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Are Zr_6-based MOFs water stable? Linker hydrolysis *vs.* capillary-force-driven channel collapse†

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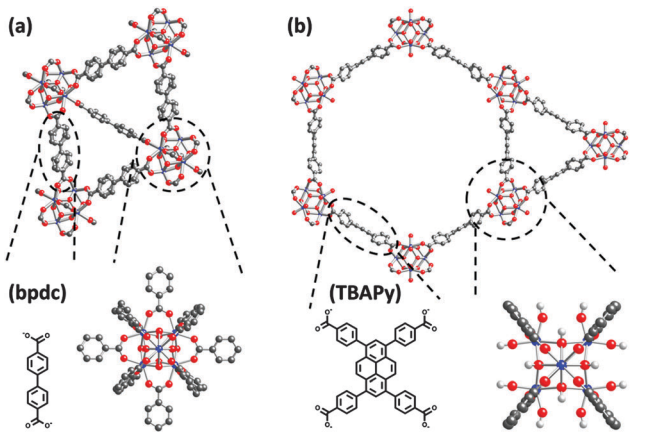
Metal–organic frameworks (MOFs) built up from Zr_6-based nodes and multi-topic carboxylate linkers have attracted attention due to their favourable thermal and chemical stability. However, the hydrolytic stability of some of these Zr_6-based MOFs has recently been questioned. Herein we demonstrate that two Zr_6-based frameworks, namely UiO-67 and NU-1000, are stable towards linker hydrolysis in H_2O, but collapse during activation from H_2O. Importantly, this framework collapse can be overcome by utilizing solvent-exchange to solvents exhibiting lower capillary forces such as acetone.

Metal–organic frameworks (MOFs) are a rapidly growing class of porous solid-state materials built up from inorganic nodes and organic linkers.[1] An important and emerging area of interest has been assessing the stability of MOFs. Surprisingly, of the approximately 20 000 known MOFs,[2] only a few dozen exhibit both the thermal and chemical stability desired for certain applications (such as catalysis in harsh environments).[3] Examples of unusually stable MOFs include various zeolitic imidazolate frameworks (ZIFs),[4] MILs,[5] pyrazolate containing frameworks,[6] and MOFs constructed from Zr_6-based nodes and carboxylate-terminated linkers.[3] The prototypical example is UiO-66, a MOF built up from $Zr_6(O)_4(OH)_4$ nodes and benzene dicarboxylate linkers; UiO-66 is thermally (up to 500 °C),[3] mechanically,[7] hydrolytically, and chemically stable in a variety of organic solvents as well as acidic and basic aqueous media.[3,8] The stability of Zr_6-based MOFs is attributed to the highly oxophilic nature of the Zr^{IV} sites and their Coulombic interaction with negatively charged termini of linkers.

Despite this, the hydrolytic stability of some Zr_6-based MOFs has recently come in to question. For example, it was reported that UiO-67 (Scheme 1)—a MOF isoreticular with UiO-66, but containing extended biphenyl dicarboxylate (bpdc) linkers—is not stable to H_2O exposure.[8,9] This lack of stability was attributed to linker hydrolysis engendered by clustering of H_2O molecules near the Zr_6-based node (a phenomenon observed for other carboxylate containing MOFs[10]) and rotational effects of the extended linker.[8] In contrast to these observations, others have found excellent hydrolytic stability in Zr_6-based MOFs with linkers of similar length to bpdc and even in MOFs with larger linkers and hence pores.[11]



Scheme 1 Idealized molecular representations of (a) UiO-67 and (b) NU-1000.

In the context of our labs' recent efforts utilizing Zr_6-based MOFs,[12] as well as our continuing efforts to elucidate the effects of activation on the stability and porosity of MOFs,[13] we hypothesized that failures at the activation stage, as opposed to inherent hydrolytic Zr–carboxylate bond stability, could be the cause of the reported degradation of various Zr_6-based MOFs. Recall that activation entails removing guest molecules, such as solvent or other chemicals utilized during synthesis, from the MOF while maintaining its permanent porosity. We find that addressing issues related to activation can often yield permanently porous MOFs. Chief among these issues are destructive

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(*i.e.*, channel-collapsing) capillary forces which are greatest when solvent surface tension is high and when solvent molecules adhere well to MOF cavities or channels (*e.g.*, *via* strong hydrogen bonding). Processes such as solvent-exchange,[14] supercritical CO_2 ($scCO_2$) activation,[15] and freeze-drying have all been employed to help avoid channel collapse in MOFs.[16]

Herein we demonstrate that two Zr_6-based MOFs, UiO-67 and NU-1000, are stable to linker hydrolysis under our experimental conditions. However, both frameworks are susceptible to capillary-force-driven channel collapse when activated directly from H_2O. Notably this can be overcome by simple solvent-exchange to acetone. Understanding the differences between linker hydrolysis and capillary-force-driven channel collapse will have a profound impact on the practical limitations of these Zr_6-based MOFs. For example, the former calls into question the viability of these frameworks for applications involving humid atmospheres, chemical catalysis, and electrocatalysis. In contrast, applications like dehumidification based cooling[17] could indeed prove problematic if the H_2O-condensation limit is reached as capillary forces would then come into play during MOF regeneration.

UiO-67 was synthesized using the procedure recently reported by Katz *et al.*[12b] The resultant powder X-ray diffraction (PXRD) pattern, Fig. 1a black line, nicely matches the simulated pattern of UiO-67 (gray line) confirming the bulk phase purity of the material. Next we placed UiO-67 in H_2O for 24 h and examined its PXRD pattern. As one might expect given the reported stability of the UiO series,[3] the PXRD pattern is unaltered. However, upon heating the sample to 150 °C under vacuum and removing the H_2O molecules from the pores of UiO-67 (*i.e.*, activating the sample), a noticeable broadening of the peaks at angles (2Θ) of 5.8 and 6.7 degrees was observed along with nearly complete disappearance of the peaks at higher 2Θ (Fig. 1a, red trace).We suspected this loss of crystallinity was due to capillary forces that in turn cause partial or complete framework collapse during activation. To circumvent this problem we exchanged the H_2O molecules to acetone and subsequently activated the sample thermally (Fig. 1a, blue line). Pleasingly the crystallinity of UiO-67 was maintained after solvent-exchange to acetone. We also rigorously quantified the relative crystallinity for these UiO-67 samples (and NU-1000, *vide infra*) in the ESI.†

To further elucidate the effects of activating UiO-67 from both H_2O and acetone, N_2 adsorption isotherms of thermally activated UiO-67 (*i.e.*, DMF synthesis solvent evacuated), a sample activated directly from H_2O, and a sample activated *via* solvent-exchange to acetone (Fig. 1c) were measured. Activation directly from H_2O (red triangles) leads to a complete loss of porosity. However, when solvent-exchange to acetone is utilized the porosity of UiO-67 is retained, Fig. 1c (comparison of black circles and blue squares).

Next we turned our attention to the MOF NU-1000 ($[Zr_6(OH)_{16}(TBApy)_2]$) which is built up from $Zr_6(OH)_{16}$ containing nodes and 1,3,6,8-tetrakis(benzoate)pyrene (TBApy) linkers (Scheme 1).[12a] NU-1000 has triangular micropores as well as exceptionally large mesopores (*ca.* 30 Å diameter). In this regard, NU-1000 should facilitate the permeation of H_2O throughout its structure and ensure H_2O molecules can readily access its node. Using the procedure detailed by Mondloch *et al.*,[12a] NU-1000 was synthesized as a microcrystalline powder. The PXRD pattern and N_2 adsorption isotherms are shown in Fig. 1b and d (black line and black circles). Examination of the PXRD patterns of NU-1000 soaked in H_2O for 24 h but not activated (Fig. 1b, green a line), activated directly from H_2O (Fig. 1b, red line), and solvent-exchanged to acetone followed by thermal activation (Fig. 1b, blue line) reveal that the crystallinity is maintained except when NU-1000 is activated directly from H_2O. In particular the reflections centered at 5 and 7.5 degrees have broadened, while the peaks at higher angles have decreased in intensity. Consistent with the UiO-67 sample, N_2 adsorption isotherms (Fig. 1d) demonstrate that the sample activated directly from H_2O (Fig. 1d, red triangles) exhibits significantly less porosity than either the pristine NU-1000 sample or the one activated *via* solvent-exchange (Fig. 1d, black circles and blue squares). For example, the BET surface area of the sample activated from H_2O is 480 $m^2\ g^{-1}$, while pristine NU-1000 has a surface area of 2040 $m^2\ g^{-1}$.

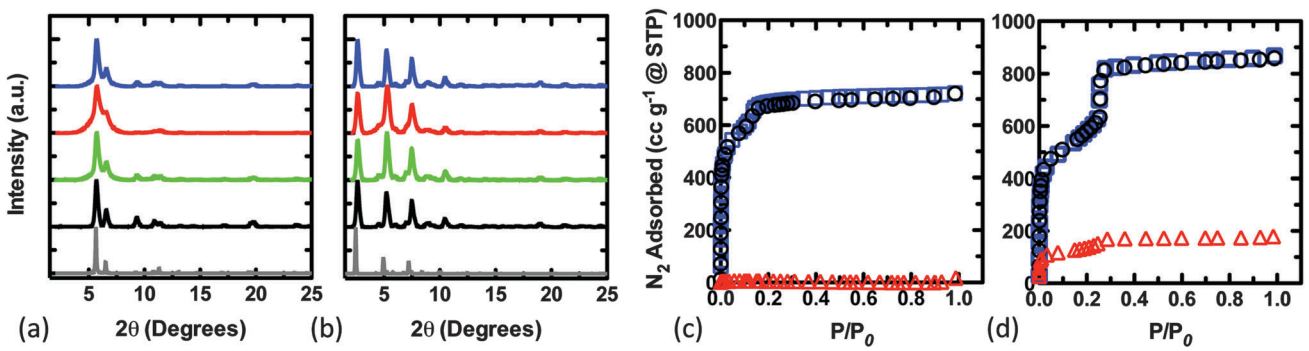

Fig. 1 Normalized PXRD patterns of the simulated structures (gray line), parent MOFs (black line), MOFs in H_2O (green line), MOFs thermally activated from H_2O (red line), and MOFs solvent-exchanged to acetone and subsequently activated (blue line) for UiO-67 (a) and NU-1000 (b). For UiO-67 (c) and NU-1000 (d): N_2 adsorption isotherms of samples activated *via* thermal evacuation of the synthesis solvent (DMF or acetone, black circles), thermal evacuation of H_2O from the pores (red triangles), and exchange of H_2O for acetone, and then thermal evacuation (blue squares). For clarity only every other data point is displayed in the isotherms.

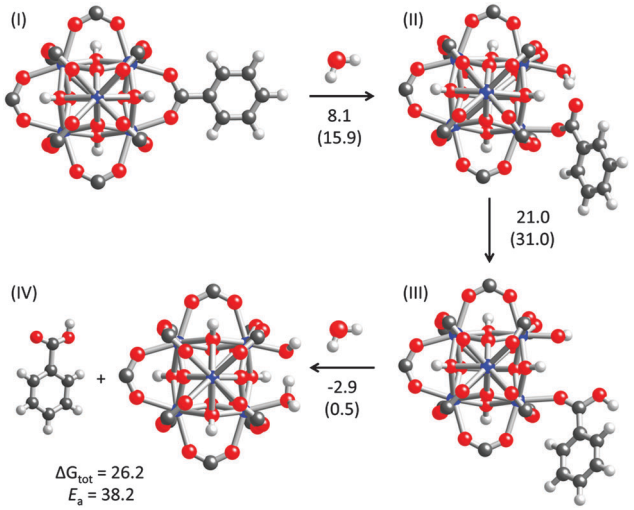

Fig. 2 Molecular representations and DFT free energies (in kcal mol^{-1}) associated with the hypothetical hydrolytic degradation of UiO-67. In parenthesis, the corresponding activation free energy.

We further ruled out the hydrolytic pathway in UiO-67 and NU-1000 through a combination of NMR and IR spectroscopies (ESI†) as well as quantum chemical characterization. ^{1}H NMR of the filtrate from the H_2O soaked samples showed no residual sign of their linkers in solution. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) demonstrated that both the UiO-67 and NU-1000 frameworks stayed intact after exposure to H_2O, solvent exchange to acetone, and finally thermally activating the samples. In contrast, DRIFTS of the samples activated directly from H_2O show broad stretches consistent with the presence of free carboxylates and loss of framework porosity (*i.e.*, node-linker bond breaking occurring during activation). Interestingly we also performed *in situ* DRIFTS experiments (ESI†). Exposure of UiO-67 and NU-1000 to H_2O vapour, followed by removal of excess H_2O yielded no detectable change in the DRIFTS spectra, a result suggesting that the stability of these frameworks towards H_2O vapor is different than for condensed phase H_2O. Finally, cluster model density functional theory, DFT, calculations (at the M06-L level, see ESI†) are consistent with the node of UiO-67 being stable towards hydrolytic attack. The computed free energies of the proposed degradation pathway are summarized in Fig. 2; the net free energy is approximately +26 kcal mol^{-1} with an overall activation energy of 38 kcal mol^{-1}. This is in good agreement with recent calculations from Vermoortele *et al.* demonstrating that removal of CF_3COO^- anions from Zr_6 containing nodes is also thermodynamically uphill.[18]

Rather than hydrolytic instability through H_2O clustering, our data demonstrate instability arises from the presence of capillary forces experienced during activation. Notably, mild activation strategies—such as solvent-exchange (or $scCO_2$, no surface tension)—can be utilized to overcome framework collapse. While the surface tension of H_2O is significantly larger than that of acetone (72 mN m^{-1} *vs.* 26 mN m^{-1} at 25 °C),[19] a discussion based on the geometrical properties of the pores of UiO-67 and NU-1000, as well as the literature on confined H_2O (ESI†), brings additional insight into the behaviour of H_2O molecules and capillary forces in Zr_6-based MOFs. Although additional data would be required to quantify these effects, our initial exploration suggests that H_2O does not behave as a liquid in UiO-67, while it should partially behave as a liquid in the larger pores of NU-1000. This in turn implies that solvent-framework intermolecular forces are significant in driving channel collapse for Zr_6-based MOFs when activated from H_2O.

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