

IV.C.1b Hydrogen Storage by Spillover

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Objectives

- Achieve the 6 wt% storage target at room temperature by 2009 by using nanostructured carbons or other sorbents aided by spillover.
- Develop a mechanistic understanding for hydrogen spillover that leads to hydrogen storage.

Approach

- To develop hydrogen storage materials with capacities in excess of 6 wt% at room temperature.
- To develop and optimize our new bridge-building techniques for spillover to enhance hydrogen storage.
- To obtain a mechanistic understanding for hydrogen spillover in nanostructured carbon-based materials for the purpose of hydrogen storage.

Accomplishments

- Developed a simple technique for bridge-building that can significantly enhance spillover at ambient temperature thereby increasing storage.
- Using this technique, we have achieved a storage amount of near 4 wt% at 298 K and 10 MPa for a bridged IRMOF-8 sample.
- Studied the kinetics of hydrogen adsorption and desorption on bridged IRMOF-8 by hydrogen spillover at 298 K.

- Developed a simple mechanistic, working model for hydrogen spillover that leads to hydrogen storage.
- Our results on the bridged IRMOF-8 at 298 K were independently reproduced and the results validated by the DOE-designated validation laboratory, Southwest Research Institute (SwRI), on a sample prepared by following our publication by a group at the Institute of Nuclear Energy Research (INER) in Taiwan.
- Developed a direct doping technique for doping metal on carbon, and achieved hydrogen storage of 1.2 wt% at 298 K at 100 atm on Pt/AX-21.



Results

The results on IRMOF-8 and that with spillover with carbon bridges are shown below.

The results on three bridged IRMOF-8 samples that were prepared during the year are shown. The isotherms were measured using a standard (and calibrated) volumetric technique. The Pt/AC was a commercial catalyst with 5 wt% Pt supported on activated carbon. By using a physical mixture of Pt/AC catalyst and IRMOF-8, a substantial spillover is observed. However, the spillover was further enhanced by applying our bridge-building technique. At 10 MPa and 298 K, our three samples yielded hydrogen storage capacities ranging from 2.2–4 wt%. The storage capacities of the INER sample were measured by SwRI using a gravimetric technique, and are compared with our results in Figure 1.

The uptake rates on the bridged IRMOF-8 were measured at different temperatures. From the temperature dependence of the rates, the activation energy for surface diffusion was determined to be 9.3 kJ/mol, which is 1/3 to 1/2 of the adsorption energies and is very reasonable. The high pressure uptake rates and desorption rates at 298 K are shown in Figure 2.

Surface diffusion of the spillover hydrogen at near ambient temperature was a slow process, which resulted in slow hydrogen uptake rates especially at higher pressures (higher surface concentrations). Desorption rates were relatively faster, and also decreased with increasing pressure or surface concentration. Desorption appeared to follow a reverse spillover process. From the kinetic data, it is seen that the diffusion time constant increased with surface concentration (or uptake amount). This is strong evidence that the spillover H₂ serves as bridges for further spillover.

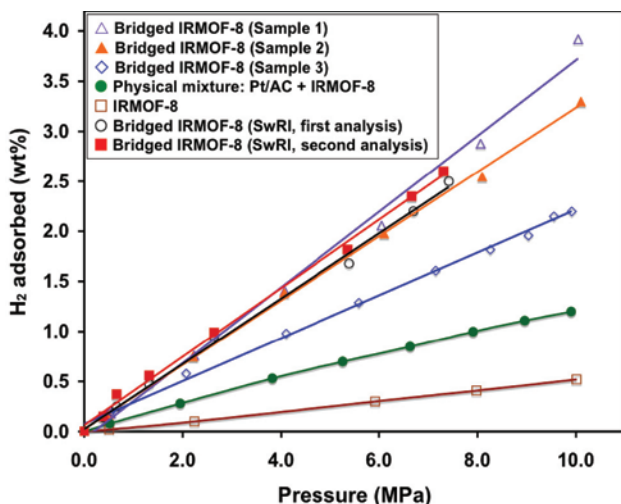


FIGURE 1. Hydrogen storage by bridged IRMOF-8 at 298 K. Comparison of INER-SwRI data and University of Michigan data on three samples. The INER-SwRI data are from M. A. Miller and R. Page, DOE Annual Merit Review Meeting, Washington, D.C., May 14-17, 2007, Paper STP 36, "National Testing Laboratory for Solid-State Hydrogen Storage Technologies."

A simple mechanistic model was formulated for the equilibrium isotherm for spillover hydrogen. The relationship between the chemisorbed hydrogen and the gas phase was obtained by using Langmuir's original (1918) dissociative chemisorption (H_2 on Pt). The resulting isotherm for the spillover system is:

$$q = \frac{K_1 k_1 \sqrt{P_{H_2}}}{1 + k_2 \sqrt{P_{H_2}} - K' k_1 \sqrt{P_{H_2}}}$$

The model is capable of interpreting various shapes of isotherms, i.e., concave, convex or nearly linear isotherms.

The hydrogen storage on the super-activated carbon, AX-21 (Brunauer-Emmett-Teller surface area of $\sim 2,800 \text{ m}^2/\text{g}$) at 298 K is shown in Figure 3. Using a direct doping technique, the hydrogen storage capacities were significantly increased by doping 6 wt% Pt on the sample, also shown in Figure 3. Here, again, spillover significantly enhanced H_2 capacity on AX-21. The results of four doped samples are shown in the figure, with a very small standard deviation, indicating high reproducibility of the sample preparation. The data on Pt/AX-21 have been validated by the National Renewable Energy Laboratory/DOE.

Future Directions

- Storage by spillover with bridge-building on other high surface area MOFs: MIL-101, COF-1 (covalent organic framework), and MOF-177.

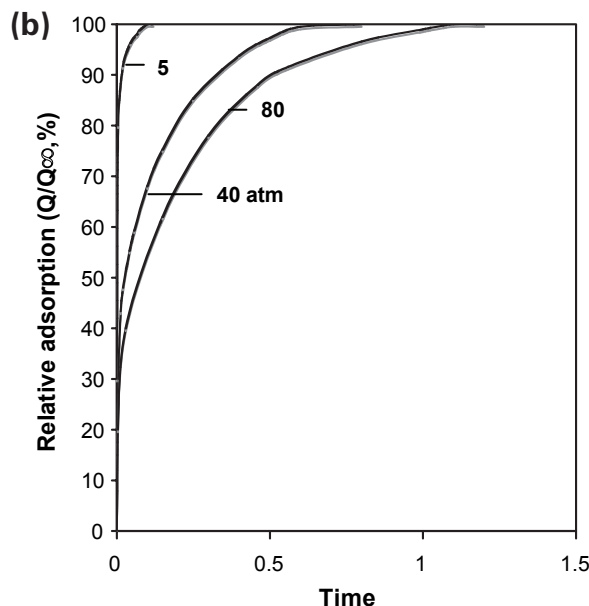
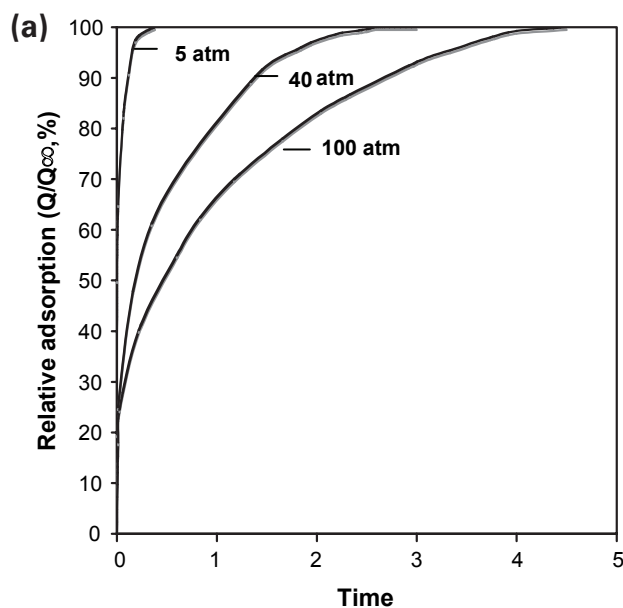


FIGURE 2. Rates of adsorption (l), and desorption (r) at different pressures (5-100 atm) on the bridged IRMOF-8 sample ($T = 298 \text{ K}$). Q_∞ is the equilibrium adsorption (a), or desorption (b) amount at each end pressure. Three pressure-changing steps are shown: 0-5 atm, 20-40 atm, 80-100 atm for adsorption, and the reverse steps for desorption.

- New direct doping techniques on AX-21 and other ultra-high surface area carbons.
- Test other promising receptors (sorbents) (for sorbent candidates, see R. T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley, New York, 2003).
- Test different catalysts and bridge-building precursors, as well as techniques for bridge building.

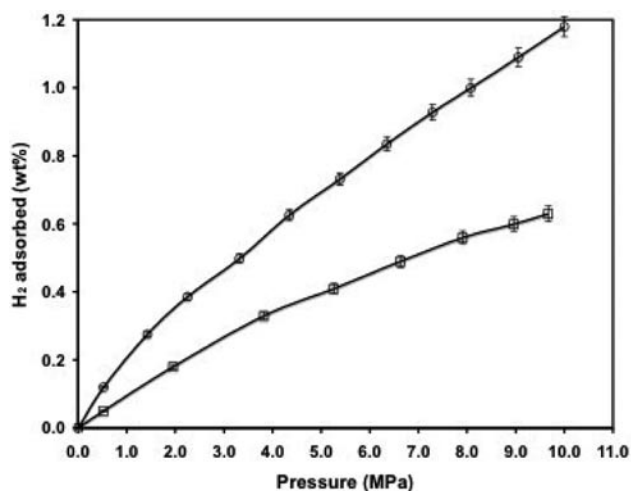


FIGURE 3. High-Pressure Hydrogen Isotherms at 298 K on 6 wt% Pt/AX-21 by a New (Direct) Doping Technique (Error Bars are Based on 1σ of Four Samples)

- Obtain basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope.
- To achieve the 4.5 wt% (36 g/L) DOE (interim) system target at 298 K in FY 2007.
- To address issues on fueling rates and other DOE targets.

Publications

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4. Y. W. Li and R. T. Yang, "Significant Enhancement of Hydrogen Storage Capacity in Metal-Organic Frameworks via Spillover," *J. Am. Chem. Soc.*, **128**, 726 (2006).
5. Y. W. Li, F. H. Yang and R. T. Yang, "Kinetics and Mechanistic Model for Hydrogen Spillover on Bridged Metal-Organic Frameworks," *J. Phys. Chem. C*, **111**, 3405 (2007).
6. R. T. Yang, Y. W. Li, A. J. Lachawiec and G. Qi, "Chemical Bridges for Enhancing Hydrogen Storage by Spillover and Methods for Forming the Same," U.S. Patent application filed (Serial No. 11/442,898, May, 2006).