J|A|C|S
COMMUNICATIONS

Hydrogen Storage in Metal−Organic Frameworks by Bridged Hydrogen Spillover

Yingwei Li and Ralph T. Yang*
Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109

Received March 10, 2006; E-mail: yang@umich.edu

The utilization of hydrogen as the energy source for fuel-cell vehicles relies in part on the development of a viable hydrogen storage system.[1] The U.S. Department of Energy (DOE) has established a multistage target for hydrogen storage capacity for fuel-cell applications. The design targets for an on-board hydrogen storage system are 4.5 wt % by 2007, 6 wt % by 2010, and 9 wt % by 2015, at moderate temperatures and pressures.[2] Among the currently available candidate storage materials, none is capable of meeting the DOE criteria for personal transportation vehicles.[3,4] Recently, new porous metal−organic frameworks (MOFs) were realized to also be promising candidates for hydrogen storage.[5] Férey et al. reported a high hydrogen storage capacity of 3.75 wt % in a nanoporous chromium terephthalate-based material, MIL-101, at 77 K and 2 MPa.[6] However, the hydrogen uptake by MIL-101 at room temperature was ∼0.45 wt % at 2 MPa.

The phenomenon of "hydrogen spillover" has long been observed over supported metal catalysts, which is defined as the dissociative chemisorption of hydrogen on the metal and the subsequent migration of atomic hydrogen onto the surface of the support such as alumina, carbon, and so on.[7] The support can be considered as the primary receptor for atomic hydrogen. Spillover to a secondary material is referred to as secondary spillover. In our previous work, we have demonstrated that it is possible to use secondary spillover to increase the hydrogen storage capacities in nanostructured carbon materials by mixing the carbon material with a small amount of supported catalyst that is capable of dissociating hydrogen.[8] Secondary spillover requires intimate contacts between the two unlike materials because there exist tremendous physical/energy barriers for surface diffusion of hydrogen atoms from one material to another. To create physical "bridges" between these two materials is helpful for increasing the contacts and, hence, facilitating secondary spillover.[8d] Here we report results of hydrogen storage in MOFs by hydrogen spillover with bridges. This work focused on IRMOF-1 and IRMOF-8, which are constructed by linking tetrahedral $[Zn_4O]^{6+}$ clusters with linear carboxylates.[5a] It was found that the hydrogen uptakes of MOFs could be enhanced markedly by secondary spillover via a simple technique for building carbon bridges. Thus, the storage capacity of IRMOF-8 was enhanced to 4 wt % at 298 K and 10 MPa. This uptake amount is 8X higher than that of pure IRMOF-8 under the same conditions. Furthermore, the storage was shown to be totally reversible and rechargeable at room temperature.

IRMOF-1 and IRMOF-8 samples were prepared following the reported procedures[9,10] and characterized by elemental analysis, IR, XRD, and N_2 adsorption analysis.[11] A catalyst containing 5 wt % Pt on active carbon (Pt/AC) was used as the source for H_2 dissociation. Active carbon was the primary receptor for hydrogen spillover.[7a,8b] IRMOF-1 or IRMOF-8 was the secondary receptor. Carbon bridges were formed by carbonization of a hydrocarbon precursor that was previously introduced into a physical mixture of the MOF and catalyst. In our previous work, we have found that carbon bridges could indeed be built between an activated carbon and a Pd/AC catalyst by carbonizing an added glucose precursor at 673 K.[8d] To build carbon bridges in MOFs by using this technique would seem to be difficult because MOFs are thermally unstable at temperatures >573 K.[5a] Here we used sucrose as the precursor and employed an effective temperature program for building carbon bridges and, at the same time, protecting the MOF crystals from collapsing. The ternary physical mixture of sucrose, Pt/AC catalyst, and MOF was first heated (in He) to 473 K (melting point of sucrose = 463 K) for 3 h. This step was designed to allow the sucrose to melt thoroughly and to fill the interstices (by capillarity) between the particles of the catalyst and the MOF (Figure 1b). Then the temperature was finally increased to 523 K. Complete carbonization of sucrose by this heating protocol was confirmed by thermogravimetric analysis (TGA) in a separate experiment. When the same temperature program was used, the TGA results showed that approximately 20% of the initial sucrose mass remained with no further weight loss on heating to 873 K. Therefore, using this heat treatment protocol, carbon bridges were introduced into the interstices between the particles of the metal, AC support, and MOF (Figure 1). Furthermore, this bridge-building technique did not lead to any decomposition of MOF materials, as confirmed by XRD and N_2 adsorption analysis (Supporting Information, Table S1 and Figure S1).

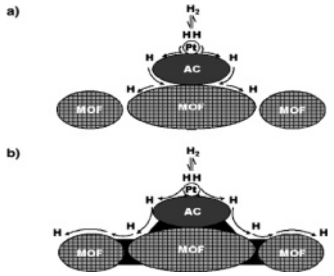

Figure 1. (a) Primary spillover of atomic hydrogen from Pt metal to the activated carbon support and secondary spillover to the MOF receptor that has limited contacts with the support. (b) Facilitated primary and secondary spillover by using carbon bridges (dark black zone).

High-pressure H_2 adsorption measurements were performed with a specially designed Sievert's apparatus. The apparatus and our measurement procedure have been proven highly accurate and reproducible by calibration using $LaNi_5$ alloy powder at 298 K.[8d] As shown in Figure 2, IRMOF-1 prepared in this study had a H_2 uptake of ∼0.4 wt % at 298 K and 10 MPa. We also measured hydrogen uptakes by IRMOF-1 at 77 K (1.3 wt % at 1 atm). These results are all in good agreement with the results of Panella et al.[9] and the latest corrected results of Roswell et al.[5g] under the same conditions. By simply mixing IRMOF-1 with Pt/AC catalyst, the H_2 storage capacities were markedly increased, especially at high pressures. Considering the relatively low H_2 uptake of Pt/AC (1.0 wt % at 10 MPa) and the small amount of Pt/AC in the mixture (10 wt %), it is clear that secondary hydrogen spillover had occurred on the surface of IRMOF-1. By building carbon bridges, the uptakes can be further increased substantially. It can be seen from Figure 2 that the bridged sample exhibits the highest hydrogen uptake of ∼3 wt % at 10 MPa. It represented an enhancement factor of 2

10.1021/ja061681m CCC: $33.50 © 2006 American Chemical Society

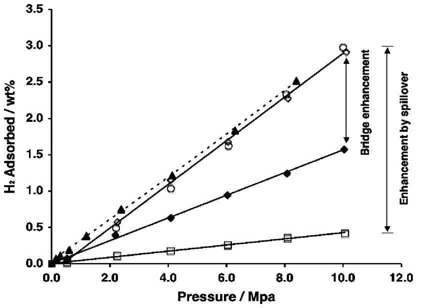

Figure 2. High-pressure hydrogen isotherms at 298 K for pure IRMOF-1 (□), Pt/AC and IRMOF-1 physical mixture (1:9 weight ratio; ◆) and for a bridged sample of Pt/AC-bridges−IRMOF-1: first adsorption (○), desorption (▲), and second adsorption (◇).

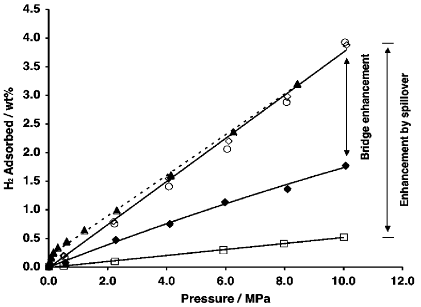

Figure 3. High-pressure hydrogen isotherms at 298 K for pure IRMOF-8 (□), Pt/AC and IRMOF-8 physical mixture (1:9 weight ratio; ◆) and for a bridged sample of Pt/AC-bridges−IRMOF-8: first adsorption (○), desorption (▲), and second adsorption (◇).

compared with the physical mixture without bridges. This enhancement was clear evidence of the success of the bridge-building technique. Compared with pure IRMOF-1, it is remarkable that the hydrogen adsorption amount of IRMOF-1 has been enhanced by a factor of 8. This increase was attributed to secondary spillover of hydrogen atoms from the catalyst to the surface of the MOF material. These results indicated that the creation of carbon bridges was crucially important for achieving a high hydrogen adsorption capacity by spillover.

Similar enhancement of hydrogen storage by spillover was also observed on IRMOF-8. Figure 3 summarizes the hydrogen adsorption results of pure IRMOF-8, a physical mixture, and a bridged sample. By using the bridge-building technique, the H_2 uptake was increased from 0.5 wt % on pure IRMOF-8 to 4 wt % at 10 MPa. This uptake amount is equivalent to ~34 H per formula unit ($Zn_4O(C_{12}H_6O_4)_3$), which is much lower than the total number of atoms in IRMOF-8, assuming H per surface atom. Furthermore, our unpublished ab initio molecular orbital calculation results indicated that it is favorable for one surface atom (such as oxygen) to adsorb two H atoms at the same time. Thus, the theoretical maximum storage would be at least 6.5 wt %. This can be supported by our results. As seen in Figure 3, no apparent saturation value was approached for the bridged sample; as the isotherm was linear even at 10 MPa. The absence of a saturation value suggests that a further increase in capacity can be expected at pressures >10 MPa; for example, 6 wt % storage is expected at 15 MPa, a viable pressure for practical automotive applications.

Reversibility was evaluated by measuring the desorption branch down to 1 atm. It can be seen from Figures 2 and 3 that the desorption branches nearly followed the adsorption branches for the bridged samples, although there appeared to be a slight hysteresis. The samples were then evacuated to a pressure of 1 Pa (7.5×10^{-3} Torr) for 12 h at 298 K. It is interesting to note that the second adsorption branches were in complete agreement with the first adsorption branches. These results indicate that hydrogen adsorption in the bridged materials were fully reversible at 298 K.

The adsorption/desorption kinetics of the bridged materials were studied by monitoring the changes in H_2 pressure versus time upon each pressure-changing step. It was observed that nearly 70% of the total hydrogen capacity was reached in 1 h. For desorption, it was found that >60% completion was achieved in 10 min upon each pressure-drop step. The heat of adsorption was measured to be in the range of 20−23 kJ/mol by using the Clausius−Clapeyron equation for the H_2 adsorption isotherms measured at two different temperatures (298 and 323 K).

The results from this work have demonstrated that hydrogen storage by spillover is a viable technique to achieve high hydrogen storage by MOFs. The bridge-building technique has been shown to be effective for building carbon bridges to MOFs for facilitating the spillover and, hence, storage. The rechargeable and reversible hydrogen capacity was 4 wt % at 298 K and 10 MPa on the bridged IRMOF-8 material. The isotherm was nearly linear and showed no saturation up to 10 MPa. Our technique may find broad application with other MOFs and nanostrutured materials for hydrogen storage because of their similar structures as IRMOF-1 and IRMOF-8.[12] Our results suggest that the enhancement factor by spillover would be a weak function of the MOF receptor and that the hydrogen capacity of the pure MOF would be the predominant factor in determining the overall hydrogen uptake via spillover. Therefore, it can be expected that further increases in capacity can be achieved with new MOFs having higher hydrogen uptakes than IRMOF-8 by spillover.

Acknowledgment. This work was supported by the U.S. Department of Energy through the Center of Excellence on Carbon-Based Hydrogen Storage. We thank A. J. Lachawiec for the TGA analysis of carbonization of sucrose.

Supporting Information Available: Experimental details, N_2 adsorption results, and powder XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353−358.
(2) U.S. Department of Energy, Energy Efficiency and Renewable Energy (EERE), Hydrogen, Fuel cells & Infrastructure Technologies Program, Multi-Year RD&D Plan, 2005. http://www.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf (accessed June 2005).
(3) Dillon, A. C.; Heben, M. J. *Appl. Phys. A* **2001**, *72*, 133−142.
(4) Züttel, A. *Mater. Today* **2003**, *6*, 24−33.
(5) (a) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keefee, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127−1129. (b) Suh, M. P.; Ko, J. W.; Choi, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 10976−10977. (c) Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T. *AIChE J.* **2004**, *50*, 1090−1095. (d) Pan, L.; Sander, M. B.; Huang, X. Y.; Li, J.; Smith, M.; Bittner, E.; Bockrath, B.; Johnson, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 1308−1309. (e) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376−9377. (f) Zhao, X. B.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. *Science* **2004**, *306*, 1012−1015. (g) Rowsell, J. L.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem.* Soc. **2004**, *126*, 5666−5667. (h) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32−33. (i) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 72−75. (j) Kubota, Y.; Takata, M.; Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kato, K.; Sakata, M.; Kobayashi, T. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 920−923.
(6) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040−2042.
(7) (a) Robell, A. J.; Ballou, E. V.; Boudart, M. *J. Phys. Chem.* **1964**, *68*, 2748−2753. (b) Srinivas, S. T.; Rao, P. K. *J. Catal.* **1994**, *148*, 470−477. (c) Conner, W. C.; Falconer, J. L. *Chem. Rev.* **1995**, *95*, 759−788.
(8) (a) Yang, F. H.; Yang, R. T. *Carbon* **2002**, *40*, 437−444. (b) Lueking, A.; Yang, R. T. *J. Catal.* **2002**, *206*, 165−168. (c) Lueking, A.; Yang, R. T. *Appl. Catal. A* **2004**, *265*, 259−268. (d) Lachawiec, A. J.; Qi, G. S.; Yang, R. T. *Langmuir* **2005**, *21*, 11418−11424.
(9) Panella, B.; Hirscher, M.; Pütter, H.; Müller, U. *Adv. Funct. Mater.* **2006**, *16*, 520−524.
(10) 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*, 105−114.
(11) Li, Y. W.; Yang, R. T. *J. Am. Chem. Soc.* **2006**, *128*, 726−727.
(12) Yang, R. T.; Li, Y. W.; Qi, G. S.; Lachawiec, A. J. *U.S. Patent application filed*, 2005.

JA061681M