Saturation of Hydrogen Sorption in Zn Benzenedicarboxylate and Zn Naphthalenedicarboxylate

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We report excess hydrogen saturation values from high-pressure isotherms of metal organic framework structures taken at 77 K. Zn benzendicarboxylate (IRMOF-1) and Zn naphthalendicarboxylate (IRMOF-8) linker structures show identical saturation values of 137 hydrogen molecules on a per unit cell basis, despite the higher sorption potential of IRMOF-8 of 6.1 kJ/mol over that of IRMOF-1 of 4.1kJ/mol. Charge transfer between linker and vertex, as well as surface area, appear to dominate the sorption behavior, over that of linker length in these two systems.

Improvements to gas sorbents will require high local site potentials for adatom/molecule interactions in addition to large surface areas. Site heterogeneities, even in well-defined crystalline structures that display Type 1 isotherm behavior, complicate our comprehension of sorption over that of traditional Langmuir isotherm studies of surfaces.[1] Still, the possibility of manipulating site potentials in such structures would be a boon to gas sorbent technology. Such manipulation could result from geometric alteration, as is done in promoting edge and pore sites from a graphitic base structure as in activated carbons. The straightforward addition of atomic or molecular species, that enable charge transfer, might also promote the number of attractive sites available to adsorbates. Materials with high sorptive capacity for hydrogen would be especially important for fuel cell applications, and metal organic frameworks (MOFs) are reported to display high capacities for hydrogen.[2] Because the linker structures of MOFs consist of benzene or graphitic units similar to the relevant active sites in activated carbons, the sorption behavior of these materials might be expected to be similar. The reported gravimetric hydrogen isotherm of IRMOF-1 (previously named MOF-5), a zinc benzenedicarboxylate structure, exhibited unusual behavior, showing an immediate 4 wt % uptake of hydrogen at 77 K below 1 bar.[2] In a subsequent paper, it was shown that the isotherm of this material actually displays Type-1-like behavior over 0 to 1 bar, reaching ∼1.3 wt % at 77 K at 1 bar.[3] In addition, the sorption capacity in the naphthalene linker IRMOF-8 structure up to 1 bar at 77 K was shown to be greater than that for IRMOF-1. Because of the longer length of the naphthalene linker, it might be natural to assume that the active sorption sites for hydrogen are located on the linker itself. However, because the ultimate saturation capacity of an adsorbent material depends on the adsorption potential, including its variation with coverage, as well as on the total number of adsorption sites, complete isotherms are necessary for accurate characterization.

In this letter, we present volumetric excess sorption isotherms of H_2 at 77 K on IRMOF-1 and IRMOF-8 that extend into the high-pressure region where saturation of the excess gravimetric sorption of these materials occur and show that > 4 wt % gravimetric density can be obtained in IRMOF-1, but that this occurs at pressures closer to 30 bar. The low-pressure volumetric data (<1 bar) we measure is consistent with previously reported gravimetric data for this material, as is our data for IRMOF-8, which also shows higher sorption of hydrogen at 1 bar than IRMOF-1.[3] The ultimate saturation value for excess gravimetric hydrogen sorption for IRMOF-8, however, is ∼3.6 wt %, i.e., lower than that for IRMOF-1. The crossover of gravimetric density of IRMOF-8 from being initially higher than IRMOF-1 at pressures up to 1 bar, but then ultimately saturating at a lower gravimetric density, shows the importance of measuring isotherms up to a pressure of 50 to 60 bar, beyond the value where hydrogen physisorbents ultimately saturate. We note also that our results for these materials have lower gravimetric densities than that predicted by recent computational results,[4,5] which also predict higher sorption values for IRMOF-8 over that of IRMOF-1 over the pressure range of our measurements.

IRMOF-1 and IRMOF-8 samples were prepared from 1,4-benzenedicarboxylate and 2,6-naphthalenedicarboxylate linkers, respectively, according to a previously described synthesis method.[6] Yellow crystals of IRMOF-1 were synthesized by solvothermal reaction of zinc nitrate tetrahydrate ($Zn(NO_3)_2$·$4H_2O$) (1.69 g, 6.45 mmol) with 1,4-benzenedicarboxylic acid (C_6H_4-1,4-$(CO_2H)_2$) (0.36 g, 2.14 mmol) dissolved in 50 mL *N,N′*-diethylformamide. This reaction was carried out at 105 °C in a 125 mL Parr acid digestion bomb for 24 h. White powder batches of IRMOF-8 were synthesized using a mixture of 2,6-naphthalenedicarboxylic acid ($C_{10}H_6$-2,6-$(CO_2H)_2$) (0.059 g, 0.275 mmol) and zinc nitrate tetrahydrate (0.62 g, 2.4 mmol)

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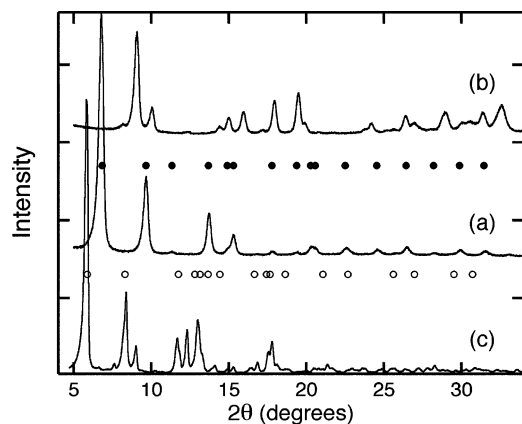
Figure 1. X-ray diffraction data and simulations from (a) IRMOF-1, showing data from the as-prepared and activated sample as the solid middle trace and the simulations that identify the peak positions as solid dots above the trace; (b) the upper trace shows the structural changes that occur in IRMOF-1 which has been allowed to sit in air for two months. (c) Shows data for the IRMOF-8 as prepared and activated sample as the lower solid trace and the simulations that identify the peak positions as open circles above the trace.

using the same synthesis procedures as for IRMOF-1 except for the use of a reaction temperature of 100 °C. After the 24 h reaction time, the Parr bomb is allowed to cool to room temperature.

For both IRMOF-1 and IRMOF-8, the products are washed with *N,N′*-diethylformamide to remove unreacted material. A subsequent exchange of high surface tension diethylformamide with low surface tension chloroform is performed while the host material remains immersed in solvent. We have found that the exchange/activation process can be completed in a few minutes when solvent is allowed to flow continuously through the IRMOF samples using filtration. This activation is necessary to yield a fully porous structure.

The crystalline phase purity of the as-prepared IRMOF samples was confirmed by X-ray diffraction analysis. Figure 1a compares the experimental and simulated X-ray patterns from IRMOF-1. The as-synthesized/activated material shows peak positions that are nearly identical to the theoretical powder diffraction data. We show in Figure 1b the instability of the IRMOF-1 structure as the activated material left in air for a couple of months displays a completely different X-ray pattern. We have also observed that the original crystalline structure is preserved for over a month when the material is stored under Ar atmosphere. Our X-ray data for IRMOF-8 also match available X-ray data.[7]

To further verify the properties of these materials for use as sorbents, 77 K N_2 coverage values of 885 mg/gm for our IRMOF-1 and 522 mg/gm for IRMOF-8 were determined[8] and compare favorably to previously reported values of 965 and 421 mg/gm, respectively.[3] Moreover, Langmuir surface area analyses were performed,[8] and surface areas of 3080 m^2/gm for IRMOF-1 and 1818 m^2/gm for IRMOF-8 are consistent with previously published[3] values of 3362 and 1466 m^2/gm.

Hydrogen excess storage analysis has been conducted at 77 K and at room temperature over a pressure range 0−70 bar using a volumetric Sieverts apparatus[9] on three different samples, including (a) a high surface area wood-based activated carbon, (b) IRMOF-1, and (c) IRMOF-8 samples. The isotherms from these materials are shown in Figure 2. The upper trace (a) is data for the activated carbon sample, which has a mean pore size of 1.1 nm and shows a maximum uptake of 5.4 wt % at 50 bar at 77 K. Trace (b) is the isotherm for IRMOF-1 and shows
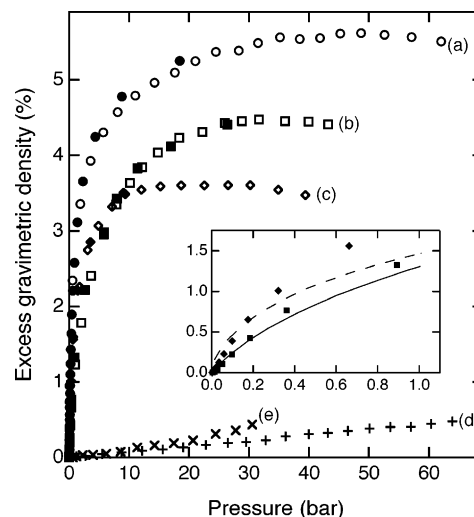

Figure 2. Isotherm traces of excess hydrogen storage densities for (a) an activated carbon with a mean pore size of 1.1 nm, where open circles are 77 K adsorption data and solid circles are desorption data, (b) IRMOF-1 where the open squares are 77 K adsorption data and the solid squares are desorption data, (c) IRMOF-8 where the open diamonds are 77 K adsorption data and the solid diamonds are desorption data, (d) IRMOF-1 room temperature adsorption data, and (e) IRMOF-8 room temperature data. The inset is an expansion of low pressure data which shows slightly higher sorption values of our experimental data points, identified above, when compared to published values from the University of Michigan for IRMOF-1 (black line) and IRMOF-8 (dotted line).

that the excess sorption saturation value of 4.3 wt % for this material is reached at a lower pressure of 30 bar. Trace (c) is the IRMOF-8 isotherm and shows a higher initial slope at low pressure than IRMOF-1, but that the saturation is reached at 3.6 wt % at 10 to 15 bar. The inset of Figure 2 shows a comparison of a small range of our desorption data over a 1 bar pressure range with that of ref 3 and shows that our materials display slightly higher sorption in this regime. We also note that the shapes of the isotherm traces for different batches of IRMOF-1 that we prepared while attempting to optimize the activation process, did vary at 77 K, but that the hydrogen saturation value for all materials eventually reached > 4 wt %. Evidently, the activation process responsible for removing solvent from the porous regions of the MOF structure is critical if optimal hydrogen sorption values are to be reached at lower pressure.

At 298 K, our isotherm data shown in Figure 2d, indicates that the maximum adsorption measured on an as-prepared/activated IRMOF-1 sample at 60 bar and room temperature is approximately 0.45 wt %. Figure 2e is IRMOF-8 room-temperature data and shows sorption of 0.4 wt % at 30 bar.

To better assess the differing roles that the benzenedicarboxylate and naphthalenedicarboxylate linkers play in hydrogen sorption behavior, we have normalized the isotherm data of IRMOF-1 and IRMOF-8 of Figure 2 to show the number of excess hydrogen molecules that are sorbed per IRMOF unit cell. These data are presented in Figure 3. There are two features of note in comparing the two traces. First is the virtually identical number of excess hydrogen molecules per IRMOF unit cell at the hydrogen saturation value, indicating that at 77 K, the unit cell of both structures accommodates the same maximum number of ∼137 hydrogen molecules at saturation, despite the larger volume of the naphthalene unit cell. This maximum number would be the equivalent of 17 hydrogen molecules per formula unit basis consisting of one vertex and three linkers.
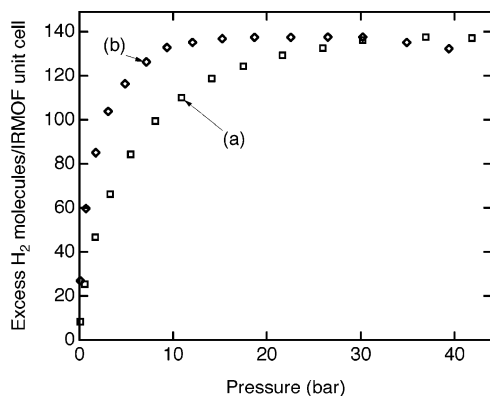
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J. Phys. Chem. B, Vol. 110, No. 3, 2006 **1101**

Figure 3. Normalization of isotherm data from Figure 2 for IRMOF-1 (a) open squares, and for IRMOF-8 (b) open diamonds, that show the excess number of hydrogen atoms sorbed/unit cell.

The lower value of excess gravimetric sorption for IRMOF-8 seen in Figure 2 results from the higher molecular weight of the naphthalene linker of this structure. The additional naphthalene linker length apparently does not improve the ultimate excess gravimetric hydrogen density. The second feature of note in Figure 3 is the sharper slope of the isotherm trace for IRMOF-8 in the Henry's law region, indicating a higher sorption potential. We can obtain the differential enthalpy of adsorption by plotting the Henry's law constant, k_H vs $1/T$. Because isotherms are nonlinear and typically consist of a limited number of data points in the low-pressure Henry's law region, the most tractable virial expansion for extracting a Henry's law constant is obtained following the analysis of Cole.[10] This analysis consists of plotting $\ln(n/p)$ vs n, where n is the gravimetric hydrogen density normalized to the 77 K saturation value, and p is the pressure. This approach yields a Henry's law constant intercept from a semilog plot and has the advantage that the linear region from which the intercept is determined extends over a pressure range that is larger than the Henry's law region,[11] enabling us to use more of the data points that are typically obtained from our Sieverts apparatus. From this analysis of data obtained at 77, 195, and 298 K, we determined the IRMOF-8 enthalpy to be ∼6.1 kJ/mol and the IRMOF-1 enthalpy from data obtained at 77, 195, and 298 K to be ∼4.1 kJ/mol, comparable to data obtained in similar systems.[12]

While we might assume that the higher sorption potential is at the naphthalene linker and that, while longer, the linker length is unable to accommodate more hydrogen molecules over that of the benzenedicarboxylate, another possibility is that the sites primarily responsible for sorption are the Zn oxide tetrahedral vertices and that the only role that the linker plays in sorption is to alter the site potential at the vertices through charge transfer from the linker to the vertices. Computational results by Sagara[13] and Mueller and Ceder[14] indicate that the latter interpretation represents the most likely physical explanation of sorption in these materials and that the site with the highest potential for attracting molecular hydrogen are the Zn oxide vertices. Recent

neutron diffraction data taken at 3.5 K do show that the initial hydrogen loading of up to 8 $D_2/4Zn$ (formula unit) occurs at two sites associated with the vertices[15] and not at sites associated with the linker, as assumed from inelastic neutron scattering data.[2] Our 77 K data is consistent with vertices as the high potential site for sorption.

We note also that the saturation limitation is a strong function of specific surface area.[16] Despite the longer linker length of IRMOF-8, this structure shows a smaller surface area than for IRMOF-1, which has a shorter linker. Alterations to the activation process might yield an IRMOF-8 sample with surface area greater than that for IRMOF-1, although we are unaware of any empirical data that show this. While several studies[17,18] do measure data in materials of these types at higher pressure, the excess sorption saturation limits are not reached, as would be noted by the eventual decrease of the gravimetric density as a function of pressure.

We expect further studies on structures with longer linkers to further clarify the role of sorption as a function of linker type and IRMOF volume. Such studies will require an analysis of high-pressure sorption data where hydrogen saturation occurs.

References and Notes

(1) Zangwill, A. *Physics at Surfaces*, Cambridge Press: Cambridge 1988, and references therein.

(2) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127−1129.

(3) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666−5667.

(4) Yang, Q.; Zhong, C. *J. Phys. Chem. B* **2005**, *109*, 11862.

(5) Garberoglio, G.; Skoulidas, A. I.; Johnson, J. K. *J. Phys. Chem. B* **2005**, *109*, 13094.

(6) Muller, U.; Harth, K.; Holzle, M.; Hesse, M.; Lobree, L.; Harder, W.; Yaghi, O. M.; Eddaoudi, M., U.S. Patent Application 20,030,148,165, 2003.

(7) Yaghi, O. M.; Eddaoudi, M.; Li, H.; Kim, J.; Rosi, N., U.S. Patent Application 20,030,004,364, 2003.

(8) Micromeritics Analytical Services, Norcross, GA.

(9) Bowman, R. C., Jr.; Luo, C. H.; Ahn, C. C.; Witham, C. K.; Fultz, B. *J. Alloys Compd.* **1995**, *217*, 185.

(10) Cole, J. H.; Everett, D. H.; Marshall, C. T.; Paniego, A. R.; Powl, J. C.; Rodriguez-Reinoso, F. *J. Chem. Soc., Faraday Trans.* **1974**, *I 70*, 2154.

(11) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*, Academic Press: New York, 1999.

(12) Kay, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506.

(13) Sagara, T.; Klassen, J.; Ganz, E. *J. Chem. Phys.* **2004**, *121*, 12543.

(14) Mueller, T.; Ceder, G. *J. Phys. Chem.* **2005**, *109*, 17974.

(15) Yildirim, T.; Hartman, M. *Phys. Rev. Lett.* **2005**, *95*, 215504.

(16) Panella, B.; Hirscher, M.; Roth, S. *Carbon* **2005**, *43*, 2209.

(17) Ferey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guégan, A. *Chem. Commun.* **2003**, 2976.

(18) Panella, B.; Hirscher, M. *Adv. Mater.* **2005**, *17*, 538.