Is catenation beneficial for hydrogen storage in metal–organic frameworks?†

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Grand canonical Monte Carlo (GCMC) simulations demonstrate that catenation can be beneficial for improving hydrogen storage in metal–organic frameworks at cryogenic temperatures and low pressures but not necessarily at room temperature.

Metal–organic frameworks[1–3] (MOFs) are a new class of materials that have shown promise for gas adsorption applications,[4,5] especially hydrogen storage.[6–8] In order to lessen the dependence on fossil fuels as a primary energy source, the US Department of Energy (DOE) has set gravimetric and volumetric storage targets for hydrogen storage on vehicles for 2010 (6 wt%, 45 g L^{-1}) and 2015 (9 wt%, 81 g L^{-1}).[9] Reports in the literature have shown promising results in a variety of MOFs, although the DOE targets have only been met at cryogenic temperatures.[10]

Catenation, where two separate frameworks self-assemble within each other,[11,12] is often suggested as a means to improve hydrogen storage in MOFs. For example, Rowsell and Yaghi[13] suggested that catenation should improve hydrogen uptake because the smaller pores would increase the strength of hydrogen binding. In addition, a second framework doubles the number of metal-corner sites, which have been shown to be strong adsorption sites for hydrogen.[6,11,14,15] On the other hand, Jung *et al.*[16] noted that catenation may hurt adsorption at high pressures, where the free volume available for guest molecules plays a key role in determining the adsorption capacity.[17] Recently, Ma *et al.*[18] reported substantial increases in hydrogen uptake at 77 K and 1 atm in a catenated MOF relative to its single-framework version.

Molecular simulations of hydrogen adsorption have been useful for elucidating how MOF characteristics, such as the heat of adsorption, surface area, and free volume, influence hydrogen adsorption in different pressure ranges.[17,19] Molecular simulations can explore wide ranges of temperature and pressure more readily than experiments. In addition, it is often difficult in experiments to isolate pure phases of catenated and non-catenated versions of the same MOF. In this communication we use these capabilities of molecular modeling to clarify whether catenation is beneficial for hydrogen storage and at what temperatures and pressures. Three related isoreticular metal–organic frameworks (IRMOFs) were chosen to investigate the effects of catenation: IRMOF-1, IRMOF-10, and IRMOF-16, which have benzenedicarboxylate, biphenyldicarboxylate, and triphenyldicarboxylate linkers, respectively.[20] The IRMOFs have Zn_4O corners connected by linker molecules to form a regular, three-dimensional lattice of cubic cavities. These structures were selected to keep the linkers as similar as possible while providing a range of pore diameters (11.2, 15.4, and 19.1 Å for IRMOFs-1, -10, and -16, respectively).[20] For each IRMOF, hypothetical interwoven and interpenetrated structures were generated on the computer by copying atoms of the original framework and translating these positions along the [111] direction. The *interwoven* configuration minimized the distance between both frameworks without atomic overlap. The *interpenetrated* configuration maximized the distance between the two frameworks, shifting the second framework exactly one half of the cavity length in the x, y, and z directions. Although the interwoven configuration is the likely preferred structure, the interpenetrated configuration is investigated as an extreme case to determine the effect of framework position on hydrogen adsorption.

GCMC simulations were performed for the non-catenated, interwoven, and interpenetrated versions of each IRMOF using our multipurpose simulation code Music.[21] Details are provided in the ESI.† A simple classical model was used. This model was shown previously to provide reasonable predictions of hydrogen isotherms and heats of adsorption in IRMOFs-1 and 8.[17,19] Additionally, more recent experimental work by Kaye *et al.* shows excellent agreement with our model at 120 bar at both 77 and 298 K, further suggesting this model reasonably describes both low and high pressure regimes (see ESI†).[22]

Hydrogen adsorption isotherms at 77 K on a gravimetric basis are shown in Fig. 1 for IRMOFs-1 and -16. Qualitatively similar results were obtained for IRMOF-10 (ESI†). At low pressures, there is a regime where catenation is clearly beneficial for hydrogen uptake. However, at higher pressures, for all three IRMOFs the curves cross and the non-catenated structures adsorb more hydrogen. It should be noted that the pressure where the curves cross increases with increasing pore size (IRMOF-1 < IRMOF-10 < IRMOF-16). Fig. 2 shows the adsorption isotherms for the same systems on a volumetric basis. Again, there is a low pressure regime where hydrogen adsorption is higher in the catenated structures than in the non-catenated MOFs, but at higher pressures the curves cross and the non-catenated MOFs exhibit higher hydrogen storage capabilities than their catenated counterparts.

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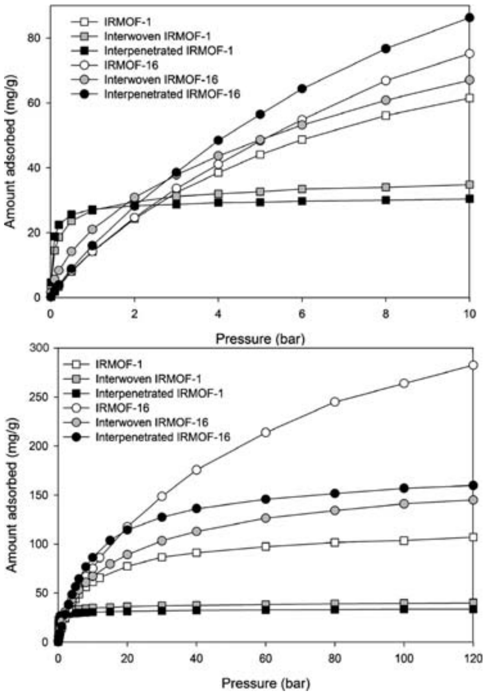

Fig. 1 Hydrogen adsorption isotherms on a gravimetric basis (mg g^{-1}) at 77 K for (top) low pressure regime and (bottom) full isotherms up to 120 bar. Note that all isotherms reported in this paper are the absolute isotherms, not the excess values.

The reasons for the higher adsorption in catenated MOFs at low pressure and the crossing of the curves are easily understood. Catenation reduces the pore size, which increases the amount adsorbed by increasing the heat of adsorption. The heat of adsorption plays an important role at low loading.[17] Similarly, catenation increases the number of metal-corner sites per unit volume, and these are known to be favorable adsorption sites. At higher pressures, however, the free volume available for adsorbed molecules limits the uptake, and the catenated structures have less free volume than their non-catenated counterparts both on a gravimetric and a volumetric basis. Thus, the arguments for and against catenation in the hydrogen storage literature are all correct, but different factors dominate under different conditions. Experiments are often performed at 77 K and 1 atm for convenience. If experiments performed under these conditions show improved hydrogen storage in catenated structures, one should be cautious in extrapolating this result to higher pressures.

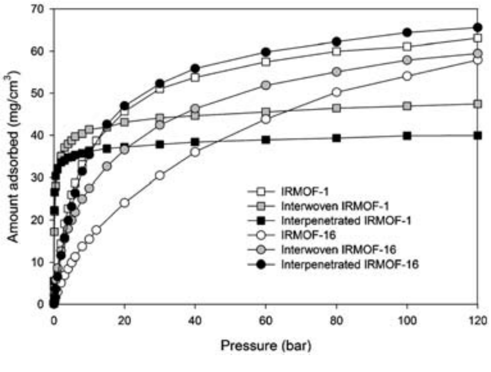

Fig. 2 Hydrogen isotherms on a volumetric basis (mg cm^{-3}) at 77 K.

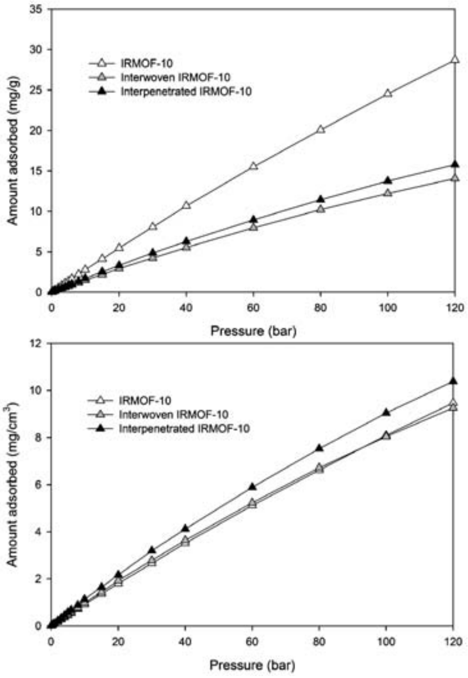

Fig. 3 Hydrogen adsorption isotherms at 298 K (top) on a gravimetric basis and (bottom) on a volumetric basis.

The extension to room temperature is shown in Fig. 3, which shows adsorption isotherms for IRMOF-10 at 298 K on both a gravimetric and a volumetric basis. These results are representative of all three IRMOFs (see ESI†). On a gravimetric basis, the loading for the catenated structures is approximately one half that of the original structure. The presence of a second framework doubles the density of the MOF and does not appear to enhance adsorption significantly at these conditions. On a volumetric basis, the amounts adsorbed in all three variations of IRMOF-10 are quite similar. The expected increase in adsorption due to catenation because of smaller pores and increased heat of adsorption is effectively offset by the loss in free volume. Again, these results indicate that even if catenation increases adsorption under some conditions (*e.g.* 77 K and 1 atm), it may not be helpful at room temperature.

Fig. 4 shows heats of adsorption at 77 K for the three variations of IRMOF-16. Both the interpenetrated and interwoven structures have higher heats of adsorption for hydrogen than the original structure across the full range of loadings. The most striking feature in Fig. 4 is the high heat of adsorption for the interwoven structure at low loading—approximately 7.3 kJ mol^{-1}, which is roughly double the value at higher loadings. However, at higher hydrogen loadings, the interpenetrated structure has the highest adsorption energy.

In order to learn more about this behavior, snapshots were generated for the various MOFs to understand where the molecules adsorb at different loadings. Fig. 5 shows representative results at two pressures (0.1 and 15 bar) in the interwoven form of IRMOF-16. The snapshots show clearly that hydrogen molecules at low pressure adsorb near the corners of

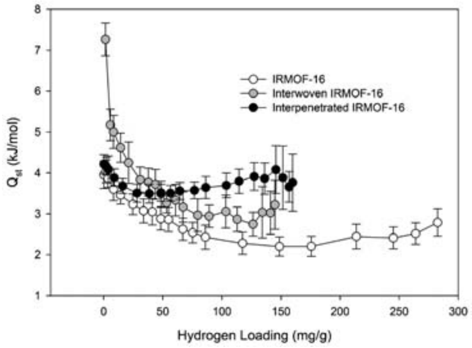

Fig. 4 Heat of adsorption in IRMOF-16 structures at 77 K as a function of hydrogen loading.

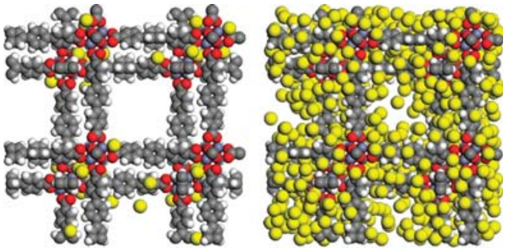

Fig. 5 Snapshots of dihydrogen (yellow) adsorption at 77 K in interwoven IRMOF-16 (a) at 0.1 bar (2.0 mg g^{-1}) and (b) at 15 bar (79.5 mg g^{-1}). Carbon, oxygen, and framework hydrogen atoms are gray, red, and white, respectively.

the frameworks, as anticipated. Additionally, for the interwoven structures, there exist pockets where hydrogen molecules can interact with two metal corner sites simultaneously, leading to the high heat of adsorption at low loading observed in Fig. 4. To understand the behavior at higher loadings, we note that the interpenetrated structures have more uniform pore dimensions than the interwoven structures, which tend to have a larger central cavity as shown in Fig. 5. After filling the corner sites, molecules adsorb along the walls of the cavities, and finally the centers of the pores fill.[23] In the larger pores of the interwoven structures, molecules cannot interact as strongly with the frameworks, leading to higher heats of adsorption in the interpenetrated structures. This is an example of the well-known trend that heats of adsorption tend to decrease with increasing pore size. These results suggest that dynamic framework movement,[24,25] where the second framework can move with respect to the other, could prove beneficial for hydrogen storage. For example, it seems likely that for an evacuated MOF the interwoven form might be preferred, as it maximizes interactions between the frameworks. If, however, guest molecules serve to drive the frameworks apart, the resulting interpenetrated structure might display increased hydrogen uptake.[26]

In conclusion, catenation of MOFs can sometimes be beneficial for improving hydrogen uptake, but the answer depends on the temperature and pressure conditions. One should be cautious in extrapolating from results at low temperatures and low pressures (where catenation is beneficial due to the increased heats of adsorption) to higher temperatures and pressures (where the reduction in free volume from catenation decreases storage capacity). This work examined three examples of the IRMOF series, but the essential physical insights should apply to other structures as well. For hydrogen storage applications at ambient temperature, our results show that, for the three IRMOFs studied, catenation does not improve adsorption and, in fact, decreases gravimetric uptake significantly. Thus, other strategies for increasing the heat of adsorption for hydrogen in MOFs should be pursued to meet DOE storage targets.

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