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# Hydrothermal breakdown of flexible metal-organic frameworks: a study by first-principles molecular dynamics

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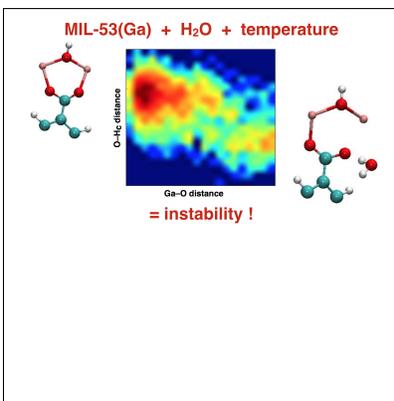
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## Abstract

Flexible metal–organic frameworks, also known as soft porous crystals, have been proposed for a vast number of technological applications, because they respond by large changes in structure and properties to small external stimuli, such as adsorption of guest molecules and changes in temperature or pressure. While this behavior is highly desirable in applications such as sensing and actuation, their extreme flexibility can also be synonymous with decreased stability. In particular, their performance in industrial environments is limited by a lack of stability at elevated temperatures and in the presence of water, leading to a rapid breakdown of the material. In this work, we demonstrate how first-principles molecular dynamics can shed light onto the hydrothermal breakdown of soft porous crystals. Focusing on the material MIL-53(Ga), we show that the weak point of the structure is the bond between the metal center and the organic linker and elucidate the mechanism by which water lowers the activation free energy for the breakdown, leading to a reduced hydrothermal stability of the material. This allows us to propose a strategy for the synthesis of MOFs with better heat and water stability.

## Graphical TOC Entry



## Keywords

MIL-53, soft porous crystals, hydrothermal stability, ab initio, DFT, NPT, flexibility

Metal-organic frameworks (MOFs) form a rapidly growing family of crystalline materials. They are built from metal centers which are connected by organic linkers to form three-dimensional nanoporous structures. The wealth of organic linker chemistry has paved the way, in the past decades, to a huge number of newly synthesized materials. Among these, Soft Porous Crystals (SPCs)<sup>1</sup> form a subclass of stimulus-responsive materials that exhibit reversible, large-amplitude structural changes when exposed to physical or chemical triggers, such as temperature, pressure or adsorption/desorption of guest molecules inside the pores of the material<sup>2,3</sup>. On the one hand, this stimulus-responsive character of Soft Porous Crystals makes them strong candidates for applications such as sensing and actuation, and there is a lot of work in the scientific literature focussing on designing novel flexible materials with targeted properties, or coupling the flexibility with novel stimuli<sup>4-6</sup>. On the other hand, their flexibility often comes at the cost of reduced stability, which limits their application at the industrial level, e.g. at elevated temperatures or in the presence of moisture or liquid water. The development of flexible yet stable MOFs depends on a better fundamental understanding of degradation mechanisms, opening the way to a rational design of novel materials.

Computational modeling of MOFs in general, and Soft Porous Crystals in particular, has greatly advanced in recent years, revealing the atomic-scale mechanisms which underly the stimuli-responsive behavior of materials, such as phase transitions induced by adsorption of guest molecules or mechanical pressure<sup>3,7-9</sup>. In a recent review, based on experimental results, criteria governing the water stability of MOFs have been proposed<sup>10</sup>. However, the issue of water stability of MOFs and its microscopic origins has only be addressed by relatively few simulation studies. In a pioneering study, Greathouse and Allendorf reproduced the experimentally observed breakdown of MOF-5 in the presence of water with classical molecular dynamics simulations<sup>11</sup>. Bellarosa *et al.* performed classical and first-principles simulations to study the hydrolysis of IRMOFs, identifying the mechanisms by which water attacks the framework and proposing strategies to make the MOF more resistant to water. They found that the basicity of water clusters inside MOFs can serve as a simple descriptor for water stability, thus providing a fast screening tool for candidate

materials<sup>12–14</sup>. De Toni *et al.* investigated the interplay of hydrophobicity and instability in the presence of water in IRMOF materials by first-principles molecular dynamics simulations<sup>15</sup>. Another recent paper showed that organic molecules adsorbed in MOF-5 undergo dynamical binding to and release from the metal center<sup>16</sup>. These studies suggest that the breakdown of the materials is initiated by water bonding to the metal center of the framework and eventually displacing an organic linker. However, these studies focused mostly on the IRMOF family of materials, that are unstable in presence of water at ambient temperature. There have been, to our knowledge, no theoretical studies of hydrothermal stability at high temperature or concerning highly flexible materials, undergoing structural transitions.

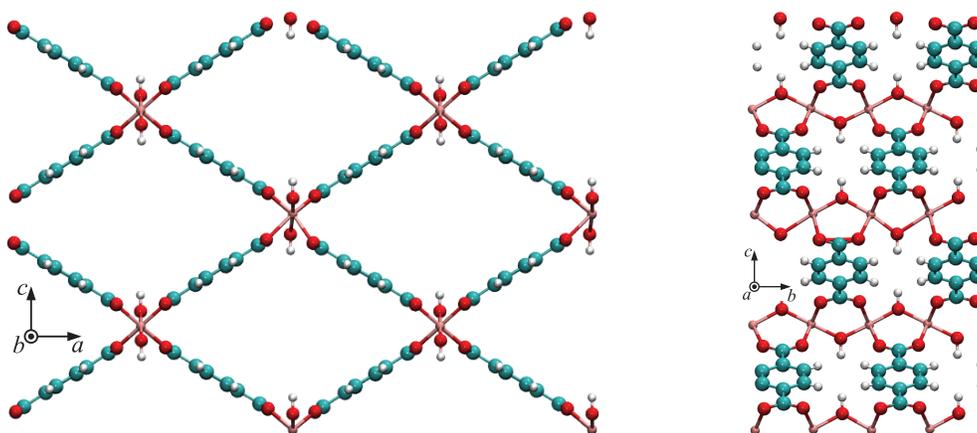


Figure 1: Large-pore structure of MIL-53(Ga), viewed along the diamond-shaped channels (left) and sideview (right). Atomic color code: Ga (pink), O (red), C (turquoise), H (white).

As a challenging test case, we study here the hydrothermal breakdown of the the gallium-based Soft Porous Crystal MIL-53(Ga)<sup>17–19</sup>. Like the other materials of the MIL-53(M) family (M = Al, Cr, Fe, Sc, ...), its structure is built from trivalent metal cations which are bridged by hydroxyl groups to form infinite –OH–Ga–OH–Ga– chains along the crystallographic *b* axis (Fig. 1). These inorganic chains are connected to each other by benzenedicarboxylate (bdc) linkers in a way that yields diamond-shaped channels along the *b* axis. MIL-53(Ga) displays a rich phase diagram and occurs in several polymorphs, depending on temperature and the amount of adsorbed guest molecules such as water<sup>20,21</sup>. This study focuses on the large-pore form which is shown in Fig. 1; the other polymorphs are not considered here. It is stable above 500 K, displays extremely

soft behavior along the  $a$  and  $c$  axes<sup>22</sup> and undergoes decomposition at approximately 650 K. Furthermore, we hypothesize that upon immersion into liquid water, the material takes on a “super-hydrated” state, structurally close to the large-pore form and of the same topology, in analogy to the Cr variant of the MIL-53 family<sup>23,24</sup>. The Al variant, MIL-53(Al), was even found to survive short exposures to boiling water, although gradual degradation was observed in the course of several hours<sup>25</sup>. To our knowledge, however, no data exists in the literature on the thermal stability of MIL-53(Ga) in liquid water.

The aim of this paper is to identify the “weak points” of the MIL-53(Ga) structure, and to study the atomic-scale mechanisms that initiate the decomposition of the material at elevated temperatures. Furthermore, we will see how water inside the channels influences the height of the relevant free-energy barrier and thus the kinetics of hydrothermal breakdown.

The first step in studying the breakdown of MIL-53(Ga) is to determine the weakest chemical bonds in the framework, i.e. those which break first and thus initiate the collapse of the material. Simulations of the non-hydrated framework were therefore performed at temperatures of 800 K, 1000 K and 1500 K, with a duration of at least 12.5 ps. We chose these relatively high temperatures in order to accelerate kinetics and to observe rare bond-breaking events even at the small time scales accessible to first-principles simulations. In these runs, the simulation box consisted of only one unit cell, containing 4 Ga(OH)(bdc). In case of a bond breaking, the periodic boundary conditions lead to a large and probably unrealistic defect density, especially along the short  $b$  axis ( $\sim 6.8$  Å). Therefore, the dynamics following the first bond breaking might not exactly represent the real material’s behavior. Nevertheless, these simulations are suitable to qualitatively identify the weakest point in the framework from short, spontaneous dynamics.

At 800 K, all chemical bonds remain intact over the whole simulation, and the unit cell fluctuates around its equilibrium structure, which is orthorhombic with a unit cell volume of  $(1500 \pm 100)$  Å<sup>3</sup> (deviation at  $1\sigma$ ). The relatively large standard deviation is a result of framework flexibility which leads to significant volume fluctuations in isobaric-isothermal simulations, unlike in rigid materials. The volume coincides, within uncertainties, with the volume derived from X-ray diffrac-

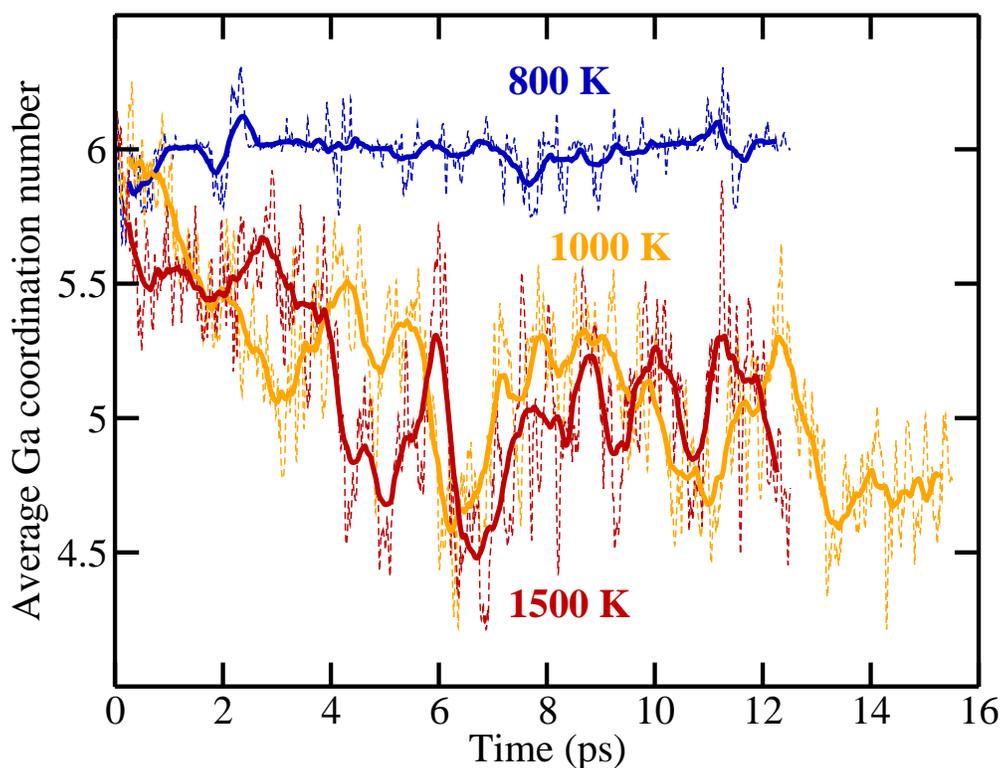


Figure 2: Evolution of the average coordination of Ga by O in non-hydrated MIL-53(Ga) at three different temperatures (dashed lines): 800 K (blue), 1000 K (orange), 1500 K (red). For better visibility, we also plot the running averages over a time interval of 0.5 ps (solid lines). The cutoff distance for Ga–O coordination is at 2.8 Å, corresponding to the first minimum of the Ga–O radial distribution function at 800 K. In order to obtain a continuous evolution in time, we applied a small Fermi-Dirac-like smearing to the cutoff distance.

tion experiments above 493 K<sup>18</sup> (1479.7 Å<sup>3</sup>), confirming the validity of our simulation protocol (and in particular the choice of the exchange–correlation functional and dispersion corrections<sup>26</sup>). At 1000 K and 1500 K, however, defects form within a few picoseconds, both starting with a bond breaking between gallium and an oxygen atom of the carboxyl group of the organic linker. Later in the simulations, this is followed by the breaking of the Ga–OH bonds that form the inorganic chains of the framework, eventually leading to a totally disordered state. To confirm this visual inspection, the evolution of the average coordination number of Ga by O along the simulation is shown in Fig. 2. At 1000 K and 1500 K, it exhibits a rapid drop from the initial value of 6, reaching values as low as 4.5. The bdc linkers themselves remain intact until the end of the simulation even at the highest temperature. Ga–O bond breaking is accompanied by a change of the simulation cell geometry from orthorhombic to triclinic of fluctuating shape, departing up to 30° from the orthorhombic cell shape, which reflects the decomposition of the framework. These results indicate that the structural collapse of MIL-53(Ga) at elevated temperatures is triggered by bond breaking between the Ga centers and organic linkers.

Now that the weakest points of the MIL-53(Ga) framework have been identified, we turn to the energetics of the Ga–O bond breaking and to the question of how the presence of water affects it. We focus here on the *kinetic* stability of the material: as pointed out by Burtch *et al.*<sup>10</sup>, even a thermodynamically unstable MOF may be useful in various applications if it is kinetically stable due to large free-energy barriers which preclude structural collapse. Experimental values for the temperature at which anhydrous MIL-53(Ga) starts to lose crystallinity range from 613 K<sup>18</sup> to 723 K<sup>17</sup>. However, in the simulations of the previous section, no bond breaking was observed even at 800 K. This is due to the fact that bond breaking is a rare event at the atomic scale and hence cannot be captured in a statistically meaningful way by equilibrium MD. We therefore turn to the use of an enhanced-sampling technique, well-tempered metadynamics, to study the onset of structural collapse of MIL-53(Ga) at the temperature of 650 K.

This method allowed us to compute the free energy profile along the distance between one Ga and one O on the carboxyl group of an organic linker, again with flexible size and shape of the

simulation cell. The latter was chosen to contain  $1 \times 2 \times 1$  unit cells, i.e. 8 Ga(OH)(bdc) units, in order to reduce the spurious interactions between the defect created during the metadynamics run and its periodic images (the smallest periodic image distance now being larger than 13 Å). One simulation of 49 ps duration was carried out for the non-hydrated framework (Fig. 1), and another of 38 ps duration for a fully hydrated material, containing 48 water molecules inside its pores. We chose this “super-hydrated” form for our purposes in order to highlight in the strongest possible way the effect of water. The super-hydrated form is of the same topology as the non-hydrated one, and our simulations yield a slightly larger unit cell volume of  $(1660 \pm 20) \text{ \AA}^3$ , due to pore opening along the  $c$  axis. It has not been reported for MIL-53(Ga) in the literature, but its Cr analogue has been observed after immersion into liquid water<sup>23</sup>. The number of water molecules in the simulation corresponds to the amount of adsorbed water ( $\sim 6$  water molecules per metal center) determined experimentally for MIL-53(Cr), which has a unit cell volume very similar to the Ga variant studied here. We suppose that in the hydrated state, the weakest point of the framework is still the metal-linker bond identified in the anhydrous state. This seems reasonable because adsorbed water interacts with the framework only through hydrogen bonding and does not alter the network of covalent bonds.

The resulting free energy profiles along the metadynamics variable (the Ga–O distance between metal center and organic linker) are shown in Fig. 3. From these profiles, we can accurately determine the activation free energy (*i.e.*, the barrier height), of the rupture of the Ga–O bond, but not the free-energy difference between the bonded and the dissociated state, because the system was precluded from sampling Ga–O distances beyond  $\sim 3.8 \text{ \AA}$ . This was done for computational reasons: first, since we are interested in kinetic stability only, we wanted to avoid sampling irrelevant parts of the phase space. Second, in preliminary simulations without restrictions on the Ga–O distance, Ga–O bond breaking was observed to entail further bond disruptions after a few picoseconds, making it impossible to define in a simple way a unique “broken” state with a single metadynamics variable. With the Ga–O distance restricted to below  $3.8 \text{ \AA}$ , we made sure that all other bonds remained intact for the duration of the simulation and that we accurately describe the

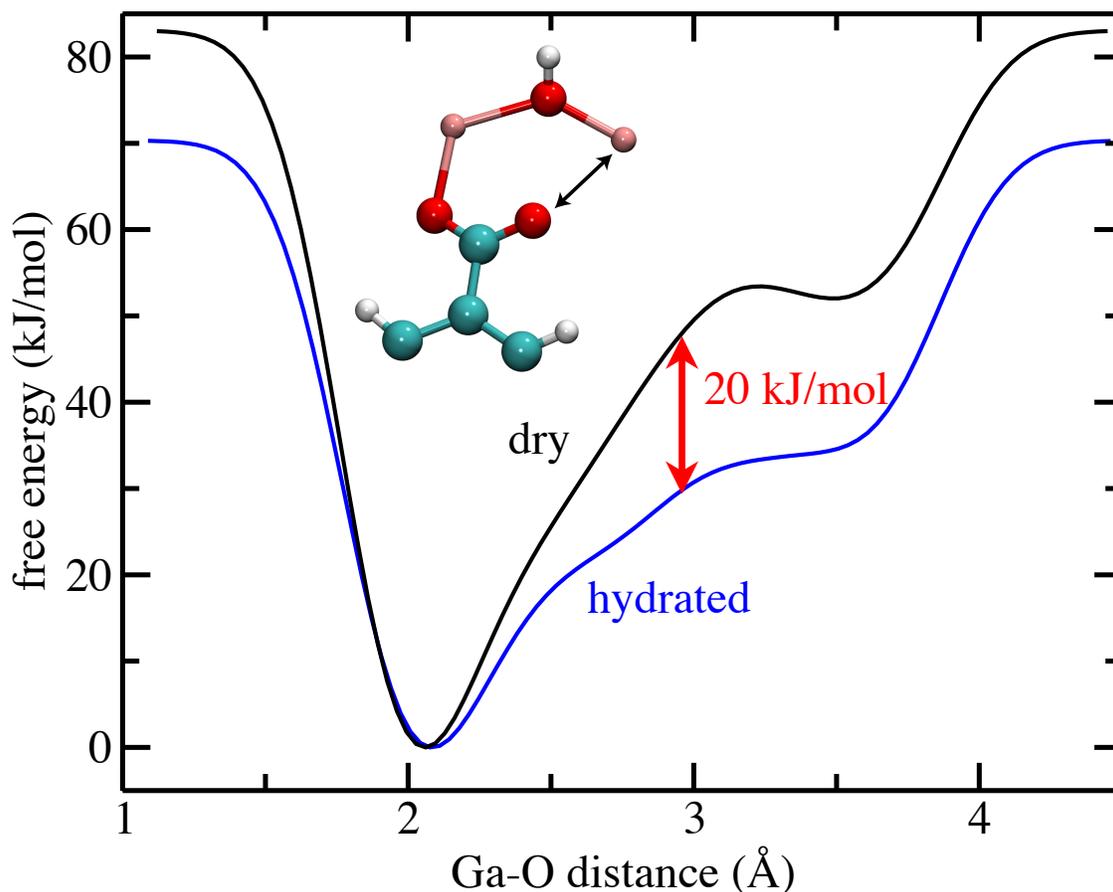


Figure 3: Free energy profiles of Ga–O bond breaking for dry (black) and hydrated (blue) MIL-53(Ga) at 650 K. The minimum of each curve has been set to zero. The black arrow in the structure model indicates the metadynamics variable, i.e. the Ga–O distance. Atomic color code: Ga (pink), O (red), C (turquoise), H (white). Note that for computational purposes, the sampled Ga–O distances were limited to about 3.8 Å, hence the free-energy profiles at larger distances are not physical (see text).

initial step of the hydrothermal instability of MIL-53(Ga). In addition to this study of kinetic stability, we note that the MD simulations above already showed that the Ga–O bond also becomes thermodynamically unstable at high temperatures.

In both the anhydrous and the hydrated case, the minimum of the curve and hence the Ga–O equilibrium distance is at 2.07 Å, slightly larger than the value of 1.96 Å determined from X-ray diffraction at 293 K<sup>17</sup>. The difference can be explained by the much higher temperature, 650 K, of the simulations (thermal expansion) and possibly by the tendency of the PBE exchange-correlation functional to overestimate bond lengths by a few percent. In the dry framework, Ga–O bond breaking requires overcoming a free-energy barrier of  $\Delta G_{\text{dry}}^{\ddagger} = 53$  kJ/mol located at a Ga–O distance of 3.2 Å. This barrier is lowered by 20 kJ/mol in the hydrated material, at  $\Delta G_{\text{hydrated}}^{\ddagger} = 33$  kJ/mol. This indicates that Ga–O bond breaking is greatly facilitated by the presence of water, with a kinetic constant for the bond breaking multiplied by a factor of  $\exp(-\Delta\Delta G^{\ddagger}/RT) = 40$  in presence of water. This shows quantitatively how free energy simulations can show the impact of water on the kinetic stability of MIL-53(Ga) at high temperature. We note, in passing, that this free energy barrier in the presence of water is twice that of IRMOF-0h in the presence of water, with  $\Delta G^{\ddagger}/kT = 6.1$  here, while  $\Delta G^{\ddagger}/kT = 3.2$  for IRMOF-0h at low hydration ( $\Delta F^{\ddagger} \simeq 8$  kJ/mol at 300 K).<sup>15</sup> This can help explain the difference in behavior between the two materials, where unfunctionalized IRMOF structures are unstable even in the presence of water vapor, while MIL-53(Ga) is stable in such conditions.

In addition to this quantitative information, atomistic simulations can elucidate in detail at the microscopic level how water facilitates the disruption of metal-linker bonds in MOFs. The most obvious mechanism would be water oxygen attacking the metal site of the framework and eventually displacing the organic linker. This behavior was reported in simulations of hydrated IRMOF structures where adsorbed water directly attacks metal centers, temporarily increasing the coordination of the metal center to form a pentavalent  $\text{Zn}^{2+}$  intermediary, before the linker–metal bond is broken to retrieve the tetrahedral coordination.<sup>15</sup> However, in the case of MIL-53(Ga), our simulations suggest a more complex process. In fact, water oxygen atoms never come closer

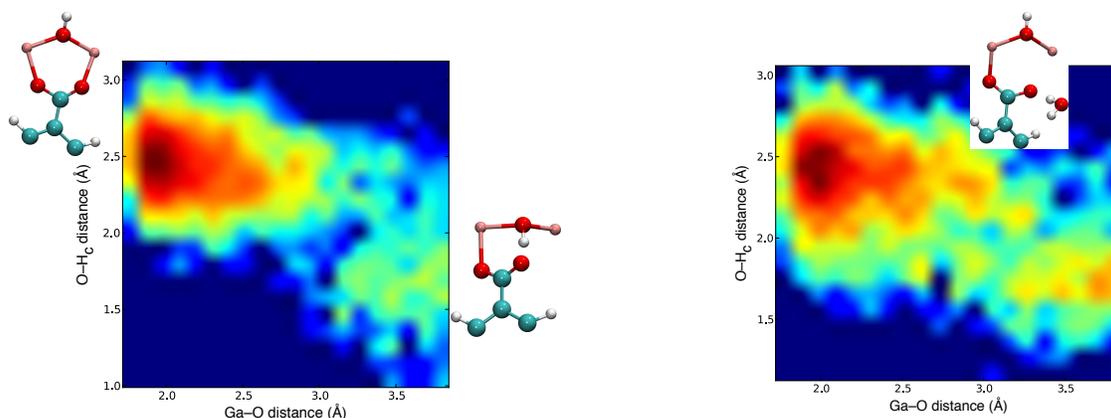


Figure 4: Color-coded histogram describing atomic configurations found during metadynamics simulations of the non-hydrated (left) and the hydrated (right) MIL-53(Ga) framework. The logarithmic color scale ranges from blue (rarely visited) to red (often visited). The abscissa represents the distance between O on the organic linker and Ga, the ordinate represents the distance between that O and the closest hydrogen atom  $H_c$ . The structure models refer to the configuration in nearby regions of the histograms.

than 3 Å to the Ga atom from which the linker is detached. This can be explained by the 6-fold coordination of Ga which sterically hinders a close water approach. The radial distribution function of water oxygen around this Ga is very similar to the one of water around the other Ga atoms which remain in octahedral coordination during the metadynamics simulation (SI, Fig. 1). In IRMOF structures, on the other hand, the metal site is only 4-fold coordinated, which allows water to approach it closely. This shows that in MIL-53(Ga), the lowering of the free-energy barrier for metal-linker separation in the hydrated framework is not due to water bonding to the unsaturated metal center after disruption of the metal-ligand bond.

Instead, the oxygen participating in the bond breaking is stabilized by forming hydrogen bonds to surrounding water molecules. This can be seen from Fig. 4 where we plot a color-coded histogram of configurations visited during the metadynamics simulations. The two-dimensional configuration space is spanned by the Ga–O distance (i.e. the metadynamics variable) and the distance between O and the closest hydrogen atom, which is termed  $H_c$  here and can either be part of the MOF or of a water molecule. The figure visualizes two distinct states of the system: (1) in both the non-hydrated and the hydrated framework, the system spends most of the time in a state with an intact Ga–O bond of approximately 2 Å length and an O– $H_c$  distance around 2.5 Å.  $H_c$  is mostly

one of the hydrogen atoms of the BDC linker (see leftmost structure model in Fig. 4), but in the hydrated MOF, also water hydrogen contributes. This state corresponds to the minimum of the free-energy curves in Fig. 3. (2) The second configuration frequently visited by the systems, both dry and hydrated, features a broken Ga–O bond ( $\sim 3.5$  Å) and an O–H<sub>c</sub> distance close to 1.7 Å, implying a hydrogen bond. Here, H<sub>c</sub> is mostly the hydrogen atom of a neighboring OH group of the framework (see middle structure model in Fig. 4), but again, in the hydrated MOF, also water hydrogen contributes. This configuration corresponds to the minimum or plateau of the free-energy curves in Fig. 3 at Ga–O distances beyond 3 Å. The main difference between the dry and the hydrated framework in Fig. 4 lies in the intermediate region between the two states just described: it is far more frequently visited by the hydrated system than by the dry one. It corresponds to configurations where the Ga–O bond is already broken but the hydrogen bond between O and the OH group of the framework has not yet formed. In the non-hydrated system, the dangling O atom has no bonding partner, leading to an energetically unfavorable situation. In the water-saturated system, however, the O atoms form hydrogen bonds with the surrounding water molecules, lowering the energy penalty of Ga–O bond breaking (see rightmost structure model in Fig. 4).

In conclusion, we have demonstrated on the case of MIL-53(Ga) soft porous crystals how first-principles molecular dynamics simulations can help gain microscopic insight and quantitative information about the hydrothermal breakdown of metal–organic frameworks, by combining direct dynamics and free energy methods (in this case, metadynamics). The mechanism for the breakdown of MIL-53(Ga) at high-temperature is initiated by the breaking of the metal–linker bond, which constitutes the weak point of the structure. Subsequently, the linker turns away from Ga, and the dangling O atom on the linker forms a hydrogen bond with the OH group of the inorganic –OH–Ga–OH– chain. This prevents the linker from re-bonding to Ga quickly. The free-energy barrier for this process was computed to be 53 kJ/mol, but it is lower by 20 kJ/mol in the presence of water in the channels of the framework, providing hydrogen bonds to the dangling oxygen. The kinetic thermal stability is therefore expected to decrease significantly in the presence of water. The present study also serves as a proof of concept that it is feasible to address the hydrothermal

stability of complex materials such as flexible MOFs with first-principles methods.

In the perspective of rational design of materials, the atomic-scale insights into the structural breakdown of the framework allow us to propose guidelines for synthesizing MIL-53 materials with higher hydrothermal stability. First, and rather obviously, the metal–linker bond should be made as strong as possible, a conclusion that is in line with recommendations reported in the literature<sup>10</sup>. A possible way to achieve this goal could be to choose more electropositive trivalent metal centers (e.g., Y or Sc). Secondly, our simulations highlight the destructive role of OH groups in the inorganic chains of the MIL-53 framework. It should be checked if these OH groups can be replaced by F, which would prevent the displaced linker from being stabilized in a distorted configuration by hydrogen bonding. Partially fluoridized MIL-53(Ga) has already been synthesized successfully<sup>17</sup>. Third, functionalization of the organic linker with small functional groups has been proposed to protect the metal center from a close approach of water molecules<sup>10</sup>. However, our simulations show that the metal site in MIL-53 is already hardly accessible for water, due its 6-fold coordination. Still, functionalization of the linker might be a promising route, even though for a different reason: it could be tuned to prevent the close approach of water to the O atoms on the carboxyl group. More experimental and computational work is needed to investigate if these recipes are experimentally feasible and if such candidate materials would still possess the desirable properties of the MIL-53 family, such as flexibility and adsorption properties. Moreover, while we studied here the large-pore polymorph of MIL-53(Ga) in its dry and super-hydrated state, it seems worthwhile to investigate, in future work, the interplay between repeated structural transitions of the MIL-53 framework (e.g. in switching applications), different hydration levels and hydrothermal stability.

## Computational methods

The systems were studied by means of density functional theory (DFT)-based molecular dynamics (MD) simulations, using the QUICKSTEP module<sup>27</sup> of the CP2K code package<sup>28</sup>. In contrast

to the few classical force fields available for flexible MOFs, this method allows for an accurate description of bond breaking between the metal centers and organic linkers. Since the soft material is anticipated to undergo massive structural changes in the process, all simulations were performed in the  $(N, \sigma, T)$  ensemble with variable size and shape of the simulation cell, following the methodology outlined in previous work<sup>26</sup>. As pointed out in the literature<sup>11,15</sup>, simulations at constant volume are not able to fully capture structural degradation, as they artificially impose a given cell geometry. Finally, whereas MD simulations provide full dynamical information about the simulated process, free energies are harder to obtain. Here, we use both “free” MD as well as metadynamics simulations<sup>29,30</sup> to study the free energy barriers associated with the onset of hydrothermal breakdown. This allows us to quantify the influence of water on the stability of the material at elevated temperatures. Details concerning the computational methods can be found in the Supporting Information.

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## Supporting Information Available

Computational methods and radial distribution functions.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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