Impact of the Metal Centre and Functionalization on the Mechanical Behaviour of MIL-53 Metal-Organic Frameworks


To cite this version:


HAL Id: hal-02363957
https://hal.archives-ouvertes.fr/hal-02363957
Submitted on 14 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Impact of the metal center and functionalization on the mechanical behavior of the MIL-53 Metal Organic Frameworks


Abstract: An extended series of MIL-53 (M)_X (MIL stands for Materials of Institute Lavoisier) with M=Al, Cr, Fe, Sc and X=Cl, -CH_3 and –NO_2 was considered to systematically explore the impact of the nature of both the metal center and the grafted functions on the mechanical behavior of this highly flexible framework under the application of an external pressure up to 3 GPa. The high-pressure X-ray diffraction measurements allowed the characterization of the pressure-induced phase transitions of the hydrated structures, the associated volume changes/pressure transitions and their mechanical resilience via the determination of their bulk moduli.

Introduction

The family of flexible dicarboxylate-based MIL-53 or MIL(OH)(BDC) with M=Al, Cr, Fe, (MIL for Materials of Institute Lavoisier) MOFs has been widely explored for their potential use in diverse societally relevant applications in the field of gas/liquid separation because of their intriguing highly flexible behavior.[1-3] Drug encapsulation,[4] and more recently mechanical energy storage.[5,6] Following our previous experimental and theoretical studies on the mechanical behaviour of the MIL-53 solids and derivatives in their dehydrated states,[7,8] the present work aims to explore the pressure-induced structural changes of a series of water loaded MIL-53s which are known to exist in a narrow pore form typically of monoclinic symmetry.[10-12] This study, based on the use of advanced high-pressure X-ray diffraction in ex situ techniques, considers the impact of both the nature of the metal center (Al, Cr, Fe, Sc) and the presence of terephthalate linkers bearing apolar or polar functional groups (-Cl, -CH_3, -NO_2) on (i) the nature of the pressure-assisted phase transformation, (ii) the associated unit cell volume and symmetry changes and (iii) the mechanical resilience via the value of the transition pressure and the determination of the bulk modulus using an equation of state. Although a few studies have been recently reported on the mechanical behaviour of the functionalized MIL-53(Al)_NH_2 and MIL-53(Al)_NH_2[13] in their hydrated states and the guest-loaded MIL-53(Cr),[15] this article reports the first systematic study on the mechanical behavior of the breathing MIL-53 solids that is interpreted in light of (i) the local structural features of the host framework and (ii) the intra-molecular interactions between the grafted functions and the μ-OH groups as well as the sterically hindered organic linkers.

Results and Discussion

All the MIL-53 studied have been previously hydrated (under ambient air); by this way all solids if one except the scandium version were obtained in their narrow pores versions (NP, S.G. C2/c (n=15)).

Supporting information for this article is given via a link at the end of the document.
Figure 1 reports the evolution of the X-ray powder diffraction (XRPD) patterns collected for the air-hydrated MIL-53(Cr) as a function of the applied pressure up to 2.0 GPa. The Bragg peaks initially present under atmospheric pressure are assigned to the Narrow Pore (NP) form of MIL-53(Cr) characterized by a monoclinic symmetry, (S.G. C2/c) and a unit cell volume of 983.4(2) Å³ (Table 1 and Fig. S1), consistent with that previously reported for the same solid.[7,8] One can further observe that the whole XRPD pattern remains unchanged up to 0.2 GPa. Above this pressure, a structural switching occurs and leads to the formation of a more contracted phase labeled as the Very Narrow Pore form (VNP) that has been successfully indexed in the triclinic system S.G. P-1 (n=2). (Figure S2) with a characteristic peak around 3° (Figures 1, S2 and S6). This structure is characterized by a unit cell volume of 939.6(2) Å³ similar to those experimentally (967.8 Å³) and theoretically (931.0 Å³) evidenced for the Closed Pore (CP) form of the empty MIL-53(Cr) under about the same applied pressure [0.30 GPa].[7] This observation clearly emphasizes that in such a contracted phase, the presence of water does not play a pivotal role on the mechanical properties of the solid. This differs with the behavior previously depicted for the Large Pore (LP) structure by Ma et al.,[15] the water allowing in this case the enhancement of the compressibility of the solid with a lower transition pressure from the LP to the NP forms as compared to the empty case. The evolution of the unit cell volume as a function of the applied pressure reported in Figure 2a shows a step-change above 0.2 GPa corresponding to the NP-VNP phase transition. This structural change involves a much lower volume variation (ΔV=4.5%) than that evidenced for the dehydrated LP form (ΔV=35%).[7,8] The bulk modul for both NP and VNP were further estimated from this plot using the Murnaghan equation of state.[17] The corresponding values of 4.3 GPa and 3.4 GPa respectively (Table 2) are higher than the value we previously reported for the LP form (1.8-2 GPa).[7, 18] Taking into account the number of point in the NP domain we can suppose that the bulk modulus is underestimated. This observation indicates a comparable degree of compressibility of these contracted phases, consistent with the presence of strong π–π repulsions between the phenyl rings facing each other that prevents a much more contraction of the structure.
pressure up to 1.20 GPa. Above this pressure, a significant change occurs with a broadening of the XRPD patterns associated with position and intensity changes of some Bragg peaks. A structural switching is observed from the NP form to a new phase indexed in the triclinic system S.G. P-1 (Figure S4) with a unit cell volume of 805 Å³. The so-obtained VNP phase evidenced for the first time for the Al version of MIL-53, shows a unit cell volume even smaller as compared to the triclinic MIL-53(Fe) previously evidenced by Millange et al. (V=892 Å³). Figure 2b further reports the corresponding pressure dependence of the unit cell dimensions of this air hydrated MIL-53(Al). Using again the Murnaghan equation of state, the NP form of MIL-53(Al) shows a bulk modulus of 10.7 GPa which is significantly higher than the value estimated for the Cr-analogue. This observation emphasizes a lower degree of compressibility for the Al-phase, higher mechanical resilience allowing the NP form to exist in a wider range of applied pressure as reported in Figure 2b. This trend can be understood by the fact that the NP form is more contracted for Al thus leading to stronger π-π stacking interactions between the opposite pore walls at the origin of a higher stabilization of the Al phases towards a mechanical perturbation.

Table 1. Unit cell volumes and symmetry for the different pressure-induced phases of the air hydrated MIL-53(M)\(^{[a]}\).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Pressure (GPa)</th>
<th>Symmetry</th>
<th>Form</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-53(Cr)</td>
<td>Atm</td>
<td>C2/c</td>
<td>NP</td>
<td>983.4(2)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>P-1</td>
<td>VNP</td>
<td>939.6(2)</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>Atm</td>
<td>C2/c</td>
<td>NP(^{[b]})</td>
<td>851.6(3)</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>P-1</td>
<td>VNP (^{[c]})</td>
<td>804.5(2)</td>
</tr>
<tr>
<td>MIL-53(Fe)</td>
<td>Atm</td>
<td>C2/c</td>
<td>NP</td>
<td>985.3(3)</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>P-1</td>
<td>VNP</td>
<td>942.7(5)</td>
</tr>
<tr>
<td>MIL-53(Cr)_Cl</td>
<td>Atm</td>
<td>C2/c</td>
<td>NP</td>
<td>1031.5(4)</td>
</tr>
<tr>
<td></td>
<td>1.21</td>
<td>C2/c</td>
<td>NP</td>
<td>961.9(1)</td>
</tr>
<tr>
<td>MIL-53(Cr)_CH(<em>3)</em></td>
<td>Atm</td>
<td>C2/c</td>
<td>NP</td>
<td>1039.6(1)</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>C2/c</td>
<td>NP</td>
<td>958.0(1)</td>
</tr>
<tr>
<td>MIL-53(Al)_NO(<em>2)</em></td>
<td>Atm</td>
<td>C2/c</td>
<td>NP</td>
<td>1036.7(1)</td>
</tr>
<tr>
<td></td>
<td>2.84</td>
<td>C2/c</td>
<td>NP</td>
<td>921.1(1)</td>
</tr>
<tr>
<td>MIL-53(Sc)</td>
<td>Atm</td>
<td>P-1</td>
<td>VNP</td>
<td>1917.5(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(958.8(1))(^{[d]})</td>
</tr>
</tbody>
</table>

[a] All the unit cell parameters are available in Table S1. [b] NP stands for Narrow Pore. [c] VNP stands for Very Narrow Pore. [d] Unit cell volume divided by 2 for comparison to take into account the difference of unit cell of the MIL-53(Sc) and MIL-53(Al, Cr, Fe).

This observation is consistent with the findings some of us recently reported on the CP form Al which was shown to be deeply bound than its Cr or V-analogues.\(^{[3]}\) The number of point recorded for the VNP-form did not allow us to extract the bulk modulus for this phase.

The pressure-induced structural behavior obtained for the MIL-53(Fe) is similar to that obtained for the Cr analogue. Indeed, a phase transition occurs from the monoclinic NP (SG. C2/c, V=985.3(3) Å³) (Figure S5) to the triclinic VNP (SG. P-1, V=942.7(5) Å³) (Figure S6) implying a similar unit cell volume variation of 4.3%. However, Figure 2c which reports the pressure-induced unit cell volume variation indicates that the evolution is more gradual and the transition pressure occurs at higher pressure vs the Cr form (around 400 MPa) that suggests a higher compressibility of the Fe-NP form. This is confirmed by a higher bulk modulus of 10 GPa as reported in Table 2.

Table 2. Equation of state parameters obtained using the Murnaghan model for all the air hydrated MIL-53(M).\(^{[a]}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>V₀ (Å³)</th>
<th>K₀ (GPa)</th>
<th>Kₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-53(Cr)</td>
<td>C2/c</td>
<td>987.2(1)</td>
<td>4.29(1)</td>
<td>2.1(1)</td>
</tr>
<tr>
<td></td>
<td>P-1(^{[a]})</td>
<td>909.2(1)</td>
<td>3.4(1)</td>
<td>9.6(1)</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>C2/c</td>
<td>939.92(1)</td>
<td>10.7(1)</td>
<td>12.4(1)</td>
</tr>
<tr>
<td>MIL-53(Fe)</td>
<td>C2/c</td>
<td>986.1(1)</td>
<td>10.1(1)</td>
<td>1.5(1)</td>
</tr>
<tr>
<td></td>
<td>P-1(^{[b]})</td>
<td>946.9(1)</td>
<td>7.4(1)</td>
<td>106.7(1)</td>
</tr>
<tr>
<td>MIL-53(Cr)_Cl</td>
<td>C2/c</td>
<td>1016.7(1)</td>
<td>12.4(1)</td>
<td>18.6(1)</td>
</tr>
<tr>
<td>MIL-53(Cr)_CH(<em>3)</em></td>
<td>C2/c</td>
<td>1052.9(1)</td>
<td>3.7(1)</td>
<td>31.8(1)</td>
</tr>
<tr>
<td>MIL-53(Al)_NO(<em>2)</em></td>
<td>C2/c</td>
<td>1036.5(1)</td>
<td>7.3(1)</td>
<td>16.5(1)</td>
</tr>
<tr>
<td>MIL-53(Sc)</td>
<td>P-1</td>
<td>1902.5(1)</td>
<td>10.3(1)</td>
<td>23.6(1)</td>
</tr>
</tbody>
</table>

[a] Pressure of reference was taken at 0.5 GPa. [b] Pressure of reference was taken at 0.4 GPa.
Typically, Figure 3 reports the evolution of the XRPD patterns for the MIL-53(Cr) Cl as a function of the pressure. All the collected patterns are successfully indexed up to 2.0 GPa in the space group C2/c (See Fig S7 and Table S1) that revealed the absence of any phase transition towards the triclinic VNP as evidenced for the non-functionalized solid. The Bragg peaks are only slightly shifted towards high angles. This behavior is associated with a progressive contraction of the unit cell volume as reported in Figure 4a with a maximum magnitude change of 6.5% at 1.20 GPa. The same behavior is evidenced for the –CH₃ functionalized form of MIL-53(Cr) (see Figures 4b, S8 and S12) with an associated slightly larger unit cell volume change of 7.8%. The bulk moduli estimated from the application of the Murnaghan equation of state to these plots are 12.4 GPa and 4.7 GPa for the chloride and methyl functionalized forms respectively. One observes that the bulk modulus evolves as follows: MIL-53(Cr) Cl > MIL-53(Cr) CH₃ > MIL-53(Cr) H. This shows that the functionalization of the organic linker induces a significant lower degree of compressibility of the solid. This can be again explained in light of the structural features of the functionalized NP forms. In addition to the steric hindrance related to the presence of the functional group, the Cl atoms are expected to form intra-framework interactions with the µ₂-OH groups present at the MOF surface as it was previously revealed for the functionalized MIL-53(Fe)s.[19] These additional interactions, combined with the steric hindrance of the Cl groups, thus contribute to enhance the mechanical resilience of the corresponding solid. In addition, the even more bulky and apolar –CH₃ group acts as a steric constraint which is also expected to withstand the external applied pressure leading to a decrease of the compressibility of the solid as compared to the pristine MIL-53(Cr). However the bulk modulus of this functionalized solid remains lower than for the –Cl analogue. This observation supports that the mechanical stability of this family of NP form is driven by both the intra-framework interactions and the steric hindrance created by bulky functional groups.

Figure 2. Evolution of the unit cell volume of the Narrow Pore (NP in black square) and Very Narrow Pore (VNP in red circle) forms of (a) MIL-53(Cr), (b) MIL-53(Al) and (c) MIL-53(Fe).

Mechanical behaviour of the air-hydrated MIL-53(Cr) and MIL-53(Al) with grafted functions

Two series of MIL-53 have been studied varying the grafted functions on the terephthalate and the nature of the metal centre: MIL-53(Cr) Cl, _CH₃ and MIL-53(Al) NO₂. (Figure S12)
The MIL-53(Al)$_{\mathrm{NO}}_2$ exhibits a similar pressure-induced structural behavior than the other functionalized MIL-53(Cr)$_x$. Indeed as observed in Figures 4c and S12 no phase change is observed in the whole range of applied pressure. All the diffraction patterns collected have been indexed in the space group C2/c (Figure S9) and the unit cell parameters for the air-hydrated phase under atmospheric pressure are in good agreement with the one published by Biswas et al.$^{[20]}$ Grafting the NO$_2$ functions leads a volume change of 9.7% which is higher than for the pristine solid leading to a bulk modulus of 7.4 GPa slightly lower than the MIL-53(Al)$_x$. This can be explained by the fact that the NP form of the air-hydrated NO$_2$-functionalyzed solid is significantly larger than that of the pristine form.

**Figure 3.** Powder X-ray diffraction patterns ($\lambda = 0.694120$ Å) obtained for the MIL-53(Cr)$_x$Cl as a function of the applied pressure at room temperature.

**Figure 4.** Evolution of the unit cell volume of the air-hydrated Narrow Pore form (S.G. C2/c) of (a) MIL-53(Cr)$_x$Cl, (b) MIL-53(Cr)$_x$CH$_3$ and (c) MIL-53(Al)$_{\mathrm{NO}}_2$.

**Mechanical behaviour of the air-hydrated MIL-53(Sc)**

The air-hydrated MIL-53(Sc)$_x$ was found to be in a triclinic form (Figure S10) with unit cell parameters in very good agreement with that published by Chen et al.$^{[21]}$ All the XRPD patterns were indexed in the whole range of pressure up to 2.0 GPa using the
same S.G. P-1 corresponding to the VNP form. This means that no phase transition was evidenced in this pressure range. This evolution was found to be comparable with that observed for the VNP versions of the MIL-53(Al, Cr, Fe) in the range of applied pressure as described above (Figure 5). The corresponding bulk modulus of this phase is 10.3 GPa which is much more higher than the value obtained for the NP forms of the Cr and Fe analogues while within the same range of value than the Al NP form.

This evolution was found to be comparable with that observed for the VNP versions of the MIL-53(Al, Cr, Fe) in the range of applied pressure as described above (Figure 5). The corresponding bulk modulus of this phase is 10.3 GPa which is much more higher than the value obtained for the NP forms of the Cr and Fe analogues while within the same range of value than the Al NP form.

Figure 5. Powder X-ray diffraction patterns (\(\lambda = 0.51000 \text{ Å}\)) obtained for the MIL-53(Sc) (S.G. P-1) as a function of the applied pressure at room temperature.

Figure 6 shows the evolution of the unit cell volume as a function of the applied pressure. The compression of the structure gives a variation of volume at 1 GPa close to 4.0%. Considering that the unit cell twice larger compared to the iron analogue the compression leads to a unit cell volume variation from 958 to 920 Å\(^3\) which is similar to the Al, Cr and Fe based MIL-53's.

![Figure 6: Evolution of the pressure-induced unit cell volume of the Very Narrow pore form of MIL-53(Sc).](image)

Conclusions

This high-pressure X-ray diffraction systematic study performed on the series of hydrated MIL-53 solids has evidenced that:

(i) the nature of metal center in the case of MIL-53(Cr, Al, Fe) modulates the transition pressure corresponding to the structural switching between the monoclinic Narrow Pore and the triclinic Very Narrow Pore forms, while the associated volume change remains almost unchanged. The bulk modulus of the Narrow Pore form has been also shown to significantly depend on the nature of the metal.

(ii) MIL-53(Sc) behaves differently. This solid remains in its initial triclinic Very Narrow Pore form in the whole range of applied pressure.

(iii) the nature of the grafted functions allow tuning of the compressibility of the MIL-53 solids, the –Cl leading to the higher bulk modulus due to the existence of intra-framework interactions between the –Cl and the \(\mu_2\)-OH groups at the MOF surface. It was observed that the functionalization tends to maintain the structure in its monoclinic Narrow Pore form whatever the apolar or polar nature of the substituent.

Experimental Section

Sample preparation

All samples have been synthesized following the procedures previously published\(^{[10-12, 20-24]}\). Prior to the high pressure X-ray diffraction experiments, all the sample were exposed to air for hydration to ensure that the solids are present in their narrow pore (NP) form with a monoclinic symmetry C2/c or a triclinic symmetry P-1 (MIL-53(Sc)) consistent with previous findings\(^{[11, 20, 21]}\).

Synchrotron X-ray Powder diffraction
In situ X-ray powder diffraction was carried out on Swiss Norwegian Beamlines (BM01A), High Pressure Beamline (ID27) at the European Synchrotron Radiation Facility (Grenoble, France) and CRISTAL beamline at the French national synchrotron source “Synchrotron Soleil,” Saint-Aubin, France. The patterns were collected at room temperature using a monochromatic beam with the wavelength of λ=0.69412 Å (BM01A), λ=0.37380 Å (ID27) and λ=0.51000 Å (CRISTAL). The sample distance-detector, parameters of the detector and wavelength were calibrated using NIST standard LaB₆. All the two dimensional images were integrated using Fit2D software [25]. The samples were initially kept under ambient atmosphere and were loaded under air. Hydrostatic conditions were ensured by the addition of silicon oil (AP 100, Aldrich) as pressure transmitting media. During the experiment the pressure generated by Pressure was generated using a diamond anvil cell (DAC) or membrane diamond anvil cell (MDAC) to generate the external pressure and was determined from the shift of the ruby R1 fluorescence line [26]. The diffraction patterns obtained for all the hydrated solids were first indexed using DICVOL06 [27] and unit-cell parameters were determined by refining the X-ray powder patterns, using JANA 2006 suite [28].

Acknowledgements

French National Agency for Research ANR "MODS" (ANR-12-BS10-0005) is thanked for its financial supports. The authors want to thank the European Synchrotron Radiation Facility (Grenoble, France) and the French national Synchrotron radiation source "Synchrotron Soleil" (Saint-Aubin, France) for beamtime at the Swiss Norwegian Beamline (BM01A), High Pressure Beamline (ID27)) and CRISTAL beamline. G.M. thanks Institut Universitaire de France for its support.

Keywords: Metal Organic Frameworks • Hydrated MIL-53 • Mechanical behaviour • High pressure X-ray diffraction • Bulk modulus