4. J. D. Termine, E. D. Eanes, D. J. Greenfield, M. U. Nylen, R. A. Harper, *Calcif. Tissue Res.* **12**, 73 (1973).
5. B. B. Tomazic, W. E. Brown, E. D. Eanes, *J. Biomed. Mater. Res.* **27**, 217 (1993).
6. H.-M. Kim, C. Rey, M. J. Glimcher, *J. Bone Miner. Res.* **10**, 1589 (1995).
7. C. Ramanathan, J. L. Ackerman, *Magn. Reson. Med.* **41**, 1214 (1999).
8. Y. Wu *et al.*, *J. Bone Miner. Res.* **17**, 472 (2002).
9. E. E. Berry, *J. Inorg. Nucl. Chem.* **29**, 317 (1967).
10. R. M. Biltz, E. D. Pellegrino, *Calcif. Tissue Res.* **7**, 259 (1971).
11. J. D. Termine, D. R. Lundy, *Calcif. Tissue Res.* **13**, 73 (1973).
12. N. C. Blumenthal, A. S. Posner, *Calcif. Tissue Res.* **13**, 235 (1973).
13. C. Rey, J. L. Miquel, L. Facchini, A. P. Legrand, M. J. Glimcher, *Bone* **16**, 583 (1995).
14. C.-K. Loong *et al.*, *Bone* **26**, 599 (2000).
15. W. P. Rothwell, J. S. Waugh, J. P. Yesinowski, *J. Am. Chem. Soc.* **102**, 2637 (1980).
16. W. P. Aue, A. H. Roufosse, M. J. Glimcher, R. G. Griffin, *Biochemistry* **23**, 6110 (1984).
17. J. Arends *et al.*, *J. Cryst. Growth* **84**, 515 (1987).
18. K. Beshah, C. Rey, M. J. Glimcher, M. Shimizu, R. G. Griffin, *J. Solid State Chem.* **84**, 71 (1990).
19. Y. Wu, M. J. Glimcher, C. Rey, J. L. Ackerman, *J. Mol. Biol.* **244**, 423 (1994).
20. Y. Wu *et al.*, *Calcif. Tissue Int.*, in press.
21. J. P. Yesinowski, H. Eckert, *J. Am. Chem. Soc.* **109**, 6274 (1987).
22. R. A. Santos, R. A. Wind, C. E. Bronnimann, *J. Magn. Reson. B* **105**, 183 (1994).
23. See supporting data on *Science* Online.
24. S. Schwarzinger, G. J. Kroon, T. R. Foss, P. E. Wright, H. J. Dyson, *J. Biomol. NMR* **18**, 43 (2000).

25. We thank J. P. Yesinowski, M. J. Glimcher, P. V. Hauschka, and C. E. Bronnimann for insightful discussions, and R. Millea for assistance with procurement of the human bone specimens. A. Bielecki and D. Rice obtained preliminary demonstration spectra of test specimens. Supported by NIH grants AR42258 (National Institute of Arthritis, Musculoskeletal, and Skin Disorders) and RR03264 (Division of Research Resources).

Supporting Online Material

www.sciencemag.org/cgi/content/full/300/5622/1123/DC1

Materials and Methods

Figs. S1 and S2

16 September 2002; accepted 11 April 2003

Hydrogen Storage in Microporous Metal-Organic Frameworks

Nathaniel L. Rosi,[1] Juergen Eckert,[2,3] Mohamed Eddaoudi,[4] David T. Vodak,[1] Jaheon Kim,[1] Michael O'Keeffe,[5] Omar M. Yaghi[1]*

Metal-organic framework-5 (MOF-5) of composition $Zn_4O(BDC)_3$ (BDC = 1,4-benzenedicarboxylate) with a cubic three-dimensional extended porous structure adsorbed hydrogen up to 4.5 weight percent (17.2 hydrogen molecules per formula unit) at 78 kelvin and 1.0 weight percent at room temperature and pressure of 20 bar. Inelastic neutron scattering spectroscopy of the rotational transitions of the adsorbed hydrogen molecules indicates the presence of two well-defined binding sites (termed I and II), which we associate with hydrogen binding to zinc and the BDC linker, respectively. Preliminary studies on topologically similar isoreticular metal-organic framework-6 and -8 (IRMOF-6 and -8) having cyclobutylbenzene and naphthalene linkers, respectively, gave approximately double and quadruple (2.0 weight percent) the uptake found for MOF-5 at room temperature and 10 bar.

The development of hydrogen-fueled vehicles and portable electronics will require new materials that can store large amounts of hydrogen at ambient temperature and relatively low pressures with small volume, low weight, and fast kinetics for recharging (*1*, *2*). A design target for automobile fueling has been set by the U.S. Department of Energy at 6.5% hydrogen by weight.

Metal hydride systems have been intensely examined in this respect (*3*), but there are many problems associated with their use, including cost, low specific uptake by weight, unfavorable kinetics requiring heating cycles, and susceptibility to contamination by impurities. Various carbon-based adsorbents (e.g., porous carbon, intercalated graphite, and nanotubes) have also been studied and, while promising, have been beset by mixed results (*4*, *5*). For these materials, it has been difficult both to systematically engineer their molecular structure and to identify specific hydrogen binding sites. Here we report very favorable hydrogen sorption properties obtained at 78 K or ambient temperature under safe pressures (up to 20 bar) with crystalline metal-organic frameworks (MOFs) (*6*) having cubic cavities of uniform size and internal

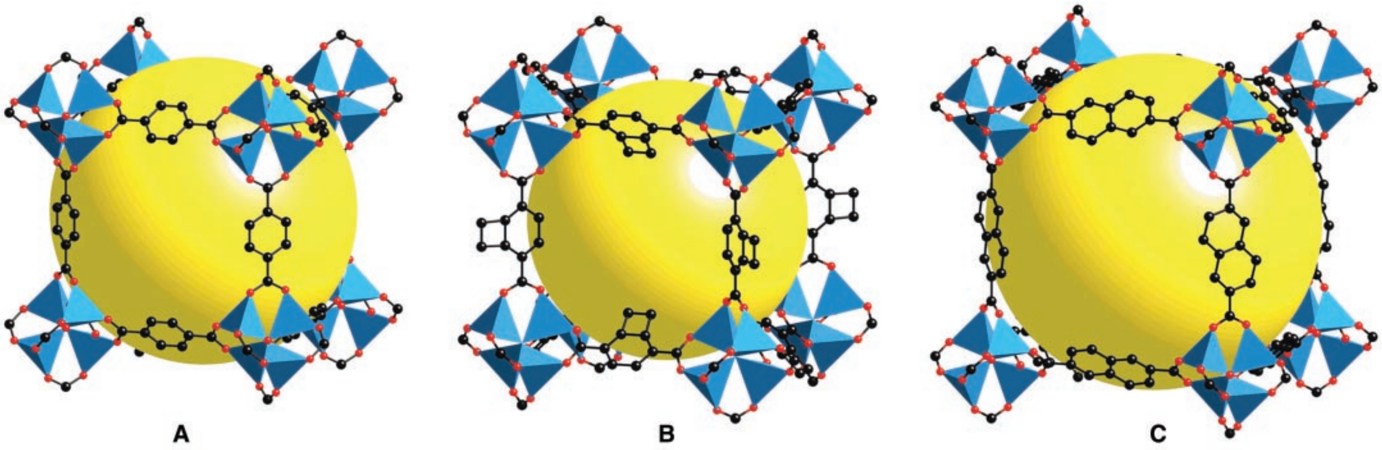

Fig. 1. Single-crystal x-ray structures of MOF-5 (**A**), IRMOF-6 (**B**), and IRMOF-8 (**C**) illustrated for a single cube fragment of their respective cubic three-dimensional extended structure. On each of the corners is a cluster $[OZn_4(CO_2)_6]$ of an oxygen-centered Zn_4 tetrahedron that is bridged by six carboxylates of an organic linker (Zn, blue polyhedron; O, red spheres; C, black spheres). The large yellow spheres represent the largest sphere that would fit in the cavities without touching the van der Waals atoms of the frameworks. Hydrogen atoms have been omitted.

---

[1]Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA. [2]Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA. [3]Los Alamos Neutron Science Center, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. [4]Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, SCA 400, Tampa, FL 33620–5250, USA. [5]Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA.

*To whom correspondence should be addressed. E-mail: oyaghi@umich.edu

structure. Inelastic neutron scattering (INS) spectroscopy has allowed us to identify the hydrogen binding sites.

We focused on MOF-5 (Fig. 1A) (*7*), in which inorganic $[OZn_4]^{6+}$ groups are joined to an octahedral array of $[O_2C\text{-}C_6H_4\text{-}CO_2]^{2-}$ (1,4-benzenedicarboxylate, BDC) groups to form a robust and highly porous cubic framework. The MOF-5 structure motif and related compounds (*8*) provide ideal platforms on which to adsorb gases, because the linkers are isolated from each other and accessible from all sides to sorbate molecules. The scaffolding-like nature of MOF-5 and its derivatives leads to extraordinarily high apparent surface areas (2500 to 3000 m^2g^{-1}) for these structures. On a practical level, the preparation of MOFs is simple, inexpensive, and of high yield. For example, the formation reaction for MOF-5 is $4Zn^{2+} + 3H_2BDC + 8OH^- \rightarrow Zn_4O(BDC)_3 + 7H_2O$. The MOF family also has high thermal stability (300° to 400°C).

We have recently shown that MOF-5 and isoreticular metal-organic framework-6 (IRMOF-6) (Fig. 1B) outperform other materials in methane adsorption at ambient temperature (*8*). Thus, we sought to determine their capacity for hydrogen storage, beginning with MOF-5 as an important representative of this set.

We measured hydrogen gas uptake by MOF-5 at 78 K by introducing small amounts of H_2 into a chamber containing the guest-free form of the material and monitoring the weight change as a function of increasing doses of H_2 (*9*). The measured sorption isotherm shows a type I behavior (*10*), in which the saturation is reached at low pressures followed by a pseudoplateau at higher pressure of H_2 with a maximum uptake of 45 mg of H_2 per gram of MOF-5 [4.5 weight % = 17.2 H_2 per $Zn_4O(BDC)_3$ formula unit] (Fig. 2A). The observed sharp uptake of H_2 at lower pressure indicates favorable sorption interactions between the MOF-5 framework and H_2 molecules. We note that, similar to the reversible sorption of gases and organic vapors (N_2, Ar, CO_2, $CHCl_3$, CCl_4, C_6H_6, and C_6H_{12}) in MOF-5 (*7*, *11*), adsorbed H_2 molecules can also be reversibly desorbed from the pores by reducing pressure.

We next evaluated the H_2 sorption in conditions that mimic a typical application environment, namely, room temperature and pressures considered safe for mobile fueling. A different sorption apparatus was constructed, in which a 10-g sample of guest-free MOF-5 was charged with H_2 up to 20 bar and the weight change monitored as a function of H_2 uptake and release (*9*). MOF-5 showed substantial H_2 uptake that increased linearly with pressure, giving 1.0 weight % at 20 bar (Fig. 2B). These findings demonstrate the potential of MOFs for H_2 storage applications. The isotherm at ambient temperature is expected to be approximately linear as observed because the material is noticeably undersaturated with H_2 in the pressure range explored and, in principle, at higher pressures can take up more H_2, up to at least the amount observed at 78 K (compare Fig. 2, A and B) (*10*).

To understand the H_2 sorption properties of MOF-5 and hence to potentially control the characteristics of H_2 binding, we carried out INS spectroscopy of the rotational transitions of the adsorbed hydrogen molecules. Neutrons are scattered inelastically far more strongly by hydrogen than by any other element, which facilitates the observation of rotational tunnel splitting of the librational ground state of the H_2 molecule (*12*). This splitting is akin to the ortho-para transition for free H_2, and this mode is forbidden in optical spectroscopy (*13*). This splitting is an extremely sensitive measure of the rotational potential-energy surface, a feature that has made it possible to determine fine details of hydrogen adsorption by INS in a wide variety of materials, including zeolites (*14–18*), nanoporous nickel phosphate VSB-5 (*19*), and carbon nanotubes (*20*, *21*).

The INS spectra for MOF-5 are shown in Fig. 3 for three levels of H_2 loadings corresponding to 4, 8, and 24 H_2 per formula unit (*9*). First, the observed peaks are much sharper than those found for H_2 in zeolites, VSB-5, and carbon materials. Thus, the adsorption sites for H_2 in MOF-5 are well defined compared with those in zeolites (*3*, *4*), in which the molecule has a variety of binding sites available that are close in energy. Second, the richness of the spectrum immediately leads us to conclude that more than one type of binding site is present in MOF-5 even though rotational transitions other than 0-1 can be observed (*22*). Some progress in assigning peaks can be made with the use of a model for the rotational potential. For reasons of simplicity, we use the energy eigenvalues for the rotations of H_2 with two angular degrees of freedom in a double-minimum potential. Thus, we can assign the peaks at 10.3 and 12.1 meV to the 0-1 transitions for the two sites, which we subsequently refer to as I and II, and we assign the remaining peaks to the 0-2 and 1-2 transitions (*22*). These assignments are verified by comparison with the INS spectrum of 4 D_2 molecules per formula unit and scaling the rotational energy level diagram by the respective rotational constants of H_2 and D_2. The rotational barriers associated with sites I and II are found to be 0.40 and 0.24 kcal mol^{-1}, respectively.

We can make some inferences about the nature of the binding sites from our study of the dependence of the INS spectra on H_2 loading. As the average loading is increased from 4 to 8 H_2 per formula unit, the intensity of the 12.1-meV band (site II) roughly doubles, whereas that of the 10.3-meV band (site I) remains constant. We associate site I with Zn and site II with the BDC linkers. Further increases in loading (24 H_2 per formula unit) (Fig. 3, bottom panel) show that the line at 12.1 meV splits into four lines, and therefore we associate four slightly different sites with the BDC linker. This result suggests that further increases in the sorption capacity for these types of materials could be achieved by the use of larger linkers. Indeed, we observed a small peak near 14.5 meV at this high loading corresponding to a small amount of solid H_2 (for which the 0-1 transition occurs essentially at the free rotor value of 14.7 meV), indicative of saturation coverage in MOF-5. As noted above, our 78 K sorption data suggest that 17.2 H_2 per formula unit is close to saturation.

The barrier to rotation for the binding site near Zn is somewhat greater than those on the BDC, as one might expect, but also slightly lower than that for the extra-framework Zn^{2+} cation in ZnNaA zeolite, for which the rotational transition was observed at ~8 meV (*23*). Various factors could contribute to this difference, including different degrees of accessibility of the Zn and the strong electrostatic field in the zeolite supercage. The barriers found for MOF-5 are noticeably higher (0.40 and 0.24 kcal mol^{-1}) than those found in carbons, including single-walled nanotubes (*20*), in which it is ~0.025 kcal mol^{-1}. Moreover, the rotational band in that case has a width of nearly 2.5 meV compared with 0.5 meV in our case. This value corroborates the much lower mobility (and hence stronger in-

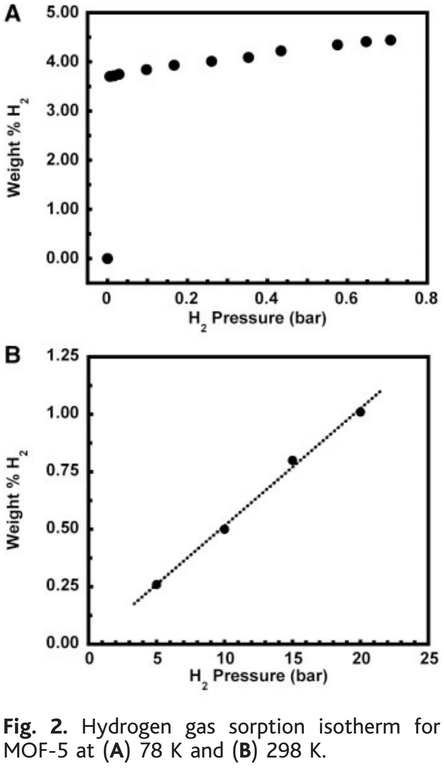

Fig. 2. Hydrogen gas sorption isotherm for MOF-5 at (**A**) 78 K and (**B**) 298 K.

teraction) for H_2 in MOF-5 than in carbons.

Our INS results for hydrogen in MOF-5 point to the importance of the organic linkers in determining H_2 uptake levels. Accordingly, using the same experimental setup and details outlined above for the room-temperature measurements on MOF-5 (*9*), we examined H_2 sorption in IRMOF-6 and IRMOF-8 (Fig. 1, B and C). Here we found that the specific H_2 uptake is approximately doubled and quadrupled, respectively, for IRMOF-6 and -8 relative to that found for MOF-5 at the same (room) temperature and pressure (10 bar). Specifically, for IRMOF-8, the H_2 uptake under those conditions is 20 mg of H_2 per gram (2.0 weight %)—a capacity well above those found for "active" carbon (0.1 weight %) (CECA, France) and "graphitic" carbon (0.3 weight %) (BASF, Germany, proprietary).

The percent uptake found for MOF-5, IRMOF-6, and IRMOF-8 at room temperature and 10 bar is equivalent to ~1.9, 4.2, and 9.1 H_2 per formula unit, respectively. These capacities are well below the saturation level as determined at 78 K for MOF-5 (17.2 H_2 per formula unit), which points to the potential for higher uptake at ambient temperature and higher pressures. The capacity of these structures for hydrogen at room temperature is comparable to the highest capacity achieved for carbon nanotubes at cryogenic temperatures, although the capacity of those materials is very sensitive to preparation conditions and appears to saturate at lower pressures (*24*). We anticipate that further increases in performance can be expected, with new IRMOFs having similar but larger organic linkers.

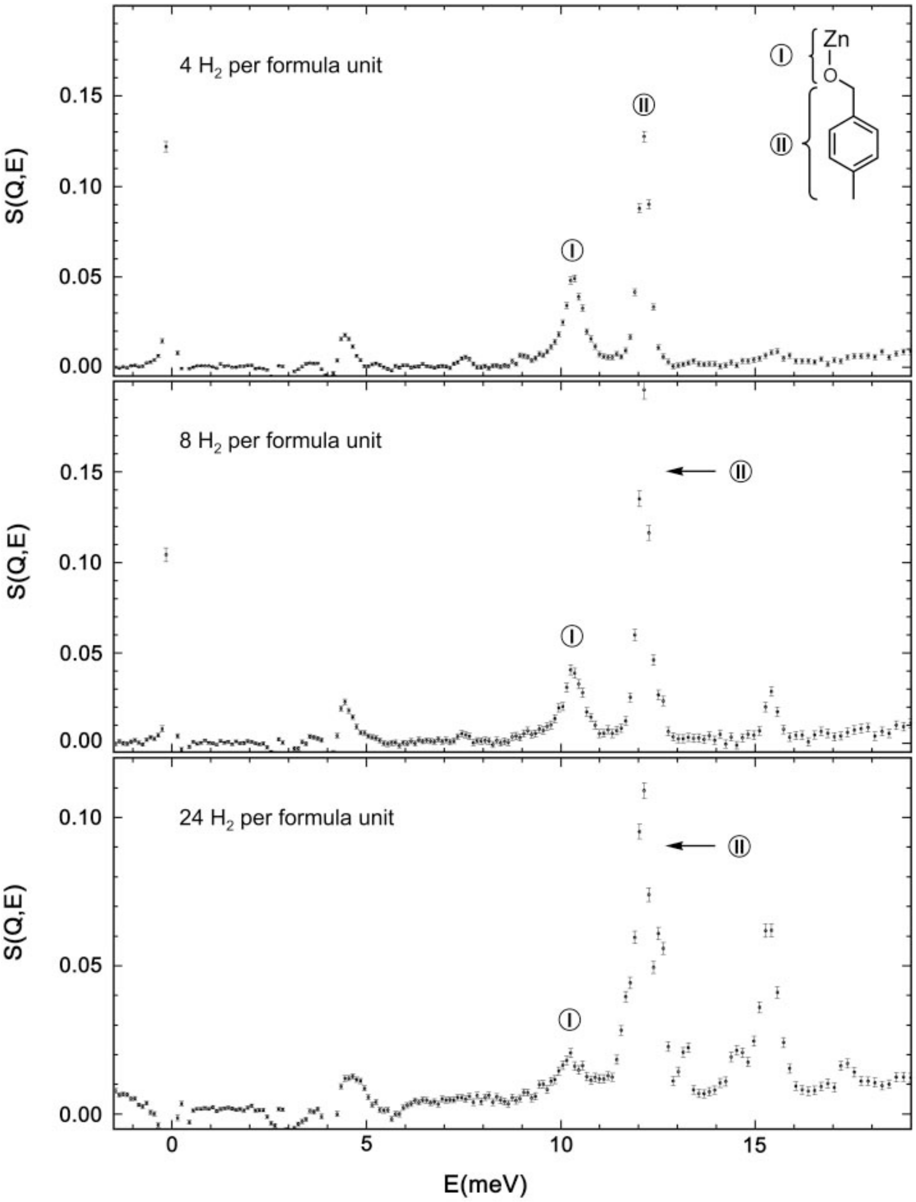

Fig. 3. INS spectra ($T = 10$ K) for hydrogen adsorbed in MOF-5 with loadings of 4 H_2 (**top**), 8 H_2 (**middle**), and 24 H_2 (**bottom**) per formula unit $[Zn_4O(BDC)_3]$ obtained on the QENS spectrometer at IPNS, Argonne National Laboratory. The spectrum of the guest-free (blank) MOF-5 sample was subtracted in each case. The very slight oversubtraction near 4 meV arises from a peak in that region of the blank sample, which cannot be removed by heating under vacuum. Assignments are based on the use of a model potential and observed isotope shifts from a spectrum of D_2 in MOF-5. Peaks at 10.3 and 12.1 meV are assigned to the 0-1 transitions for the two principal binding sites (I and II, labeled on the spectra). Other tentative assignments are 4.4 meV (1-2, site II), 15.5 meV (0-2, site II), 7.5 meV (1-2, site I), 17.5 meV (0-2, site I), and 14.5 meV (solid H_2). The regions of MOF-5 corresponding to sites I and II are shown schematically in the top right corner.

References and Notes

1. G. D. Berry, S. M. Aceves, *Energy & Fuels* **12**, 49 (1998).
2. Alliance of Automobile Manufacturers, www.autoalliance.org/fuel_cells.htm.
3. L. Schlapbach, A. Züttel, *Nature* **414**, 353 (2001).
4. R. Dagani, *Chem. Eng. News* **80**, 25 (14 January 2002).
5. G. E. Froudakis, *J. Phys. Condens. Matter* **14**, R453 (2002).
6. M. Eddaoudi *et al.*, *Acc. Chem. Res.* **34**, 319 (2001).
7. H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **402**, 276 (1999).
8. M. Eddaoudi *et al.*, *Science* **295**, 469 (2002).
9. Details of the H_2 uptake and INS experiments are available as supporting material on *Science* Online.
10. S. J. Gregg, K. S. W. Sing, *Adsorption, Surface Area, Porosity* (Academic Press, London, ed. 2, 1982).
11. M. Eddaoudi, H. Li, O.M. Yaghi, *J. Am. Chem. Soc.* **122**,1391 (2000).
12. J. Eckert, G. J. Kubas, *J. Phys. Chem.* **97**, 2378 (1993).
13. I. F. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).
14. J. Eckert, J. M. Nicol, J. Howard, F. R. Trouw, *J. Phys. Chem.* **100**, 10646 (1996).
15. J. M. Nicol, J. Eckert, J. Howard, *J. Phys. Chem.* **92**, 7117 (1988).
16. C.-R. Anderson, D. F. Coker, J. Eckert, A. L. R. Bug, *J. Chem. Phys.* **111**, 7599 (1999).
17. J. A. MacKinnon, J. Eckert, D. A. Coker, A. L. R. Bug, *J. Chem. Phys.* **114**, 10137 (2001).
18. B. L. Mojet, J. Eckert, R. A. van Santen, A. Albinati, R. E. Lechner, *J. Am. Chem. Soc.* **123**, 8147 (2001).
19. P. M. Forster *et al.*, *J. Am. Chem. Soc.* **125**, 1309 (2003).
20. C. M. Brown *et al.*, *Chem. Phys. Lett.* **329**, 311 (2000).
21. Y. Ren, D. L. Price, *Appl. Phys. Lett.* **79**, 3684 (2001).
22. Transitions for the hindered H_2 rotor are labeled (e.g., 0-1) as being between energy levels that are numbered 0, 1, and 2, with increasing energy. These numbers are not to be taken as the rotational quantum number J, which is only appropriate for the free rotor.
23. I. J. Braid, J. Howard, J. M. Nicol, J. Tomkinson, *Zeolites* **7**, 214 (1987).
24. B. K. Pradhan *et al.*, *J. Mater. Res.* **17**, 2209 (2002).
25. Supported in part by NSF (M.O'K. and O.M.Y.), U.S. Department of Energy (DOE) (O.M.Y.), and BASF (O.M.Y.). We thank U. Mueller, W. Harder, and O. Metelkina (BASF Aktiengesellschaft, Germany) for performing the ambient temperature measurements under conditions mimicking the application environment and R. Connatser for experimental assistance on the quasielastic neutron spectroscopy (QENS). This work has benefited from the use of facilities at the Intense Pulsed Neutron Source (IPNS), a national user facility funded by the Office of Science, U.S. DOE.

Supporting Online Material

www.sciencemag.org/cgi/content/full/300/5622/1127/DC1

Materials and Methods

13 February 2003; accepted 1 April 2003