Direct Observation of Hydrogen Adsorption Sites and Nano-Cage Formation in Metal-Organic Frameworks (MOF)

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The hydrogen adsorption sites in MOF5 were determined using neutron powder diffraction along with first-principles calculations. The metal-oxide cluster is primarily responsible for the adsorption while the organic linker plays only a secondary role. Equally important, at low temperatures and high-concentration, H₂ molecules form unique interlinked high-symmetry nano-clusters with inter-molecular distances as small as 3.0 Å and H₂-uptake as high as 10-wt%. These results hold the key to optimizing MOF materials for hydrogen storage applications and also suggest that MOFs can be used as templates to create artificial interlinked hydrogen nano-cages with novel properties.

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The success of future hydrogen and fuel-cell technologies is critically dependent upon the discovery of new materials that can store large amounts of hydrogen at ambient conditions. Metal-organic framework (MOF) compounds, which consist of metal-oxide clusters connected by organic linkers, are a relatively new class of nano-porous material that show promise for hydrogen storage applications because of their tunable pore size and functionality. Yet despite numerous experimental studies of hydrogen adsorption in MOF materials, the nature of the MOF-hydrogen interaction and the manner in which hydrogen molecules are adsorbed onto the structure are still unknown. Answers to these questions hold the key to optimizing these materials for practical hydrogen storage applications.

Here using the difference-Fourier analysis of neutron powder diffraction data along with first-principles total-energy calculations, we directly determined the H₂ adsorption sites in MOF5 (the most widely studied MOF material, which consists of ZnO₄ clusters linked by 1,4-benzenedicarboxylate (BDC)). Surprisingly, the MOF5 host lattice has the enough space available to hold many hydrogen molecules, up to 10 wt-% at low temperatures. The ZnO₄-cluster is responsible for most of the adsorption while the organic linker plays only a secondary role.

Equally important, we find that at high-concentration loadings hydrogen molecules form unique 3-dimensional (3D) networks of H₂ nano-clusters with intermolecular distances of 3.0 Å, which is significantly shorter than the intermolecular distances of 3.6 Å in pure solid hydrogen. These findings suggest that MOF materials can also be used as templates to create artificial, interlinked hydrogen nano-cages. Such materials could exhibit very unexpected properties due to confinement effects and small intermolecular separation, such as metallic behavior.

Due to the large incoherent cross section of H₂, the neutron diffraction data were collected on a deuterated-MOF5 sample, which was synthesized as described in detail in Ref.13. Because of the large cubic crystallite sizes obtained from the synthesis, we ground the sample in a helium-filled glovebox prior to neutron powder diffraction to eliminate the effects of preferred orientation. Figure 1 shows the diffraction data from the deuterated-MOF5 host lattice which was obtained on BT-1 at NIST. The pattern was taken over a period of 8 h with the 2.5 gram sample loaded into a vanadium cell at 3.5 K. The agreement between the data and refinement is excellent. We note that the neutron diffraction data allowed the determination of the hydrogen atom positions of the BDC linker, which were not previously observed.

Having characterized the MOF5 host lattice, we next studied the adsorption of hydrogen in MOF5 as a function of D₂ concentration per formula unit (i.e. 4Zn). The hydrogen loading was achieved by first filling a well-known dosing-volume to a target pressure and then ex-

FIG. 1: The neutron powder diffraction pattern (\(\lambda=2.08\) Å) of the deuterated-MOF5 host lattice at 3.5 K (dots) plus the Rietveld refinement (solid), using space group Fm̅3m and \(a=25.909\) Å, and difference plot (bottom). The inset shows the high-angle portion of the data along with the fractional atomic positions and thermal factors. The refinement was characterized by \(\chi^2=1.195\).
posing it to the MOF5 sample at 70K. The sample was then cooled down to 30K at which point the pressure decreased to a negligible value as the D$_2$ was adsorbed. Once the system was equilibrated at 30 K, the sample was further cooled down to 3.5 K before the measurements. The sample was loaded with the following concentrations; nD$_2$=4,8,14, 26, 34, and 46 D$_2$ per molecular formula (i.e. per 4Zn) [14]. We note that one D$_2$/4Zn corresponds to about 0.255-wt% hydrogen uptake. For the nD$_2$=46, the final pressure at 30 K was non-zero, and we briefly pumped the system to remove free D$_2$. None of the structural refinements of the deuterium loaded-samples showed any evidence for solid D$_2$, indicating that the deuterium was adsorbed onto the MOF5. This was further supported by the total amount of hydrogen obtained from the refinements as shown in Fig. 2(a). Apart from the last point where we had to remove unadsorbed deuterium gas, the target and refined values for the total amount of deuterium molecules adsorbed in MOF5 lattice are in very good agreement. It is quite interesting to note that at cryogenic temperatures, the MOF5 host structure actually has enough space to hold up to 10-wt% hydrogen. If we can find a way to engineer MOF5-H$_2$ interactions in these materials to hold the hydrogen molecules in the structure at ambient temperatures, one could easily store enough hydrogen for practical applications. Figure 2(b) shows that there is a small contraction of the lattice upon hydrogen loading. We attribute this to a small charge transfer ($\approx 0.1e$) to the hydrogen molecules which result in an attractive Madelung Coulomb energy. In the rest of this letter, we discuss where and how the hydrogen molecules are packed into the MOF5 structure as a function of D$_2$-loading.

Figure 3 shows the diffraction pattern from MOF5 which was loaded with 4D$_2$/4Zn. In order to locate the hydrogen adsorption sites, we first performed a Rietveld structural refinement using the model for the the MOF5 host structure, ignoring the adsorbed D$_2$ molecules. The difference-Fourier scattering-length density based upon this model, shown in the inset to Fig. 3, was then used to locate the adsorbed D$_2$ molecules. The Fourier plot clearly shows where the hydrogen molecules are adsorbed (red-yellow-green region). Isosurfaces of the three-dimensional difference-Fourier scattering-length density for a loading of 8D$_2$/4Zn are shown in Fig. 4(a). The first adsorption sites (blue) are the positions at the center of the three ZnO$_3$ triangular faces, which resemble a cup shape and were termed the "Cup-site". There are four such sites, forming a tetrahedral cluster (blue region in Fig. 4a). Having determined the location of the first-adsorption sites, we then further refined the structural model, explicitly including the D$_2$ molecules at the first adsorption site. The positions, isotropic-thermal factors, and fractional occupancies of the adsorbed D$_2$ molecules were refined. The deuterium molecules were treated as point scatterers with double occupancy. The final refinement for a deuterium loading of 4D$_2$/4Zn is shown in Fig. 3. The agreement between data and the fit is very good. For the 4D$_2$/4Zn loading, we also observed a small amount of D$_2$ (i.e. 10% ) adsorbed at a secondary adsorption sites (green isosurface in Fig. 4(a)). For 8D$_2$/4Zn loading, these two adsorption sites are almost fully occupied[12]. Unlike the cup-sites, the second adsorption sites are on top of a single ZnO$_3$ triangles and were hence denoted as the "ZnO$_3$-site". These sites also form a tetrahedron about the metal-oxide cluster. We observed that with further hydrogen loading (i.e. 14 and 26 D$_2$/4Zn), there are two additional adsorption sites which start to populate in almost equal proportion. These sites are shown in Fig. 4(b) as light-blue and brown spheres. The adsorption sites just above the two oxygen ions are called the "ZnO$_2$-site" (see Fig. 4(b)). The fourth adsorption site is basically the top of the hexagonal linkers, which we termed the "Hex-site". The refined

**FIG. 2:** (a)The target versus refined values for the hydrogen loading of MOF5 host lattice. (b) The lattice parameter as a function of hydrogen loading.

**FIG. 3:** The neutron powder diffraction pattern ($\lambda = 2.08A$) of the MOF5-4D$_2$ at 3.5 K (dots) plus the Rietveld refinement (solid) with space group Fm3m and a=25.9097 Å, and difference plot (bottom). The inset shows the real-space Fourier-difference scattering-length density superimposed with the MOF5 structure, indicating the location of cup-sites for the first hydrogen adsorption (red-yellow-green region). The refinement was characterized by $\chi^2=2.736$ and R$_{wp}=5.54\%$. 

\[ \text{Number of } \text{D}_2/4\text{Zn (target)} \]
The calculated binding energies for the "Hex-site" and most energetically stable, followed by the "ZnO$_2$-site". The binding energies are in good agreement within 0.5 meV/atom.

340 eV was found to be enough for total energies to converge, which contains 106 atoms$^{[14]}$. A cutoff energy of 106 eV was found to be enough for total energies to converge; indicating some disorder. However, with increasing the hydrogen loading to 46 D$_2$/4Zn, we observed that the cubic cage is destabilized with respect to the more occupied sites when H$_2$ molecule is parallel and perpendicular to the 3-fold axis near the adsorption sites.

Fractional positions of these four sites are summarized in Fig. 4. At 26 D$_2$/4Zn loading, structural refinement indicates that these four adsorption sites are almost totally occupied$^{[13]}$, yielding 6.63-wt% deuterium uptake.

It is important to know if the adsorption sites reported above make sense in terms of hydrogen host-lattice interactions and energetics. Hence, we have also performed total energy calculations from density functional theory (DFT). The calculations were performed within the plane-wave implementation$^{[15]}$ of the local-density approximation (LDA) to DFT. We used Vanderbilt ultrasoft pseudopotentials$^{[16]}$. We relax only the hydrogen molecules inside the primitive cell of the MOF5 structure, which contains 106 atoms$^{[14]}$. A cutoff energy of 340 eV was found to be enough for total energies to converge within 0.5 meV/atom.

The energies of the four adsorption sites are summarized in Table 1 for two different orientation of the hydrogen molecule. The binding energies are in good agreement with the experimental finding the "Cup-site" is the most energetically stable, followed by the "ZnO$_3$-site". The calculated binding energies for the "Hex-site" and "ZnO$_2$-site" are quite close each other, in agreement with the equal population of these sites observed experimentally. Finally, we also point out that the "Hex-site" and "ZnO$_2$-site" are further stabilized by the intermolecular interactions amongst the adsorbed deuterium molecules. For example, each "ZnO$_3$-site" is surrounded by three "ZnO$_2$-site" due to local 3-fold symmetry. Upon initial hydrogen loading, the molecules first go to the biggest cavities, namely the "cup-site" and the corner sites (i.e. "ZnO$_3$-site"). After that, each hydrogen molecules is surrounded by three hydrogen molecules (of the "ZnO$_2$-site" and "Hex-site"). In this way, the packing of the hydrogen molecules are optimized due to both H$_2$-ZnO-cluster interaction and the H$_2$-H$_2$ interactions. Finally, we note that the adsorption energy of the first three sites show significant anisotropy (about 30 meV) with respect to the orientation of the H$_2$ molecule. Therefore we expect significant splitting of the ortho-para transition for the hydrogen molecule at the "Hex-site". These results seem to be consistent with the available inelastic neutron data on H$_2$ in MOF5$^{[5,17]}$. We also observe that the exact location of the H$_2$ molecule at the adsorption sites depends on the H$_2$ orientation within 0.2 Å , suggesting that a proper treatment of translation-rotation coupling of the H$_2$ quantum dynamics is required to explain the inelastic neutron data$^{[17]}$.

So far we have discussed hydrogen loading up to 26 D$_2$/4Zn, at which point the adsorption sites discussed above are almost fully occupied. Figure 5 shows the neutron powder diffraction patterns and Rietveld structural refinements at two more deuterium loadings of 34 and 46 D$_2$/4Zn, indicating that MOF5 structure is capable of adsorbing more hydrogens. The difference Fourier analysis indicated that at these high-coverages, hydroge molecules form quite interesting nano-cages in the cubic-cavities of the MOF5 structure as shown in Fig. 6. The first two hydrogen positions listed in Fig. 5 generate the cubic and almost spherical D$_2$ nano-cages shown in Fig. 6(a) and (b), respectively. Due to the hydrogen atoms on the organic linker, the cubic nanocage shown in Fig. 6(a) is slightly bent along the edges. For 34 D$_2$/4Zn loading, these two cage structures have about equal population; indicating some disorder.

| Adsorption Site | $\Delta E_{\text{par}}$ (eV) | $\Delta E_{\text{perp}}$ (eV) |
|-----------------|---------------------|---------------------|
| Cup-site        | 0.133               | 0.160               |
| ZnO$_3$-site    | 0.086               | 0.115               |
| ZnO$_2$-site    | 0.056               | 0.108               |
| Hex-site        | 0.092               | 0.106               |

TABLE I: The calculated binding energies for four-adsorption sites when H$_2$ molecule is parallel and perpendicular to the 3-fold axis near the adsorption sites.

FIG. 4: The hydrogen absorption sites obtained from difference Fourier analysis. Top: The first (blue) and second (green) absorption sites, respectively. Bottom: A view along the 3-fold axis, showing the four absorption sites together. In addition to the first two absorption sites (blue and green), ZnO$_2$ (brown) and Hex-sites (light-blue) are shown.
symmetric and exotic looking cage shown in Fig. 6(b). The intermolecular distances in these nano-cages are on the order of 3.0 Å, much shorter than those found in solid H₂[10,11]. At the maximum coverage of 46D₂/4Zn, we also determined three additional hydrogen sites which are listed in Fig. 5. These hydrogens basically sit on the top of the square faces of the nano-cage shown in Fig. 6(b), creating quite remarkable 3D interlinked nano-cage structures. These results suggest that the MOF host lattices may be used as a template to build new artificial hydrogen nano-structures, which could have quite interesting properties due to the quantum nature of the molecules, confinement effects, and small intermolecular distances. The structure of solid hydrogen under very high-pressures has been a focus of intense research for a long time due to theoretical predictions for metallic behavior[12]. Hence, we hope that our initial results for the high-concentration hydrogen loading will give a different perspective and direction to this important field of research[11, 12]. We note that due to the construction of the vanadium sample holder used in this study, we were not able to apply high pressures to load the MOF5 sample with even more hydrogen molecules. The fractional occupancies listed in Fig. 5 indicates that it should be possible to insert more hydrogen molecules into the structure. We hope to perform such high-pressure studies in the near future.

In conclusion, using Rietveld structural refinement of neutron powder diffraction data in conjunction with difference-Fourier analysis and first-principles calculations, we have determined the hydrogen adsorption sites and binding energies in MOF5. We have also discovered that hydrogen molecules form unique 3D interlinked nano-cages at high-concentrations of hydrogen loading. Surprisingly, we find that MOF host lattice has enough space to hold hydrogen molecules up to 10-wt% at low temperatures. This implies that by using different organic linkers, which make hydrogen desorption difficult by narrowing the channels connecting the network of nan-pores in MOF, one may be able to engineer these materials for practical hydrogen storage at ambient conditions. These results not only hold the key to optimizing MOF materials for hydrogen storage applications but also suggest that MOFs can be used as templates to create artificial interlinked hydrogen nano-cages with novel properties.

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