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ARTICLE TYPE

Guest-modulation of the mechanical properties of flexible porous Metal Organic Frameworks

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The highly flexible hybrid nanoporous MOF MIL-53(Cr) was evoked as a potential media to store mechanical energy via a structural switching from an open to a close pore forms under moderate applied external pressures. Herein, we show that the inclusion of a low concentration of either polar or apolar molecules into the pores can finely tune the structural and energetic behaviour of this solid under compression-decompression. This allows a modulation of the material's storage abilities in the forms of not only nano-springs/dampers but also shock adsorbers by confining *n*-alkane and water/alcohol respectively. Predicting and further understanding the impact of each guest on the mechanical properties of this MOF is achieved by molecular dynamics simulations based on a refined version of a flexible force field able to accurately capture the breathing of the framework. A careful analysis of the host/guest interactions and the preferential conformations of the confined molecules validated on *in situ* X-ray diffraction and microcalorimetry data shed light on the microscopic mechanisms at the origin of the singular mechanical behaviour of each guest loaded material.

Introduction

Crystalline hybrid solids, known as metal-organic frameworks (MOFs) built up from inorganic subunits and organic moieties are one of the most recent classes of porous solids. These materials are attracting considerable attention by virtue of their exceptional diversity in terms of surface chemistry, framework topology and pore dimension (from micro- to mesopores) leading to architectures with potential applications in different domains including gas storage/separation,¹⁻³ drug encapsulation/release,⁴ etc. While the adsorption performances of these materials have been massively explored for a wide range of gases/vapours, this is still far beyond to be the case for the characterization of their mechanical properties although it is of prime importance for a shaping purpose.⁵⁻¹⁰ More especially the studies related to the guest dependent pressure behaviour of these solids are scarce. They focused on (i) rigid MOF frameworks (MOF-5, Cu-BTC, ZIF-8), i.e. systems which are known to experience only slight changes of their unit cell parameters upon inclusion of guest molecules or under moderate applied pressure (<0.5 GPa), and (ii) a limited set of guest molecules (alcohol/water, diethylformamide, I₂) used experimentally as pressure transmitting fluids which penetrate the pores. Further, the mechanical properties of these guest loaded MOFs were primarily characterized in the high pressure domain (>1 GPa). It has been revealed for instance that while diethylformamide adsorbed in MOF-5 tends to stabilize the framework by shifting the onset of the amorphization at higher pressure,¹¹ the confinement of methanol and iso-propanol into the pores of Cu-BTC has an

extremely tiny impact on the bulk modulus of this MOF.¹² A minor influence of the guest was also observed in the case of the I₂/ZIF-8 system which undergoes an amorphization under the same temperature and pressure conditions than the empty solid.¹³ A different scenario could be envisaged in flexible MOFs with a more pivotal role of the guest molecules on the mechanical properties of the framework as suggested by the previous work reported on the NH₂-MIL-53(In).¹⁴ Herein, to confirm this, we selected the MIL-53(Cr) (MIL stands for Materials of the Institut Lavoisier) as one of the most fascinating breathing MOF upon a variety of stimuli. Several experimental¹⁵⁻²⁰ and computational^{15, 17, 21-27} studies evidenced that this solid, built up from chains of octahedral sharing μ_2 -OH vertices linker by terephthalate linkers, endures a reversible structural switching from a large pore to narrow pore forms upon the inclusion of a wide variety of guest molecules, corresponding to a unit cell variation up to 40%.¹⁵⁻²⁰ More recently, it was demonstrated by Hg-porosimetry⁵ and neutron diffraction⁶ that such a structural transition can also be induced by applying an external pressure of moderate magnitude (~53.5 MPa). This structural switching was revealed to be reversible and associated with a large hysteresis. This makes this material potentially attractive for energy storage applications in the form of molecular nano-dampers with a storage capacity of 12 J·g⁻¹ as demonstrated in ref. 5, which is significantly higher than the performance of mesoporous hydrophobic materials.²⁸⁻²⁹ Molecular dynamics (MD) simulations using a refined version of a flexible force field to represent the framework allowed us to fully capture the breathing of MIL-53(Cr) not only upon the whole range of CO₂ adsorption but also under applied external

pressure up to 300 MPa.^{6, 30} Based on this computational approach, the present work first aims at exploring the structural behaviour of MIL-53(Cr) upon the adsorption of three different vapours i.e. water, methanol and *n*-hexane in a wide range of concentration, molecules which have been previously used as pressure transmitting media in several MOFs. These simulations are further validated by *in situ* X-ray diffraction and adsorption measurements performed at the same conditions.^{16, 19-20} A further step consists of predicting the pressure behaviour of each guest loaded-MIL-53(Cr) system up to 300 MPa which are then compared to the situation for the empty solid with a special emphasis on the guest dependence of (i) the large pore to narrow pore pressure transition, (ii) the compressibility of the large pore form, and (iii) the structural behaviour (reversibility/irreversibility, hysteresis) once the pressure is switched off. These observations are analyzed in light of the strength of the host/guest interactions. A careful exploration of the preferential orientations and conformations of the molecules confined in the narrow pore form of MIL-53(Cr) at 300 MPa is presented and compared to the situation pointed out in the absence of external pressure. Beyond this fundamental interest, we emphasize how the inclusion of either polar or apolar molecule into the pores of MIL-53(Cr) can modulate its structural response under compression/decompression to potentially generate alternative storage capabilities for such a breathing MOF.

Microscopic Models and computational method

MD simulations were conducted using the DL_POLY_2.20 program³¹ in the N σ T ensemble to permit the simulation cell to change both size and shape. The thermostat and anisotropic barostat of Berendsen (with $\tau_T=1.0$ ps and $\tau_P=5.0$ ps as relaxation times) was employed in order to maintain constant both pressure and temperature while the velocity Verlet scheme coupled with the QUATERNION, SHAKE-RATTLE algorithms³¹ were selected to integrate the equations of motions. All the calculations on the MIL-53(Cr) in presence of guest molecules and under applied pressures ranging from 0.1 to 300 MPa at 300 K were performed considering MD runs of 3 ns with a time step of 1 fs, following 1 ns of equilibration. The simulation box consisted of 32 unit cells. The MOF structure was loaded with the different guest molecules for a wide range of concentration, starting with its large pore (LP) version previously reported.³² This was done through Monte Carlo simulations in the NVT ensemble using the CADSS software.³³ The flexibility of the MIL-53(Cr) framework was treated by considering our most recent refined force field.³⁰ The considered polar and apolar guests were described as follows: (i) water molecule was treated by the TIP4P-2005 model³⁴ which has been derived to reproduce the experimental vapor-liquid phase equilibrium data and (ii) methanol and *n*-hexane molecules were represented using the TraPPE-UA model,³⁵⁻³⁶ the corresponding potential parameters being fitted to the critical properties and vapor-liquid phase equilibrium data of diverse alcohols and alkanes. The Lorentz-Berthelot mixing rules were further applied to describe the Lennard-Jones interactions between the guest molecules and the framework atoms except for the interaction between the oxygen atoms of the water molecule and the carbon of the carboxylate group of the MIL-53(Cr) framework where the LJ parameters have been adjusted by our

own to capture the re-opening of the structure at high concentration of water (Table S1 in SI). A cut-off distance of 12 Å was considered to treat the van der Waals interactions and the long-range electrostatic contributions were calculated using the Ewald summation.

Results and discussion

As a preliminary step, the consistency of the selected potential parameters to describe the host/guest interactions with the flexible force field for the framework was tested by comparing the predicted and experimental structural behaviour of MIL-53(Cr) in presence of a wide range of guest concentrations without applying external pressures.

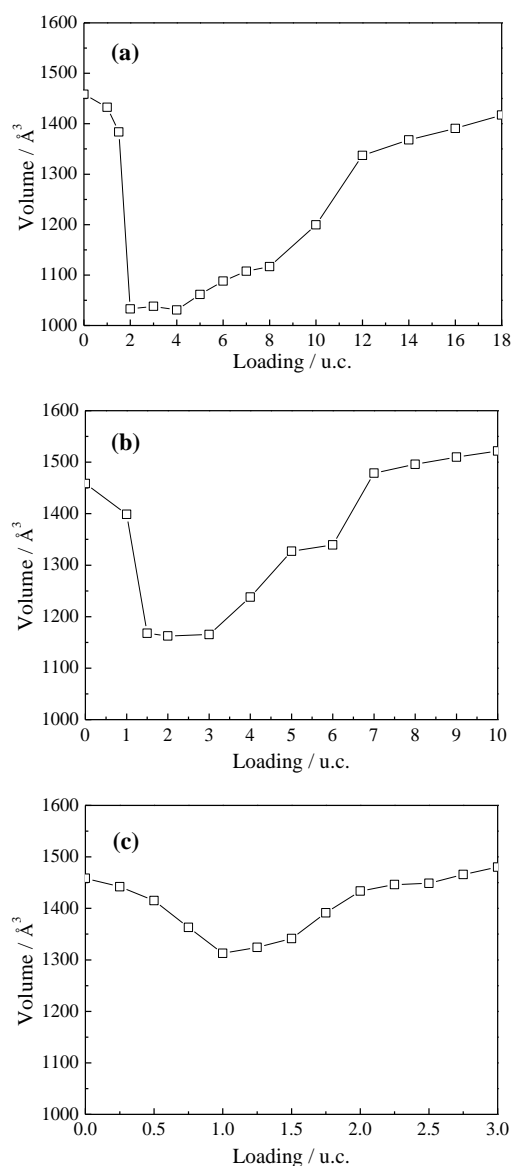


Fig. 1 MD simulated evolutions of the unit cell volume of MIL-53(Cr) at 300 K and 0.1 MPa as a function of the number of (a) water, (b) methanol, and (c) *n*-hexane molecules per unit cell.

Fig. 1(a) reports the simulated unit cell volumes for MIL-53(Cr) as a function of the water loading which varies from 1 to 18 molecules per unit cell. The structure remains in its initial LP

form of orthorhombic symmetry up to 1.5 H₂O/u.c. with an associated unit cell volume larger than 1400 Å³. A sudden drop of the unit cell volume then occurs for 2 H₂O/u.c. with a simulated unit cell volume of 1033 Å³. This agrees very well with the experimental value previously reported for the NP form loaded with a similar concentration of water (1012 Å³).³² The structure remains in this NP form with an almost constant cell dimensions up to 4 H₂O/u.c. which further gradually increases, suggesting a progressive swelling of the structure as it was already emphasized for other guest molecules.^{15, 18, 24} One can notice that the simulated unit cell volume (1417 Å³) at 18 H₂O/u.c. remains still lower than the one for the initial LP form, thus confirming the difficulty of fully reopening the MIL-53(Cr) in the presence of water vapor as previously evidenced by Infra-red and *ex-situ* X-ray diffraction.¹⁶ Fig. 1(b) first reports the simulated methanol concentration dependence of the unit cell volume from 1 to 10 molecules per unit cell to cover the whole range of the experimental adsorption isotherm previously reported.¹⁶ For 1 CH₃OH/u.c., one observes that the structure remains in its initial LP form with an orthorhombic symmetry and a unit cell volume of 1398 Å³ which is only slightly lower than the one simulated in absence of guest molecule (1450 Å³). A sudden drop in the unit cell volume then occurs for 1.5 CH₃OH/u.c. attaining 1167 Å³, which is also associated with a change of the symmetry from orthorhombic to monoclinic. This is in excellent agreement with the experimental results obtained by *ex situ* X-ray diffraction which evidenced for this loading a narrow-pore (NP) structure of monoclinic symmetry with a unit cell volume of 1168 Å³.¹⁶ The MIL-53(Cr) thus remains in this NP form up to a loading of 3 CH₃OH/u.c. and above one observes a gradual expansion of the unit cell volume up to 6 CH₃OH/u.c. corresponding to a progressive swelling of the NP structure. This predicted structural behaviour is fully consistent with the shape of the adsorption isotherm observed in the same range of concentration, (in the pressure domain $p/p^{\circ} = 0.1\text{--}0.2$) which corresponds to a continuous increase of the adsorbed amount¹⁶ instead of a distinct plateau as observed for the majority of the gases/vapours investigated so far in this solid.^{15, 17, 24} The structure then returns to the LP form for 7 CH₃OH/u.c. with a simulated unit cell volume of 1478 Å³ very close to the initial empty form. At higher loadings, the structure still slightly expands, the unit cell volume for a loading of 10 CH₃OH/u.c. corresponding to the saturation capacity of the solid, being 1522 Å³ which is in good agreement with previous experimental findings.¹⁶ Fig. 1(c) further reports the simulated structure evolution of MIL-53(Cr) as a function of the *n*-hexane loading which varies from 0.5 to 3 molecules per unit cell. One observes that below 0.5 *n*-hexane/u.c., the structure remains in its LP form (orthorhombic symmetry), with an associated unit cell volume larger than 1410 Å³. For 1 *n*-hexane/u.c., the unit cell volume decreases to 1313 Å³, which is in very good agreement with the one experimentally determined for the NP structure upon adsorption of similar concentration of *n*-hexane molecules as evidenced by *ex-situ* X-ray thermodiffraction (1302 Å³).²⁰ Meanwhile, one can notice that the symmetry remains orthorhombic and this is also consistent with what has been previously evidenced for the Al analogue.¹⁹ Finally, for 3 *n*-hexane/u.c. which corresponds to the saturation capacity of MIL-53(Cr),²⁰ the structure evolves toward

a LP form with a unit cell volume of 1480 Å³, in accordance with the experimental observation.²⁰

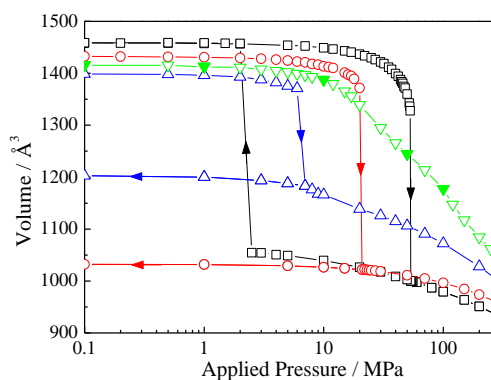


Fig. 2 Evolution of the simulated unit cell volume for MIL-53(Cr) as a function of the external applied pressure at 300 K (empty: black square symbols data taken from ref. 30; loaded with i. 1 H₂O/u.c.: red circle symbols; ii. 1 CH₃OH/u.c.: blue triangle up symbols and iii. 0.5 *n*-hexane/u.c.: green triangle down symbols. The empty and solid triangle symbols for *n*-hexane correspond to the data obtained for increasing and decreasing pressure respectively.

As a further step, we then followed the structural evolution of the MIL-53(Cr) framework in the presence of a low concentration of each guest molecule as a function of the applied pressure. Fig. 2 first compares the simulated evolutions of the unit cell volume for MIL-53(Cr) in the presence of the selected polar water and methanol molecules in a range of applied pressure up to 300 MPa. These calculations are compared with those we previously reported for the empty solid.³⁰ One first observes that for water, the simulated profile is very similar to the one obtained in the absence of any guest molecules in the compression domain. Indeed, while the structure remains initially its LP form, a sudden drop of the unit cell volume occurs at 21 MPa and attains a value of 1022 Å³ which is similar to both simulated and experimental³² structural features of the NP form in presence of 4 H₂O/u.c. at 0.1 MPa (1031 and 1012 Å³ respectively). One can notice that the so-obtained transition pressure is significantly lower than the one obtained in the absence of guest molecules (53.5 MPa). This is attributed to the fact that the confined molecule exerts an internal stress on the framework that tends to bring forward the onset of the structural switching. Such an observation emphasizes that there is a synergic combination of the chemical stimuli, through the adsorption of water, and the applied external pressure to facilitate the structural switching of this flexible MOF. Here, the role of the guest molecule thus drastically differs with the one previously reported for the water/alcohol mixtures in the relatively rigid Cu-BTC MOF, which once adsorbed within the pores show almost no impact on the pressure behaviour of this solid.¹² One can also observe that the unit cell volume change $\Delta V = (V_{\text{initial}} - V_{21\text{MPa}}) / V_{\text{initial}} \sim 30\%$ associated with this structural transition is very similar to the one previously reported for the empty case (31%).^{6, 30} Above 21 MPa, the unit cell volume of the NP structure slightly decreases, but remains higher than the one simulated for the MIL-53(Cr) in the absence of guest molecules and this holds true in the whole range of applied pressure up to 300 MPa (956 vs 931 Å³). Indeed, in this domain of pressure, the adsorbed water molecules put up resistance to the external pressure, leading to a slightly less contracted structure.

Interestingly, this loaded structure remains in the NP form when switching off the applied pressure from 300 to 0.1 MPa which differs with the reversible structural behaviour reported for the empty MIL-53(Cr).^{6, 30} The irreversible nature of the structural transition in the presence of water is mainly due to the relatively strong host/guest interactions which are not break down enough once the applied pressure is released to allow the re-opening of the structure.

A similar pressure-dependent behaviour was evidenced for the MIL-53(Cr) framework loaded with 1 CH₃OH/u.c. A structural transition occurs at 7 MPa associated with a drop of the unit cell volume from 1390 to 1183 Å³ which is much lower ($\Delta V = (V_{\text{initial}} - V_{21\text{MPa}})/V_{\text{initial}} \sim 15\%$) than for the water loaded solid (30%), consistent with a larger van der Waals volume for methanol vs water. In addition, this loaded NP shows a very similar unit cell volume both experimentally and theoretically evidenced¹⁶ in the presence of 3 CH₃OH/u.c. (1168 and 1165 Å³ respectively) at 0.1 MPa. The transition pressure is still below the one for the empty material which supports that the internal pressure exerted by the guest molecules contributes to move forward the appearance of the transition, this trend being even more pronounced for methanol (7 MPa) compared to water (21 MPa). This later observation can be related to the higher adsorption enthalpy value previously reported for methanol¹⁶ (-50.6 kJ·mol⁻¹) vs water²⁷ (-39 kJ·mol⁻¹) in the LP form. Above 7 MPa, there is a continuous contraction of the NP form up to a unit cell volume of 998 Å³ at 300 MPa which is only slightly higher than the one obtained in the presence of water, consistent with the experimental findings.¹⁶ Similarly to the case of water, the methanol loaded NP version does not re-open when the applied pressure is switched off, here again due to the relatively strong host/guest interactions. This result suggests that the presence of polar molecules within the pores tends to render irreversible the structural transition under compression/decompression.

Regarding the loaded MIL-53(Cr) with the apolar *n*-hexane molecule, a structural transition starts to be initiated at a pressure ~10 MPa very close to the one obtained for methanol (7 MPa). This result is consistent with a very similar adsorption enthalpy values obtained for both guests in the LP form (~-51.0 and -50.6 kJ·mol⁻¹ for *n*-hexane²⁰ and methanol,¹⁶ respectively). It is clearly established that the influence of the polar/apolar guest molecule on the transition pressure strongly depends on its strength of interactions with the pore wall. The simulated profile primarily corresponds to a smooth decrease of the unit cell volume from 10 MPa up to a value of 1044 Å³ at 300 MPa which is much lower than the one reported above for the NP form in presence of 1 *n*-hexane/u.c. (1313 Å³) without applying an external pressure. One observes that the resulting unit cell volume variation is much less sudden than the one obtained for the apolar molecules. This can be attributed to the larger dimension of *n*-hexane which makes this molecule highly resistant to the contraction of the structure under applied pressure. This interpretation can be quantitatively supported by introducing the guest induced relative contraction volume ΔV_c defined as follows:

$$\Delta V_c = \left[\frac{V_0 - V}{V_0} \right] \left[\frac{V_{e0} - V_e}{V_{e0}} \right] V_m \quad (1)$$

where the V_0 (V_{e0}) and V (V_e) are the volumes of the loaded (empty) MIL-53(Cr) structure at 0.1 MPa and at a given applied pressure

respectively while V_m is the volume occupied by the guest molecule estimated from the van der Waals volume of 1 methanol, 1 water and 0.5 *n*-hexane molecules respectively. This normalized contraction volume can be considered as a measure of the tendency of each investigated guest molecule to assist or withstand the structural switching of the structure when an external pressure is applied. The corresponding data are plotted in Fig. 3 for each guest in the pressure range up to 25 MPa. This result illustrates that the bulkier *n*-hexane is the more resistant molecule towards the structural contraction of the solid, consistent with the smooth transition as observed in Fig. 2.

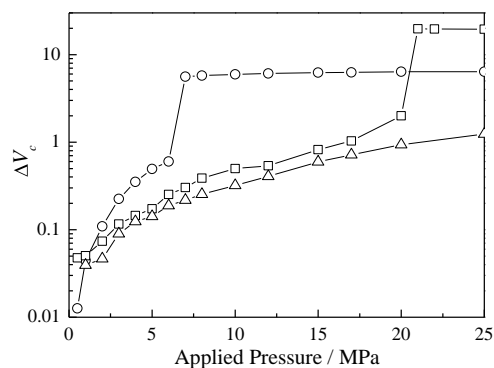


Fig. 3 Evolution of the simulated guest induced relative contraction volume of the MIL-53(Cr) as a function of the applied pressure up to 25 MPa. Square, circle and triangle up symbols represent the data for 1 H₂O/u.c., 1 CH₃OH/u.c. and 0.5 *n*-hexane/u.c. loaded MIL-53(Cr) respectively.

In addition, compared to the previous polar molecules, the structural transition of this *n*-hexane loaded MIL-53(Cr) is reversible once the pressure is switched off in the same way than the empty case, the main difference being that there is no hysteresis. Table S2 summarizes the unit cell parameters for each guest loaded MIL-53(Cr) under the whole range of applied pressure.

Fig. 2 shows that below 6 MPa, all the loaded structures remain in the LP form with a moderate gradual decrease of the unit cell volume (<3%) which reflects the reversible elastic compression of this solid. The bulk moduli of the LP form in the presence of the guest molecules were then determined in this range of pressure by using the third-order Birch-Murnaghan equation of state³⁷ to fit the evolutions of the relative unit cell volume as a function of the applied pressure (Fig. 4). The resulting bulk moduli for MIL-53(Cr) loaded with H₂O, CH₃OH and *n*-hexane are 0.96, 0.37 and 0.50 GPa, respectively, which are significantly lower than the one extracted for the empty solid (1.80 GPa). This observation emphasizes that the presence of these confined molecules induces a high degree of compressibility of the host structure which is even more pronounced for *n*-hexane and methanol. This is consistent with the corresponding higher adsorption enthalpies for the two molecules and the ability of the framework loaded with them to initiate the structural switching at lower applied pressures (Fig. 2). This trend is different from the one previously reported in the Cu-BTC MOF for which it was shown that the guest molecules offer little resistance on the compression of the framework, leading to an almost unchanged value of the bulk moduli (~30 GPa)

whatever the nature of the fluids.¹²

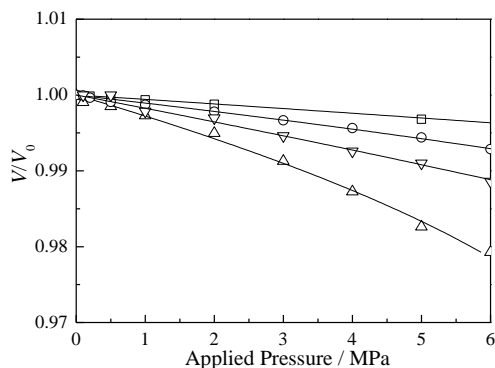


Fig. 4 Evolution of the simulated relative volume of the MIL-53(Cr) as a function of the applied pressure; V_0 corresponds to the volume of the LP form in the absence of external pressure. The solid lines correspond to the fits using the third-order Birch-Murnaghan EOS.³⁷ Square, circle, triangle up and triangle low symbols are for the empty (taken from ref. 30), 1 $\text{H}_2\text{O}/\text{u.c.}$, 1 $\text{CH}_3\text{OH}/\text{u.c.}$ and 0.5 n -hexane/ u.c. loaded MIL-53(Cr) respectively.

To finely characterize the microscopic behaviour of the guest molecules in the NP form along the whole range of applied pressure, the MD runs were carefully analyzed. Fig. 5(a) reports the radial distribution functions (RDFs) between the oxygen of the water molecules and the hydrogen of the hydroxyl $\mu_2\text{-OH}$ groups present at the MIL-53(Cr) surface. One observes that at 21 MPa, the water molecules establish a relatively strong hydrogen bond with the hydroxyls corresponding to a mean $\text{O}(\text{H}_2\text{O})\text{-H}(\mu_2\text{-OH})$ distance of 2.00 Å, which is similar to the one evidenced for the adsorption of 4 $\text{H}_2\text{O}/\text{u.c.}$ without applying an external pressure.

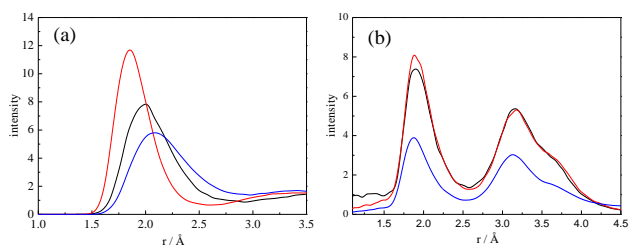


Fig. 5 Radial distribution functions between H_2O and MIL-53(Cr) for the pair (a) $\text{O}(\text{H}_2\text{O})\text{-H}(\mu_2\text{-OH})$ and (b) $\text{O}(\text{H}_2\text{O})\text{-H}(\text{H}_2\text{O})$ corresponding to a loading of (i) 1 $\text{H}_2\text{O}/\text{u.c.}$ at 21 MPa (black line) and at 300 MPa (red line), and (ii) 4 $\text{H}_2\text{O}/\text{u.c.}$ at 0.1 MPa (blue line)

The water molecules become even closer to the pore wall at 300 MPa with a mean $\text{O}(\text{H}_2\text{O})\text{-H}(\mu_2\text{-OH})$ distance of 1.85 Å. The resulting strong host/guest interaction which leads to an adsorption enthalpy of $-57 \text{ kJ}\cdot\text{mol}^{-1}$ for water in this form¹⁶ supports that MIL-53(Cr) remains in its NP form even when the external pressure is switched off. Fig. 5(b) reports the RDFs between the oxygen and the hydrogen atoms of the water molecules. Here again, the mean hydrogen bond $\text{O}(\text{H}_2\text{O})\text{-H}(\text{H}_2\text{O})$ distance is shorter (1.85 Å) at 300 MPa than at 21 MPa (1.90 Å) and in absence of external pressure for a loading of 4 $\text{H}_2\text{O}/\text{u.c.}$ (2.00 Å). This observation emphasizes the presence of a strong hydrogen bonding network once we reach 300 MPa. These whole interactions lead at 300 MPa to a preferential arrangement of the water molecules in the middle of the pores of the NP form with a

formation of strong hydrogen bonding network along the direction of the tunnel as illustrated in Fig. 6(a).

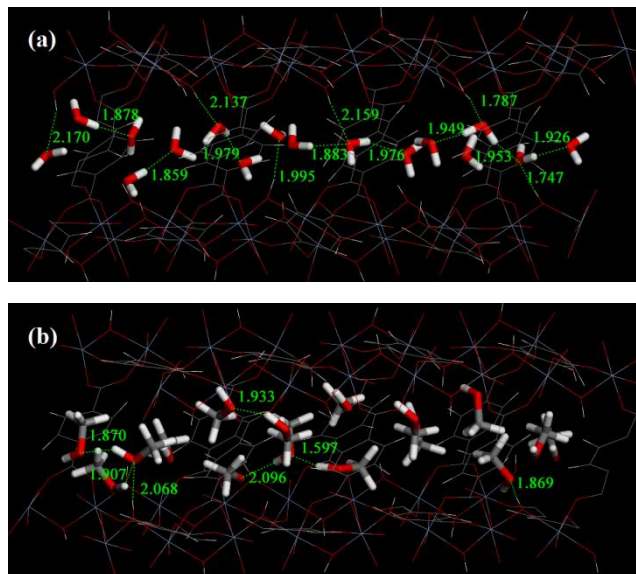


Fig. 6 Typical illustrations of the preferential arrangements of water (a) and methanol (b) in the tunnel of the NP form of MIL-53(Cr) under an applied pressure of 300 MPa extracted from the MD trajectories. View through yz plane along the direction of the tunnel. The characteristic distances are reported in Å.

The RDF between the oxygen atom of methanol and the hydrogen atom of the $\mu_2\text{-OH}$ group of MIL-53(Cr) is then plotted in Fig. 7(a). While at 7 MPa and similarly to the case for 3 $\text{CH}_3\text{OH}/\text{u.c.}$ at 0.1 MPa, the RDF is relatively broad with a mean $\text{O}(\text{CH}_3\text{OH})\text{-H}(\mu_2\text{-OH})$ distance of 2.20 Å, one observes at 300 MPa that the peak is much well defined and the mean characteristic distance of 2.00 Å is significantly shorter. This suggests a stronger interaction between methanol and the pore wall at the origin of the absence of the reopening of the structure once the applied pressure is released. This is again consistent with the relatively high adsorption enthalpy value reported for methanol in this NP form ($-60 \text{ kJ}\cdot\text{mol}^{-1}$).¹⁶ In addition, Fig. 7(b) which reports the RDFs between the oxygen and the hydrogen atoms of the methanol molecules evidences that the mean $\text{O}(\text{CH}_3\text{OH})\text{-H}(\text{CH}_3\text{OH})$ distance remains almost unchanged (1.80 Å) in the whole range of applied pressure. This is illustrated on Fig. 6(b) which shows that the methanol molecules tend to form hydrogen bonds with the neighbor molecules mainly forming dimers although they do not form a network as it is the case for H_2O .

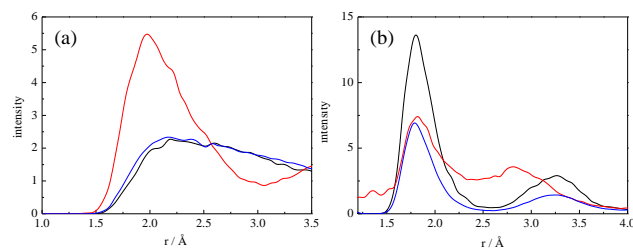


Fig. 7 Radial distribution functions between CH_3OH and MIL-53(Cr) for the pair (a) $\text{O}(\text{CH}_3\text{OH})\text{-H}(\mu_2\text{-OH})$ and (b) $\text{O}(\text{CH}_3\text{OH})\text{-H}(\text{CH}_3\text{OH})$ corresponding to a loading of (i) 1 $\text{CH}_3\text{OH}/\text{u.c.}$ at 7 MPa (black line) and 300 MPa (red line), and (ii) 3 $\text{CH}_3\text{OH}/\text{u.c.}$ at 0.1 MPa (blue line)

The preferential conformations and orientations of the *n*-hexane molecules confined within the porosity of MIL-53(Cr) at 300 MPa were further analyzed by adopting the methodology previously proposed by Bates et al.³⁸ Some of us already successfully employed to explore the geometries of long-chain *n*-alkanes in the analogue MIL-47(V).³⁹ Fig. 8(a) plots the angle formed between the end-to-end vectors of *n*-hexane and the axis corresponding to the direction along the tunnel of MIL-53(Cr). Compared to the situation obtained with 1 *n*-hexane/u.c. at 0.1 MPa, one observes that under 300 MPa, the distribution is much narrower and centered around a smaller angle value (4° vs 14°). This observation unambiguously shows that the guest molecules are increasingly aligned along the direction of the tunnel.

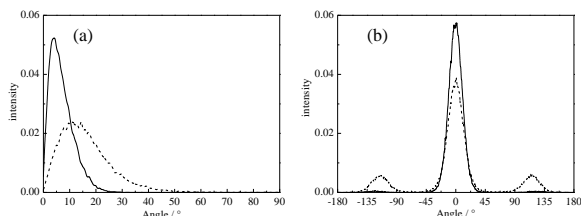


Fig. 8 Distribution of (a) the angles formed between the end-to-end vector of *n*-hexane loaded in MIL-53(Cr) and the axis corresponding to the direction of the tunnel averaged over all the conformations collected during the MD runs and (b) the dihedral angles over all bonds for *n*-hexane loaded in MIL-53(Cr). The solid and dash lines represent the data extracted in the case of MIL-53(Cr) loaded with 0.5 *n*-hexane/u.c. at 300 MPa and with 1 *n*-hexane/u.c. at 0.1 MPa, respectively.

Fig. 8(b) which reports the dihedral angle distribution for *n*-hexane in MIL-53(Cr) shows that while the guest can adopt a trans (0°) and gauche conformations (±90~135°) in the absence of an applied pressure, the scenario significantly differs at 300 MPa, *n*-hexane being mainly in the trans-conformation. This indicates that at high pressure the molecules mainly lie parallel to the direction of the tunnel. This can be illustrated in Fig. 9 which clearly states that at high applied pressure, the orientations of *n*-hexane become highly ordered along the direction of the tunnel and their conformations are predominantly linear. It should be noted that these high energy conformations are stabilized by the applied mechanical pressure. They are expected to recover to the initial low energy conformations and release energy to assist the structure expansion, leading to the reopening of the host structure when the applied pressure is switched off.

Compared to the empty case, the methanol and *n*-hexane loaded materials show both the lower transition pressure and the unit cell volume variation, leading to a drastic decrease of the energy capacity stored during a cycle of compression-decompression. For the water case, one maintains almost the same unit cell volume change while the transition pressure decreases much less than for the two other guests. Interestingly, in the presence of the apolar molecule, the structural transition is still reversible but this time with the absence of a hysteresis. This observation suggests that in complement to the potential application as nano-damper for the empty solid. Here we can envisage this *n*-alkane/MIL-53(Cr) system as potentially promising for the manufacturing of nano-spring. The scenario differs with polar molecules. In this latter case, the structural transformation of MIL-53(Cr) becomes irreversible and such a system can be proposed in the form of a shock absorber able to

store the mechanical energy during the compression without any further release. The water loaded MOF is further able to absorb a mechanical energy of ~4 J·g⁻¹ which is still higher than the storage capacity of mesoporous hydrophobic solids.²⁸⁻²⁹

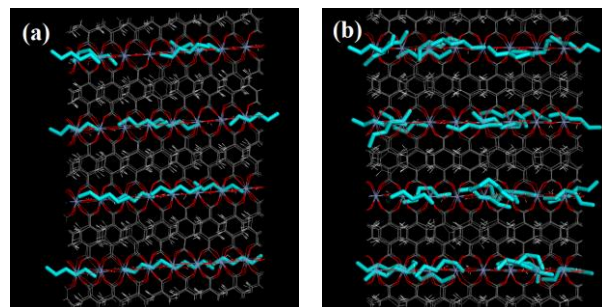


Fig. 9 Typical illustrations of the preferential arrangements of *n*-hexane in the NP structure of MIL-53(Cr) loaded with (a) 0.5 *n*-hexane/u.c. at 300 MPa and (b) 1 *n*-hexane/u.c. at 0.1 MPa.

Conclusions

To summarize, MD simulations based on a refined version of a flexible force field has been employed to explore the guest dependence pressure behaviour of the MIL-53(Cr). It was established that the inclusion of *n*-alkane allows a fully reversible structural switching under compression-decompression with the absence of any hysteresis which makes this guest loaded system potentially interesting for nano-spring applications. In complement to this, confining polar molecules into the pores leads to an irreversible structure transformation with an associated absorbed energy of 4 J·g⁻¹ for the water-loaded MIL-53(Cr) which outperforms other nanoporous reported so far. Interestingly this latter system is promising in terms of manufacturing novel shock nano-absorbers. Incorporating guest molecules of different polarities and strength interactions with the pore wall allows a massive extension of the storage abilities of this flexible material which has been previously evoked as nano-dampers by virtue of its reversible structural transition with the presence of a large hysteresis in its empty state. Such a modulation of the mechanical properties of this flexible MOF might be also envisaged by grafting the organic linker with different polar/apolar functions and by changing the nature of the metal center. This will guide the next step of our investigation on this system.

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