligands, different energetic behavior could be obtained. This will allow modulation of the storage capabilities and the manufacturing of either dampers (transition with hysteresis) or molecular springs (transition without hysteresis).

Experimental Section

The MIL-53(CR) sample was synthesized by following a published procedure.[8] Nitrogen adsorption at 77 K (results not shown) was carried out with an ASAP2010 apparatus from Micromeritics. The sample was outgassed overnight at 200 °C under a residual pressure lower than 1 Pa. Mercury intrusion–extrusion experiments were carried out with an Autopore 9220 apparatus from Micromeritics. To start the experiment with the open structure, a special treatment method was used because it is not possible to heat the sample in situ with mercury porosimeters. The sample was immersed in methanol, which is known to open the structure. Then it was outgassed at 150 °C, cooled, and transferred as soon as possible into the mercury porosimetry cell for analysis. In the mercury apparatus, a primary vacuum is realized (lower than 5 Pa).

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