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Opening the Gate: Framework Flexibility in ZIF-8 Explored by Experiments and Simulations

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S Supporting Information

ABSTRACT: ZIF-8 is a zeolitic imidazole-based metal−organic framework with large cavities interconnected by narrow windows. Because the small size of the windows, it allows in principle for molecular sieving of gases such as H_2 and CH_4. However, the unexpected adsorption of large molecules on ZIF-8 suggests the existence of structural flexibility. ZIF-8 flexibility is explored in this work combining different experimental techniques with molecular simulation. We show that the ZIF-8 structure is modified by gas adsorption uptake in the same way as it is at a very high pressure (i.e., 14 700 bar) due to a swing effect in the imidazolate linkers, giving access to the porosity. Tuning the flexibility, and so the opening of the small windows, has a further impact on the design of advanced molecular sieving membrane materials for gas separation, adjusting the access of fluids to the porous network.

Zeolitic imidazolate frameworks (ZIFs) have emerged as a very promising family of microporous metal−organic frameworks (MOFs).[1,2] They combine the advantages of MOFs (i.e., high porosity and surface area, transition metal centers, and tailored linkers) with high stability and framework diversity. Their adsorption properties can be tuned through chemical modification of the linker making them promising candidates for gas storage applications.[3,4] Furthermore, many ZIFs exhibit large cavities interconnected by small windows which allows in principle for shape- and size- selective separations.

ZIF-8 is a prototypical structure with a sodalite (SOD) topology that has been studied as a molecular sieve for the purification of hydrogen due to the narrow size of the 6-ring windows (∼3.40 Å) that connect the large cavities (∼11.6 Å of diameter).[5,6] Because of the small window size, ZIF-8 is expected to separate hydrogen (2.89 Å kinetic diameter) from larger molecules including methane (3.80 Å) and nitrogen (3.60 Å). However, it has been observed experimentally that molecules which are theoretically too large to pass through the windows of the framework (i.e., in terms of the LJ collision diameter and the assumption that the framework is rigid), such as methane and nitrogen, are adsorbed in the material.[1,7] In addition, predictions of the diffusivity of molecules in the rigid ZIF-8 structure[8] show fundamental discrepancies to experimental data.[5,6] The unexpected adsorption of large molecules and their relatively high diffusivity imply flexibility during the adsorption process. This flexibility in ZIF structures is fundamentally important since it modifies the diffusivity of gases through the porous network. A thorough understanding of this behavior is a prerequisite to exploit this phenomenon in adsorption technology. In this work, we explore structural flexibility in ZIF-8 using different experimental techniques (gas adsorption, high pressure X-ray diffraction (XRD), and *in situ* synchrotron XRD), combined with grand canonical Monte Carlo simulations (GCMC).

Previous work demonstrated the effect of pressure up to 1.47 GPa or 14 700 bar on structural changes of ZIF-8.[9] Though this pressure is far from a typical adsorption pressure (i.e., generally below 0.01 GPa or 100 bar), the structural changes observed in the diamond anvil cell experiments provide a first indication about the nature of the framework flexibility induced by adsorption at much lower pressures. At 1.47 GPa, a new phase was observed which we refer to as ZIF-8HP. This high-pressure phase maintained the *I*43*m* space-group symmetry of ZIF-8 but showed a reorientation of the imidazolate linkers, increasing the accessible pore volume and the size of the 6-ring windows. The structural change was found to be reversible after decreasing the pressure.

The experimental adsorption isotherm of N_2 at 77 K shows two steps occurring at 2×10^{-3} and 2×10^{-2} P/P_0 or 0.002 and 0.02 bar (Figure 1); the desorption process was completely reversible, and no hysteresis was found. The fitting of the BET equation to both steps revealed the uptake of N_2 for the first and second step, corresponding to 36.9 and 49.4 molecules per unit cell, respectively (Supporting Information, Table S1). This corresponds to an increase of 26% in uptake going from the first to the second step. This two-step isotherm, which has also been observed in two other ZIFs with a SOD topology (ZIF-90, ZIF-91),[10] was previously interpreted as a result of a reorganization of the adsorbed nitrogen molecules during the adsorption process, rejecting the existence of structural changes.[11]

To investigate the step in the isotherm further and to relate it to possible changes in the structure of the ZIF-8, we conducted GCMC simulations of nitrogen at 77 K using both the ZIF-8HP structure and the structure of the conventional ZIF-8 (hereafter referred to as ZIF-8AP) following a similar approach as was used previously in, for example, the study of CO_2 adsorption in the flexible MOF MIL-53.[12] In contrast to the experimental curve, a standard Type I isotherm (i.e., without any step) was found in

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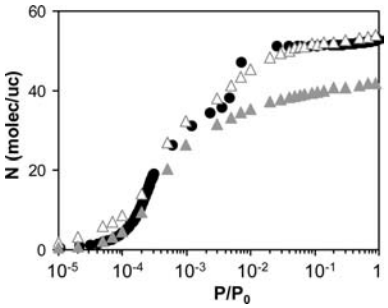

Figure 1. Semilog plot of N_2 adsorption on ZIF-8 at 77 K: experimental, circles; and simulated data on ambient pressure structure, ZIF-8, closed triangles and high-pressure structure, ZIF-8HP, open triangles.

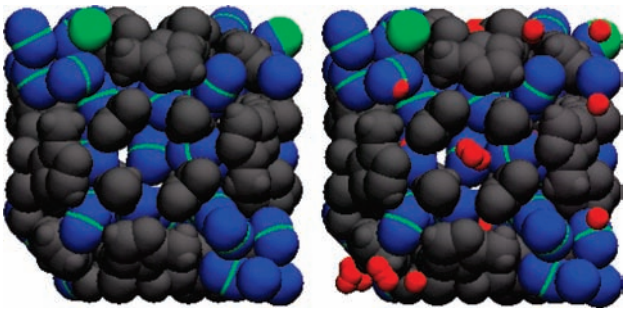

Figure 2. Snapshots of N_2, blue-green spheres, adsorption on ZIF-8HP, gray spheres, at 77 K (left) before and (right) after the step. Extra adsorbed N_2 molecules are represented by red spheres where their size has been scaled down for an easier visualization.

Table 1. Pore Volume and Surface Areas for the Different Structures Using GCMC

	Free Pore Volume [Å^3/uc][a]	Accessible Surface Area [Å^2/uc]	Accessible Surface Area [m^2/g][b]	BET Surface Area [m^2/g]
ZIF-8AP	2918	606	1332	1279
ZIF-8HP	3034	598	1296	1706

[a] Obtained using a probe molecule with a diameter of 0 Å. [b] Obtained using a probe molecule with a diameter of 3.681 Å (i.e., N_2 molecule diameter used in the BET analysis).

ZIF-8AP. The isotherm simulated in this structure fits the experimental isotherm in the low pressure range very well, correctly describing the Henry constant, which is a direct measure of the strength of the interactions. However, the prediction deviates from the experimental data when the pressure is higher than 2×10^{-4} P/P_0. In this case, the maximum uptake determined with the BET equation from the simulated isotherms corresponds to 35.8 molecules per unit cell, close to the first step of the experimental isotherm, but far below the second step. The differences between the experimental and the simulated isotherm at low and high pressures, together with the nonexistence of steps in the simulation, indicate that the rigid model for ZIF-8AP is not able to describe fully the experimental behavior.

When running the simulations on the ZIF-8HP phase previously observed at 1.47 GPa, the isotherm deviates from the experimental at low pressure but predicts the step shape of the experimental isotherm after 5×10^{-4} P/P_0 correctly. Here, the maximum uptake determined from the BET equation corresponds to 47.7 molecules per unit cell, similar to the experimental uptake after the step. This maximum uptake corresponds to a 33.4% increase compared to the simulation on ZIF-8AP. The combination of both simulated adsorption isotherms on ZIF-8AP and ZIF-8HP before and after 2×10^{-4} P/P_0, respectively, is able to match the experimental isotherm indicating that ZIF-8 is undergoing the same structural changes on adsorption as observed in the diamond anvil cell experiments under much higher pressures.

We further studied the structural change of ZIF-8 calculating geometrically the free pore volumes and accessible surface areas, and comparing them with those obtained from BET. Whereas the difference in the amount adsorbed before and after the step in the experimental isotherm (25.7%) and in the simulated maximum adsorbed in two different structures (33.4%), respectively, is substantial, no significant difference in either the free pore volumes or surface areas was observed (Table 1). This result seems counterintuitive at first, as an increase in the maximum uptake should be related to an increase in the pore volume. However, a detailed analysis of the molecular simulation results shows that the situation is more complicated. First, at 1.5×10^{-2} P/P_0, the N_2 molecules fill the same 36 positions of the nanocage as determined by Yildirim and co-workers from neutron powder diffraction experiments for the adsorption of CH_4 (Figures 2 and S2).[13] A further pressure increase does not affect greatly the uptake. In the case of ZIF-8HP, N_2 molecules fill positions similar to the ones observed in ZIF-8AP before reaching the step in the adsorption isotherm. After the step, the subtle changes in the pore structure of ZIF-8HP compared to ZIF-8AP allow additional molecules to be accommodated leading to a more efficient packing through the rearrangement of previously adsorbed molecules and the insertion of new ones close to the 4-ring windows, a situation that does not arise in the case of ZIF-8AP. Here, the linear shape of the N_2 molecules plays an important role in the packing during the adsorption process.

In order to confirm that the ZIF-8HP structure is indeed observed at high nitrogen loadings, *in situ* powder XRD measurements at 77 K were conducted on station I11 at the Diamond light source on a fully evacuated sample of ZIF-8 and a separate sample which was loaded with N_2 at a relative pressure of 0.4 (i.e., after the step). Rietveld refinements were carried out using TOPAS-A. Both the evacuated and N_2 loaded samples were refined from the ambient pressure coordinates from Moggach et al.[9] in order to not bias the final model.

On comparing the N_2 containing ZIF-8 structure with ZIF-8HP, little difference is observed between the structures, with the N_2 loaded ZIF-8 (collected at several orders of magnitude lower in pressure) showing the same reorientation of the imidazolate linkers (Figure 3). This confirms the existence of a change in the structure caused by a swing effect of the imidazolate linker.

In conclusion, we have shown that the ZIF-8 structure is modified by gas adsorption in the same way as at very high pressure in diamond anvil cell high-pressure experiments. Thus, the step in the nitrogen adsorption isotherm for ZIF-8 is caused by a structural change, which is also responsible for the non-expected adsorption of large molecules in ZIF-8 due to the enlargement of the window size. In turn, the enlargement of the window size provokes the faster diffusivity of molecules through

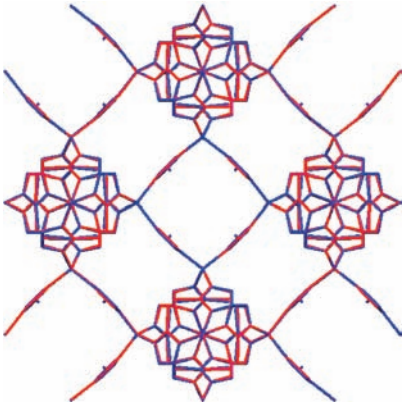

Figure 3. Overlay of ZIF-8 loaded with N_2 (blue) and ZIF-8HP (red).

the porous network.[5,6] The addition of further molecules during the adsorption process close to the 4-ring windows is only possible due to a swing effect of the imidazolate rings. Our results demonstrate that two conformations of ZIF-8 are needed to describe adsorption in this material: one derived from the crystal structure of the as-synthesized material, the other one obtained from high pressure XRD experiments. Thus, a correct description of the flexibility and structural changes of ZIF-8 is essential to precisely describe the adsorption performance over the whole range of pressure. Here, the diamond anvil cell experiments prove their usefulness for applications at much lower pressures since they are able to overcome any kinetic barrier between configurations in the same way as adsorbed fluid molecules do but are easier to carry out than in situ XRD experiments which require synchrotron radiation access.

The study of ZIF flexibility opens a new direction in the design of new porous solids. It has already been shown that ZIF-90 is suitable for postsynthesis modification and keeps the SOD topology when other functional groups are introduced in the framework.[2,10] The understanding of the role of the different building blocks and functional groups on the flexibility phenomena is of fundamental importance. Tuning this effect and so the opening of the windows between cavities by changing the functional group in the imidazolate linker will directly affect the diffusivity of fluids through the porous network, which has a fundamental impact on the performance of ZIFs as advanced molecular sieving membrane materials.

■ ASSOCIATED CONTENT

Supporting Information. Experimental and simulation procedures; BET surface area analysis; snapshots of N_2 adsorption on ZIF-8AP and ZIF-8HP; XRD data and cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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