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The Interaction of Water with MOF-5 Simulated by Molecular Dynamics

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Isoreticular metal−organic frameworks (IRMOFs) are a recently discovered class of nanoporous coordination polymers that are attracting considerable attention because of their extremely high surface areas (up to 4,500 m^2/g)[1] and interchangeable organic linkers, enabling relatively facile manipulation of pore size and surface area through judicious ligand selection.[2,3] In this communication, we present a new flexible force field for MOFs, validated by comparing the simulated lattice parameter for MOF-5 with experiment. Additionally, we report for the first time molecular dynamics simulations describing the interaction of water with MOF-5. Our simulations show that MOF-5 is stable at very low water content but unstable when exposed to ≥4% water.

Much of the experimental and theoretical attention MOFs are receiving concerns their potential application as storage media for gases, particularly hydrogen. However, MOFs can accommodate many other guest molecules.[1−4] Although there is a growing body of experimental evidence for these adsorption processes, theoretical understanding of these adsorbate−MOF interactions significantly lags that of light gases. Understanding the interaction with water is of particular importance since the MOF crystal morphology is affected by exposure to water during synthesis or after evacuation.[5] In addition, zinc-based MOFs are water sensitive, losing their high surface area after prolonged exposure to humid air.[6] Recent molecular simulations of MOF-5 (IRMOF-1) focus on their gas sorption capacity.[7] The framework itself is usually treated as a rigid body, and general force fields are used for MOF-adsorbate interactions. Such treatments cannot reproduce structural changes that occur upon absorption of guest molecules or be used to probe chemical reactions with the MOF. To our knowledge, no MOF-specific intramolecular parameters have been reported. Our hypothesis is that the interaction energy between Zn ions and water O atoms is similar to that between Zn ions and MOF O atoms. Water molecules could easily penetrate the pores and disrupt the framework. A possible mechanism might be (ignoring associated hydrolysis reactions)

$$(Zn_4O)(BDC)_3 + 4H_2O \rightarrow [(Zn_4O)(H_2O)_4(BDC)_2]^{2+} + BDC^{2-}$$

where BDC refers to the benzene dicarboxylate ion. Because Zn ions would interact with water molecules only through nonbonded (electrostatic and van der Waals) interactions, our methodology requires the use of only nonbonded force field parameters between Zn ions and MOF O atoms.

Constant-pressure molecular dynamics simulations were performed at 300 K on both pure MOF-5 and MOF-5 with up to 10% water (by mass).[8] Our approach combines a general force field (CVFF)[9] for the BDC linker with parameters optimized for the mineral zincite (ZnO). Simulated lattice parameters for zincite ($a = 3.27 \pm 0.01$ Å, $c = 5.24 \pm 0.01$ Å) are in good agreement with experiment ($a = 3.26$ Å, $c = 5.21$ Å).[10] Simulation of an isolated Zn ion in pure water resulted in a tetrahedral solvation shell (data not shown), which is consistent with concentrated Zn solutions.[11] We have not tested the zincite parameters with other general organic force fields, but that should in principle be possible.

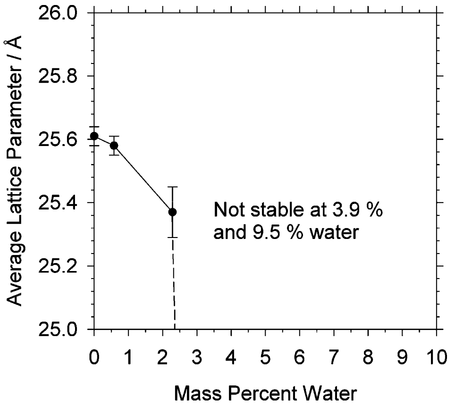

Figure 1. Simulated lattice parameter as a function of water content. The dashed line indicates the trend toward a much smaller lattice parameter (≈20 Å) at higher water content.

The lattice parameter of pure MOF-5 produced by our force field is 25.61 ± 0.01 Å, which is in good agreement with the range of reported X-ray diffraction values (25.67−25.89 Å).[2,12] Average bond and angle values also compare well with experiment,[8] although errors in nonbonded angles involving Zn are somewhat higher than those in the bonded BDC linker. These errors could be minimized by including bonding parameters (bond stretch and angle bend) between Zn and neighboring O atoms, which would require quantum chemical calculations. The good agreement with pure MOF-5 supports the combination of CVFF parameters for organic species with nonbonded parameters for ZnO. A more general force field with these additional bond and angle parameters and their application to other Zn-based MOFs are subjects of future work.

The result of added water on the simulated MOF-5 lattice parameter is shown in Figure 1. At low water content, the MOF-5 structure is maintained despite a decrease in lattice parameter to 25.37 Å (2.3% water). At higher water contents of 3.9% and 9.5%, the MOF-5 structure collapsed within 200 ps to a high density state. Equilibrium was never obtained, but lattice parameters of ≈20 Å were observed. Our results are consistent with the experimental results of Huang et al., which show a transformation in the MOF-5 XRD pattern and a decrease in surface area from ≈900 to 45 $m^2 \cdot g^{-1}$ upon exposure to water.[6] The role of water in the disruption of the MOF-5 structure becomes evident by monitoring the coordination of Zn ions to neighboring O atoms. In pure MOF-5, each Zn ion is coordinated by one inorganic O atom (O1) and three BDC O atoms (O2). Both of these coordination numbers decrease with added

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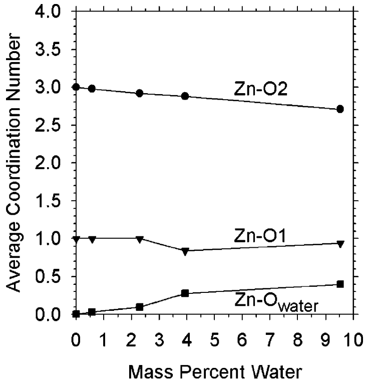

Figure 2. Changes in Zn coordination with increasing water. Zn retains tetrahedral coordination, but the relative amounts of BDC O (O2) and inorganic O (O1) decrease as they are replaced by water O atoms (O$_{water}$).

water, as seen in Figure 2. Each Zn ion retains tetrahedral coordination, with water O atoms taking positions in the first shell. With classical molecular dynamics simulations such as these, it is not possible to accurately model the protonation state of the aqueous BDC anion. Completely deprotonated BDC O atoms such as those seen in our collapsed structure would only occur in very basic solution. However, we believe that the simulations predict the initial mechanistic steps involved when a water molecule attacks a MOF-5 pore. As a water O atom approaches a ZnO_4 tetrahedron, either of the Zn−O1 or Zn−O2 first-shell interactions can be broken. Figure 2 shows that both O1 and O2 coordination have decreased by approximately 10% when the water content is 9.5%.

Our simulations indicate that water molecules interact with MOF-5 in three ways: (1) direct attack on a ZnO_4 tetrahedron in which a water O atom replaces one of the coordinating MOF O atoms (O1 or O2), (2) hydrogen bonding between a water H atom and O2, and (3) a hydrogen-bonded network of water molecules tethered (hydrogen-bonded) to one or more ZnO_4 tetrahedra. All three scenarios occur in the simulation system with 2.3% water in MOF-5 (Figure 3). Even though MOF-5 is stable at this low water content, distortions in the framework structure occur. The structure shown in Figure 3 could be analogous to the hydrolyzed form of MOF-5 (a = 25.05 Å, c = 27.00 Å) described elsewhere.[6] An example of the first and apparently most destructive mode of interaction can be seen in the Figure 3 inset. In this case, the inorganic O atom (O1) becomes triply coordinated after a water molecule has taken up position in a ZnO_4 tetrahedron. The Zn ion is still coordinated by three BDC O atoms (O2), but without the anchoring O1 atom all three BDC ligands have increased freedom of rotation. As the water content increases, water molecules continue to attack ZnO_4 tetrahedra, and the framework eventually collapses. Upon removal of water from the 0.6% and 2.3% systems, the original MOF-5 structure is recovered after constant-pressure simulation. The water adsorption process thus appears to be reversible at low water content, in agreement with experiment.[6]

The stability of MOF-5 (and other MOF compounds) in water has received little attention in the literature,[6] perhaps because they can be prepared and characterized in other solvents.[2,12] However, the technological applications of MOFs would be greatly increased if new water-resistant frameworks were developed. Our simulation techniques provide insight into the mechanism of MOF-5 dissociation that is initiated by contact with water. The relatively weak interaction between Zn ions and O atoms in MOF-5 allows for attack by water molecules. Thus, a potential solution would be to tailor the metal−linker interactions so that they are stronger than possible metal−water interactions.

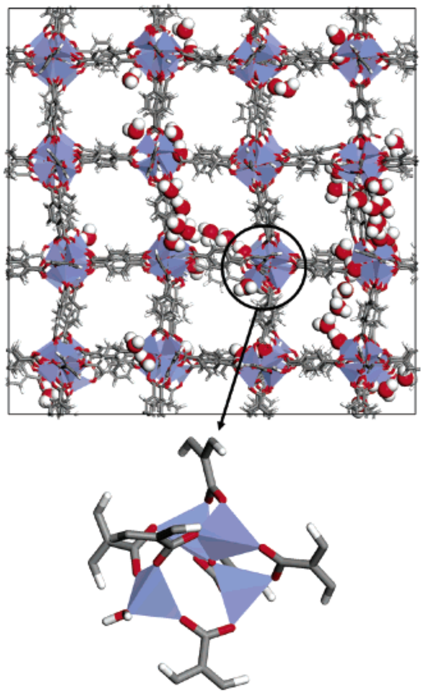

Figure 3. Disruption of the MOF-5 structure at 2.3% water (top). The color scheme is Zn (purple), O (red), C (gray), and H (white), with ZnO_4 tetrahedra represented as polygons. Also shown is a Zn_4O center in which an inorganic O atom has been replaced by a water O atom (bottom).

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Supporting Information Available: Simulation methods and structural results. This material is available free of charge via the Internet at http://pubs.acs.org.

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