

IV.C.1k Hydrogen Storage in Graphite Nanofibers and the Spillover Mechanism

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Partner Approach

To achieve the DOE hydrogen storage targets, the University of Michigan is developing nanostructured carbon and/or other sorbent materials. The focus of this effort is on characterizing and enhancing hydrogen spillover from a carbon supported catalyst to lightweight receptor materials. The University of Michigan is developing and optimizing our new bridge-building techniques for spillover to enhance hydrogen storage and is performing systematic experiments to obtain a mechanistic understanding for hydrogen spillover in nanostructured carbon-based materials for the purpose of hydrogen storage.

Partner FY 2006 Accomplishments

Developed a strategy for bridge building that involves the following steps:

- Select a proper precursor for the carbon bridge (e.g., sugars, polymers).
- Melted mixture of precursor with catalyst and sorbent/receptor.
- Followed an optimized temperature/gas environment treatment protocol (depending on the receptor, precursor and the catalyst) for optimized bridge-building.

Using this technique, we have:

- Achieved 1.8 wt% hydrogen storage at 298 K and 10 MPa by using AX-21 activated carbon and Pd/carbon catalyst with carbon bridges built for spillover.
- Achieved 1.8 wt% hydrogen storage at 298 K and 10 MPa by using IRMOF-8 and Pt/carbon catalyst by spillover (without bridges).
- Preliminary results indicate a storage amount of near 2.2-4 wt% at 298 K and 10 MPa for IRMOF-8 samples by using our bridge building technique.

The results on IRMOF-8 and those with spillover with carbon bridges are shown in Figure 1. The low pressure isotherms were measured using the commercial Micromeritics ASAP-2010 system, and the high pressure isotherms (Figure 2) were measured using our own volumetric system. The Pt/AC was a commercial catalyst with 5 wt% Pt supported on activated carbon. By using physical mixture of the Pt/AC catalyst and the IRMOF-8, a substantial spillover is already seen. The spillover was further enhanced by applying the bridge-building technique. The results obtained from the two systems were in total agreement. Furthermore, the high pressure system was calibrated/validated against sorbents with known H₂ capacities at 298 K and 100 atm, including activated carbon, AX-21, Li-X zeolite, 3 MOFs, and Pd/AC and Pt/AC (5% supported catalysts). The H₂ uptakes were all <0.6 wt% (except for

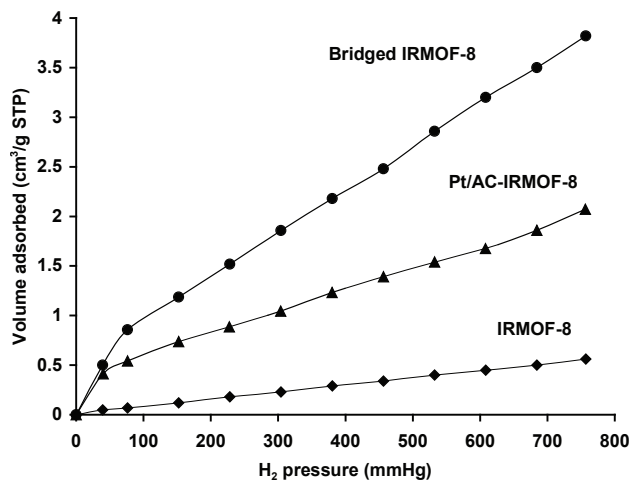


FIGURE 1. Low-pressure hydrogen isotherms at 298 K for pure IRMOF-8 (◆), 1:9 mixture of Pt/AC and IRMOF-8 (▲) and the mixture with 10% carbon bridges (●).

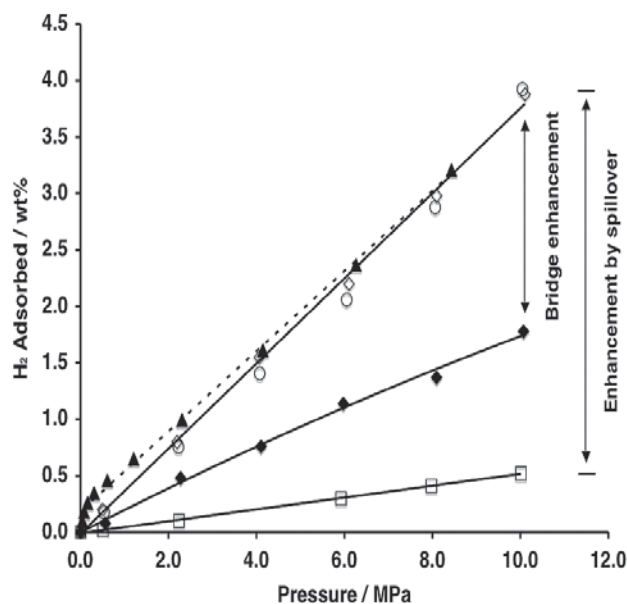


FIGURE 2. High-pressure hydrogen isotherms at 298 K for pure IRMOF-8 (\square), Pt/AC and IRMOF-8 physical mixture (1:9 weight ratio) (\blacklozenge), and for bridged sample of Pt/AC-bridges-IRMOF-8: first adsorption (\circ), desorption (\blacktriangle) and second adsorption (\diamond).

Pd/AC and Pt/AC which were ~ 1 wt% at 100 atm, and all isotherms were concave in shape. For the bridged IRMOF, repeated measurements (with several samples) were 2.2-4 wt% (at 100 atm), and the isotherms were nearly linear.

Partner FY 2007 Plans

- Test different receptors (sorbents) including MOFs and carbons.
- Test different catalysts and bridge-building precursors, as well as techniques for bridge building.
- Obtain basic understanding of the spillover process including equilibrium and kinetics.
- To achieve the DOE target of 4.5 wt% storage at 298 K in FY 2007.
- To achieve the 6 wt% DOE target at 298 K in FY 2010.
- To address issues on volumetric targets and other DOE targets.

Publications

1. A. J. Lachawiec, Jr., G. S. Qi and R. T. Yang, "Hydrogen Storage in Nanostructured Carbons by Spillover: Bridge Building Enhancement," *Langmuir*, **21**, 11418 (2005).
2. 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).
3. F. H. Yang, A. J. Lachawiec, Jr. and R. T. Yang, "Adsorption of Spillover Hydrogen Atoms on Single-Wall Carbon Nanotubes," *J. Phys. Chem. B.*, **110**, 6236 (2006).