

Direct Observation of Hydrogen Adsorption Sites and Nanocage Formation in Metal-Organic Frameworks

T. Yildirim and M. R. Hartman

NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

(Received 8 July 2005; published 16 November 2005)

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 nanoclusters with intermolecular distances as small as 3.0 Å and H₂ uptake as high as 11 wt%. These results hold the key to optimizing metal-organic framework (MOF) materials for hydrogen storage applications and also suggest that MOFs can be used as templates to create artificial interlinked hydrogen nanocages with novel properties.

DOI: 10.1103/PhysRevLett.95.215504

PACS numbers: 61.66.-f, 61.12.-q, 68.43.Bc, 68.43.Fg

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 [1,2]. Metal-organic framework (MOF) compounds, which consist of metal-oxide clusters connected by organic linkers, are a relatively new class of nanoporous material that show promise for hydrogen storage applications because of their tunable pore size and functionality [3–9]. 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 enough space available to hold many hydrogen molecules, up to 11 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 three-dimensional (3D) networks of H₂ nanoclusters with intermolecular distances of 3.0 Å, which is significantly shorter than the intermolecular distances of 3.6 Å in pure solid hydrogen [10,11]. These findings suggest that MOF materials can also be used as templates to create artificial, interlinked hydrogen nanocages. Such materials could exhibit very unexpected properties due to confinement effects and small intermolecular separation, such as metallic behavior [12].

Because of 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 glove box 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 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) [14]. The hydrogen loading was achieved by first filling a well-known dosing volume to a target pressure and then exposing it to the MOF5 sample at 70 K. The sample was

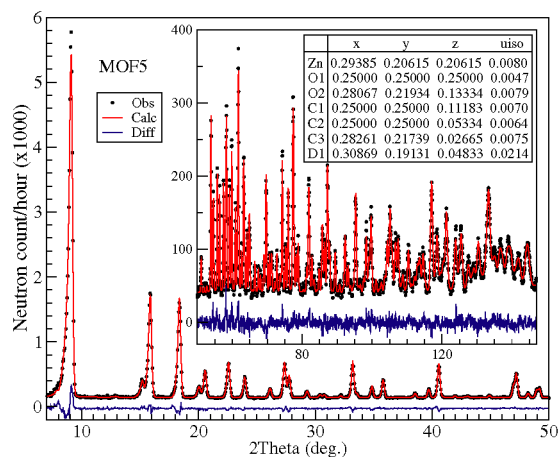


FIG. 1 (color online). The neutron powder diffraction pattern ($\lambda = 2.08$ Å) of the deuterated-MOF5 host lattice at 3.5 K (dots) plus the Rietveld refinement (solid line), using space group $Fm\bar{3}m$ and $a = 25.909$ Å, and difference plot (bottom). The inset shows the high-angle portion of the data along with the fractional atomic positions and thermal factors. The refinement was characterized by $\chi^2 = 1.195$.

then cooled down to 30 K 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 $H_2/4Zn$ corresponds to about 0.26 wt % hydrogen uptake. For the $nD_2 = 46$, the final pressure at 30 K was nonzero, 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 lattice actually has enough space to hold up to 11 wt % hydrogen. 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 results 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 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. 4(a)]. Having

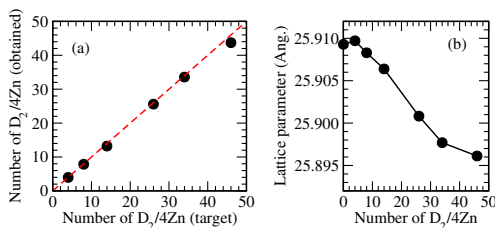


FIG. 2 (color online). (a) The target versus refined values for the hydrogen loading of MOF5 host lattice. (b) The lattice parameter as a function of hydrogen loading.

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 [13]. Unlike the cup sites, the second adsorption sites are on top of 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 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 6.8 wt % H_2 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

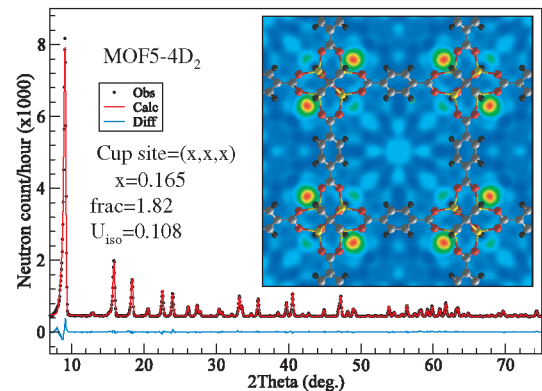


FIG. 3 (color). The neutron powder diffraction pattern ($\lambda = 2.08 \text{ \AA}$) of the MOF5- $4D_2$ at 3.5 K (dots) plus the Rietveld refinement (solid line) with space group $Fm\bar{3}m$ and $a = 25.9097 \text{ \AA}$, and difference plot (bottom). The inset shows the real-space Fourier-difference 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 $R_{wp} = 5.54\%$.

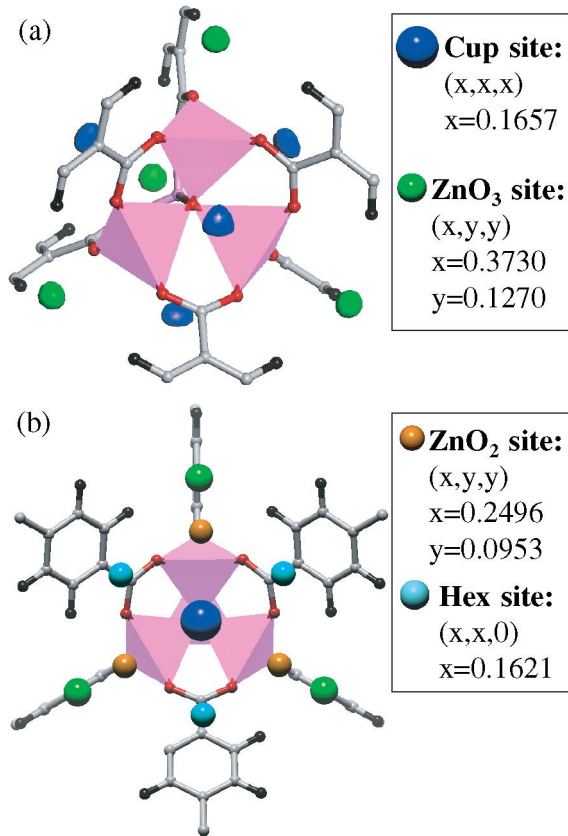


FIG. 4 (color). The hydrogen absorption sites obtained from difference-Fourier analysis. Top: The first (blue) and second (green) absorption sites, respectively. Bottom: A view along the threefold axis, showing the four absorption sites together. In addition to the first two absorption sites (blue and green), ZnO₂ (brown) and hex sites (light blue) are shown.

plane-wave implementation [15] of the local-density approximation to DFT. We used Vanderbilt ultrasoft pseudo-potentials [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 I for two different orientation of the hydrogen molecule. The binding energies are in good agreement with the experimental finding that the cup site is the most energetically stable, followed by the ZnO₃ site. The calculated binding energies for the hex site and ZnO₂ site are

TABLE I. The calculated binding energies for four-adsorption sites when the H₂ molecule is parallel and perpendicular to the threefold axis near the adsorption sites.

Cup site	$\Delta E_{\text{par}} = 0.133$ eV	$\Delta E_{\text{perp}} = 0.160$ eV
ZnO ₃ site	$\Delta E_{\text{par}} = 0.086$ eV	$\Delta E_{\text{perp}} = 0.115$ eV
ZnO ₂ site	$\Delta E_{\text{par}} = 0.056$ eV	$\Delta E_{\text{perp}} = 0.108$ eV
Hex site	$\Delta E_{\text{par}} = 0.092$ eV	$\Delta E_{\text{perp}} = 0.106$ eV

quite close to each other, in agreement with the equal population of these sites observed experimentally. Finally, we also point out that the hex site and ZnO₂ site are further stabilized by the intermolecular interactions amongst the adsorbed hydrogen molecules. For example, each ZnO₃ site is surrounded by three ZnO₂ sites due to local threefold symmetry, so that the packing of the hydrogen molecules are optimized due to both H₂-ZnO-cluster interaction and the H₂-H₂ interactions. Finally, we note that the adsorption energy of the first three sites shows significant anisotropy (about 30 meV) with respect to the orientation of the H₂ molecule. Therefore we expect significant splitting of the ortho-para transitions for H₂ molecules adsorbed at these three sites with a more isotropic transition for the hydrogen molecule at the hex site. These results seem to be consistent with the available inelastic neutron data on H₂ in MOF5 [5,17].

So far we have discussed hydrogen loading up to 26 D₂/4Zn, 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 D₂/4Zn, indicating that MOF5 structure is capable of adsorbing more hydrogens. The difference-Fourier analysis indicated that at these high coverages, hydrogen molecules form quite interesting nanocages 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 D₂ nanocages shown in Fig. 6(a) and 6(b), respectively. Because of the hydrogen atoms on the organic linker, the cubic nanocage shown in Fig. 6(a) is slightly bent along the edges. For 34 D₂/4Zn loading, these two cage structures have about equal population; indicating some disorder. However, with increasing the hydrogen loading to 46 D₂/4Zn, we observed that the cubic cage is destabilized with respect to the more symmetric and exotic

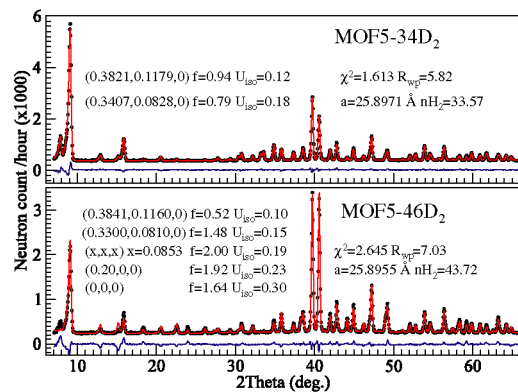


FIG. 5 (color online). The neutron powder diffraction patterns (dots), Rietveld refinements (solid line), and the difference plots (noisy line) for high-concentration hydrogen loading, $n = 34$ and $n = 46$ D₂/4Zn, respectively. In addition to the four-adsorption sites shown in Fig. 4, additional hydrogen sites, occupancies, and thermal factors are also given.

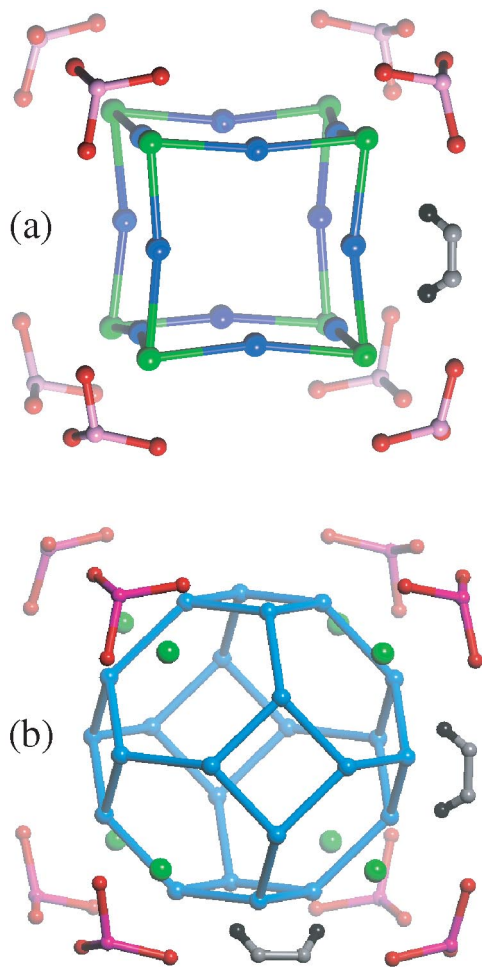


FIG. 6 (color). Two different hydrogen nanocages (blue and green spheres) obtained from Rietveld refinements at 34 and 46 $D_2/4Zn$ loading, respectively. For clarity, only some of the ZnO_3 (red-pink) and CH bonds (gray-black) are also shown.

looking cage shown in Fig. 6(b). The intermolecular distances in these nanocages are on the order of 3.0 Å, much shorter than those found in solid H_2 [10,11]. At the maximum coverage of 46 $D_2/4Zn$, 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 nanocage shown in Fig. 6(b), creating quite remarkable 3D interlinked nanocage structures. These results suggest that the MOF host lattices may be used as a template to build new artificial hydrogen nanostructures, 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].

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 nanocages at high concentrations of hydrogen loading. Surprisingly, we find that the MOF host lattice has enough space to hold hydrogen molecules up to 11 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 nanopores 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 nanocages with novel properties.

We thank B. H. Toby and Q. Huang for assistance with BT-1 and J. Eckert, J. Rowsell, and D. A. Neumann for useful discussions. This work was partially supported by DOE within the Center of Excellence on Carbon-based Hydrogen Storage Materials.

-
- [1] See the special issue *Towards a Hydrogen Economy*, by R. Coontz and B. Hanson [Science **305**, 957 (2004)].
 - [2] A. Zuttel, *Materials Today* **6**, 24 (2003).
 - [3] M. Eddaoudi *et al.*, *Science* **295**, 469 (2002).
 - [4] O. M. Yaghi *et al.*, *Nature (London)* **423**, 705 (2003).
 - [5] N. L. Rosi, *et al.*, *Science* **300**, 1127 (2003); please note that the hydrogen isotherm reported in this paper is not correct, see J. L. C. Rowsell, A. R. Millward, K. Sung Park, and O. M. Yaghi, *J. Am. Chem. Soc.* **126**, 5666 (2004).
 - [6] X. Zhao *et al.*, *Science* **306**, 1012 (2004).
 - [7] N. W. Ockwing, O. D. Friedrichs, M. O'Keeffe, and O. M. Yaghi, *Acc. Chem. Res.* **38**, 176 (2005).
 - [8] Q. Yang and C. Zhong, *J. Phys. Chem. B* **109**, 11 862 (2005).
 - [9] R. Kitaura *et al.*, *Science* **298**, 2358 (2002).
 - [10] J. van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).
 - [11] R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.* **61**, 857 (1988).
 - [12] D. E. Ramaker, L. Kumar, and F. E. Harris, *Phys. Rev. Lett.* **34**, 812 (1975).
 - [13] The details of sample synthesis, the Rietveld refinements, powder patterns, etc., can be found at <http://www.ncnr.nist.gov/staff/taner/h2>.
 - [14] The unit formula for MOF5 is $Zn_4O_{13} - (C_8H_4)_3$. The conventional unit cell (Fm $\bar{3}$ m) has eight of these formulas.
 - [15] M. C. Payne *et al.*, *Rev. Mod. Phys.* **64**, 1045 (1992).
 - [16] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
 - [17] M. R. Hartman, T. Yildirim, T. J. Udovic, C. M. Brown (to be published).