Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn₄O(1,4-benzenedicarboxylate)₃ (MOF-5)

Steven S. Kaye,[†] Anne Dailly,[‡,§] Omar M. Yaghi,[¶] and Jeffrey R. Long*,[†]

Department of Chemistry, University of California, Berkeley, California 94720, Chemical and Environmental Sciences Laboratory, General Motors Corporation, Warren, Michigan 48090, College of Engineering, Purdue University, West Lafayette, Indiana 4790, and Department of Chemistry and Biochemistry and Center for Reticular Chemistry at the California NanoSystems Institute, University of California, Los Angeles, California 90095

Received September 11, 2007; E-mail: jrlong@berkeley.edu

Due to its clean combustion and high heating value, hydrogen is under consideration as a replacement for fossil fuels in mobile applications. To achieve this goal, however, an effective means of on-board storage is required,[1] prompting the U.S. Department of Energy to set 2010 storage system performance targets of 6.0 wt % H₂ and 45 g H₂/L.[2] Recent work has exposed the considerable potential for cryogenic hydrogen storage in microporous metal-organic frameworks exhibiting robust three-dimensional network structures and high surface areas.[3] In particular, frameworks consisting of tetrahedral $[Zn_4O]^{6+}$ units linked via rigid arylcarboxylate ligands were found to adsorb large amounts of hydrogen reversibly at low temperature and moderate pressures. For example, at 77 K and pressures of up to 50 bar, $Zn_4O(BDC)_3$ (MOF-5, BDC^{2-} = 1,4-benzenedicarboxylate) was shown to adsorb 5.2 excess wt % H₂,[4] while $Zn_4O(BTB)_2$ (MOF-177, BTB^{3-} = 1,3,5-benzenetribenzoate) exhibited a record uptake of 75 mg/1075 mg = 7.0 excess wt % H₂.[5] Here, we report conditions for the synthesis and handling of $Zn_4O(BDC)_3$ that significantly increase its gas adsorption capacity, resulting in the highest gravimetric and volumetric loadings yet reported for a cryogenic hydrogen storage material.

The compound $Zn_4O(BDC)_3$ serves as a prototype for an extensive family of metal-organic frameworks in which oxo-centered Zn₄ tetrahedra (of the type encountered in basic zinc acetate) are connected through linear organodicarboxylates to give a cubic network structure.[6] As formed from a solution assembly reaction, the pores within the structure are filled with guest solvent molecules. Remarkably, these guest molecules can be evacuated to leave a rigid metal-organic scaffold that is typically stable up to 400 °C under vacuum.[6,7] Despite this apparent stability, there is considerable variation in the reported gas adsorption properties of $Zn_4O(BDC)_3$ (see Table 1).[3c,5,7-10] Depending on the preparation, the N₂ uptake at saturation varies from 11.8 to 34.4 mmol/g, while the maximum H₂ uptake varies from 1.3 to 5.2 excess wt %.

In order to resolve these discrepancies and determine the true hydrogen storage capacity of $Zn_4O(BDC)_3$, a variety of synthetic methods were explored. Ultimately, the highest surface area material was obtained by employing a modification of a previously reported method[11] in which the exposure to water and air was minimized. In this procedure, a 3:1 mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and H_2BDC is dissolved in diethylformamide (DEF) and heated at 80 °C without stirring. The reaction is monitored visually until crystal formation has ceased (usually after 10 h), whereupon the heating is immediately stopped and the mixture is transferred to a nitrogen atmosphere. The colorless cube-shaped crystals are washed with anhydrous DMF and anhydrous CH₂Cl₂, and the exchanged guest solvent is removed under reduced pressure to afford pure Zn₄O-
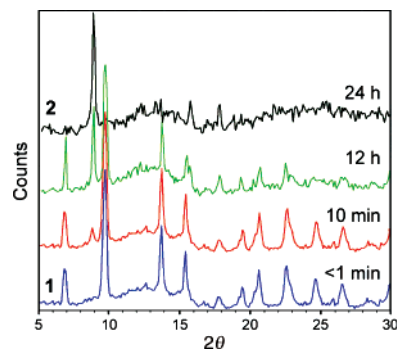
Figure 1. Powder X-ray diffraction patterns collected using Cu Kα radiation for $Zn_4O(BDC)_3$ exposed to air for <1 min (**1**), 10 min, 12 h, and 24 h (**2**). The broad hump centered at ca. 13° is due to the sample holder.

Table 1. Gas Adsorption Properties of $Zn_4O(BDC)_3$ Resulting from Various Preparations

preparation	N₂ uptake[a] (mmol/g)	SA_BET[b] (m²/g)	SA_Langmuir[b] (m²/g)	H₂ uptake[a] (excess wt %)
ref 9	11.8	570	1010	1.3
ref 8	14.5	950	1250	
ref 7	29.7		2900	
ref 10	31.6		3080	4.3
ref 3c	34.4		3362	
ref 5		3530	4170	5.2
1w	35.8	3100	3300	5.1
1	44.5	3800	4400	7.1

[a] Maximum uptake observed at 77 K. [b] Surface area determined by fitting the N₂ adsorption isotherm at 77 K to the BET or Langmuir equation.

(BDC)₃ (**1**) in 70−80% yield. Significantly, raising the temperature or extending the duration of the reaction was found to afford a yellow-tinted product with reduced surface area.[12] Although conditions were identified under which DMF could be employed as a less costly alternative to DEF (see Supporting Information), the surface area of the resulting material was generally somewhat lower.

During the course of these investigations, $Zn_4O(BDC)_3$ was observed to decompose in humid air. Exposure of a pulverized, desolvated sample of **1** to air for 10 min resulted in appearance of a new peak at $2\theta = 8.9°$ in the powder X-ray diffraction pattern, indicating partial conversion to a second phase (see Figure 1). Further exposure to air produced an increase in the relative intensity of this peak, as well as the appearance of two additional peaks at $2\theta = 15.8$ and 17.8°, suggesting formation of a compound isostructural to $Zn_3(OH)_2(BDC)_2 \cdot 2DEF$ (MOF-69C).[13] After 24 h, the conversion of **1** into a solid of formula $C_{24}H_{22}O_{18}Zn_4$ (**2** = **1·** $5H_2O$) was complete. In contrast, no reaction was observed upon exposure of **1** to dry O₂ or anhydrous organic solvents such as methanol, DMF, or DMSO. Thus, the decomposition of Zn_4O-$(BDC)_3$ can be attributed to atmospheric water. This is consistent with results concerning the immersion of nanoparticles of MOF-5 in water,[8] as well as recent calculations predicting $Zn_4O(BDC)_3$ to

[†] University of California, Berkeley.
[‡] General Motors Corporation.
[§] Purdue University.
[¶] University of California, Los Angeles.
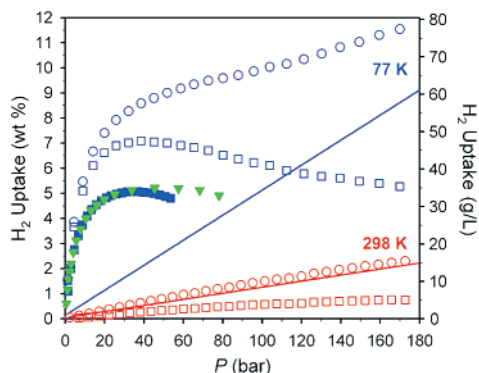
Figure 2. Hydrogen adsorption isotherms for samples of $Zn_4O(BDC)_3$ prepared with (**1w**, filled symbols) and without (**1**, open symbols) exposure to air, and as reported in ref 5 (green triangles). Data were measured at 77 (blue) and 298 (red) K and are shown as excess (squares) and total (circles) uptake.[4] All isotherms showed full reversibility without hysteresis. Solid lines indicate the density (right-hand scale) of pure H_2 gas.[17]

be unstable in the presence of more than 4% water by mass.[14] Importantly, gas adsorption measurements showed the decomposition product, **2**, to be nonporous, with no significant uptake of N_2 or H_2 at 77 K. The differences in the gas adsorption capacities reported for $Zn_4O(BDC)_3$ (see Table 1) could therefore potentially be explained as arising from variations in the degree of exposure to atmospheric or solvent water during sample preparation.[15]

Comparisons of N_2 adsorption data for samples of $Zn_4O(BDC)_3$ prepared with (**1w**) and without (**1**) exposure to air indeed reveal substantial differences. Compound **1w** was produced via a procedure identical to that utilized for **1**, but with isolation and desolvation performed in air without use of anhydrous solvents. Nitrogen adsorption measurements at 77 K revealed isotherms (see Figures S5 and S6) with maximum N_2 uptakes of 35.8 and 44.5 mmol/g for **1w** and **1**, respectively, confirming the deleterious effects of air exposure. Fitting the data with the BET equation gave respective surface areas of 3100 and 3800 m^2/g. Note, however, that a step occurring in the very low pressure region of each adsorption isotherm[16] complicates the fitting procedures used to estimate surface areas, such that the amount of N_2 adsorbed actually provides the most meaningful comparison for the materials listed in Table 1.

Even more dramatic differences are apparent in the H_2 adsorption data (see Figure 2). At 77 K and 40 bar, **1w** adsorbs 5.0 excess wt % H_2, which is comparable to the uptake of 5.2 excess wt % recently reported for a similarly prepared sample.[5] Under these conditions, **1** adsorbs 7.1 excess wt % H_2, representing the highest gravimetric capacity yet observed for a hydrogen storage material operating at 77 K. The volumetric H_2 storage capacity of a material is also of critical import[1,2] but requires knowledge of the total H_2 uptake. Using the crystallographic volume of the sample, the total H_2 uptake for **1** at 77 K was calculated to reach 10.0 wt % at the relatively safe pressure of 100 bar, and then to climb as high as 11.5 wt % at 170 bar. The corresponding volumetric storage densities are 66 and 77 g/L, respectively. Remarkably, the latter is greater than the density of liquid H_2, which is 71 g/L at 20.4 K and the lower pressure of 1 bar.[17] Note that, consistent with this record volumetric uptake capacity, the pore dimensions within $Zn_4O(BDC)_3$ are near the 10 Å diameter thought to be optimal for hydrogen storage at 77 K.[18]

Other key characteristics for a hydrogen storage material are the loading time and recyclability.[1,2] Kinetics measurements performed on **1** showed that, with an initial applied pressure of 45 bar, H_2 uptake achieved saturation in approximately 2 min (see Figure 3). In addition, the uptake was found to be fully reversible, with no detectable loss in capacity after 24 adsorption−desorption cycles.

The foregoing results demonstrate that, when protected from air, $Zn_4O(BDC)_3$ provides a promising medium for achieving the 2010 DOE hydrogen storage system targets of 6.0 wt %, 45 g/L, loading
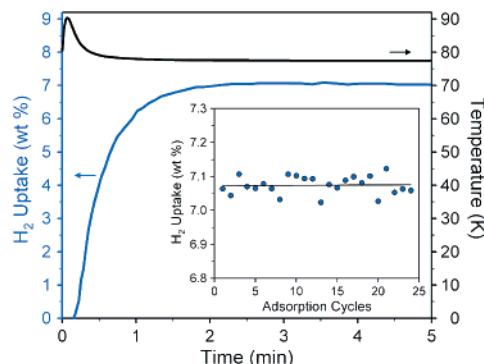
Figure 3. Kinetics trace (blue line) for excess H_2 uptake upon exposure of a liquid nitrogen-bathed sample of **1** to a pressure of 45 bar of H_2 gas at 298 K. Note that it takes almost 1 min for the temperature (black line) to return to 77 K. Inset: Excess uptake capacity of **1** measured for sequential H_2 adsorption/desorption cycles.

at 1.67 kg/min, and a lifetime of 1000 refills. Ongoing work is focused on increasing the H_2 adsorption enthalpy within such materials as a means of improving upon the low room-temperature storage capacity (see Figure 2),[3e] thereby generating materials suitable for use in noncryogenic systems.

Supporting Information Available: Details of all experimental procedures and H_2 and N_2 adsorption data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353 and references therein.
(2) Read, C.; Petrovic, J.; Ordaz, G.; Satyapal, S. *Mater. Res. Soc. Symp. Proc.* **2006**, *885*, 125.
(3) (a) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (b) Férey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guégan, A. *Chem. Commun.* **2003**, 2976. (c) Rowsell, J. L.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666. (d) Dybstev, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033. (e) Dincă, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (f) Collins, D. J.; Zhou, H. C. *J. Mater. Chem.* **2007**, *17*, 3154 and references therein.
(4) Excess uptake is the amount of gas taken up in addition to what would be present in a container with a volume equal to the pore volume within the sample. Total uptake is the amount of gas contained within the volume of the crystals, which includes both surface-adsorbed molecules and pressurized gas within the pores.
(5) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 3494.
(6) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 470.
(7) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
(8) Huang, L. M.; Wang, H. T.; Chen, J. X.; Wang, Z. B.; Sun, J. Y.; Zhao, D. Y.; Yan, Y. S. *Microporous Mesoporous Mater.* **2003**, *58*, 105.
(9) Panella, B.; Hirscher, M. *Adv. Mater.* **2005**, *17*, 538.
(10) Dailly, A.; Vajo, J. J.; Ahn, C. C. *J. Phys. Chem. B* **2006**, *110*, 1099.
(11) Yaghi, O. M.; Eddaoudi, M.; Li, H.; Kim, J.; Rosi, N. U.S. Patent Application 2003/0004364.
(12) The yellow color is likely due to decomposition of DEF to form guest oligomers that are not readily evacuated. Heating a solution of just Zn-$(NO_3)_2 \cdot 6H_2O$ in DEF indeed led to a yellow precipitate and a yellow solution containing a range of higher molecular weight organic species.
(13) Rosi, N. L; Kim, J.; Eddaouddi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504.
(14) Greathouse, J. A.; Allendorf, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 10678.
(15) Additional factors in some of the preparations may be framework interpenetration and/or the presence of zinc guest species: Hafizovic, J.; Bjørgen, M.; Olsbye, U.; Dietzel, P. D. C.; Bordiga, S.; Prestipino, C.; Lamberti, C.; Lillerud, K. P. *J. Am. Chem. Soc.* **2007**, *129*, 3612.
(16) Grand canonical Monte Carlo simulations suggest that these steps are associated with preferential initial adsorption of N_2 molecules at the corners within the framework: Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, *129*, 8552.
(17) Younglove, B. A. *J. Phys. Chem. Ref. Data* **1982**, *11*, 1.
(18) Rzepka, M.; Lamp, P.; de la Casa-Lillo, M. A. *J. Phys. Chem. B* **1998**, *102*, 10894.

JA076877G