

IV.C.1b Enhanced Hydrogen Dipole Physisorption

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Partner Approach

We have been using well-developed volumetric techniques [1] in order to measure surface excess isotherms at 77 K and room temperature (RT). This work has enabled us to validate behavior noted by other investigators wherein gravimetric density scales with surface area [2] in a wide range of carbons. Using the rule of thumb where 1 wt% hydrogen is adsorbed for every 500 m²/g of surface area of sorbent, we have been working with Carbon-Based Hydrogen Storage partner Ted Baumann of Lawrence Livermore National Laboratory (LLNL), who has been using a range of carbonization temperatures and processing techniques in synthesizing carbon aerogels. These materials can be made in monolithic form, potentially giving them packing density advantages over that of traditional high surface area carbons such as activated carbon. Moreover, we note that the addition of Ni particles that presumably act catalytically, enhance the sorption characteristics of carbon aerogels and we are pursuing strategies that will best incorporate Ni into the aerogel structures.

Partner FY 2006 Results

Isotherm temperature dependent behavior can be seen in Figure 1, which is an example of our earlier work on IRMOF-1 [3]. Because the differential enthalpy of adsorption as determined by a Henry's law analysis of the low-pressure isotherm slope is ~4 kJ/mole (or close

to thermal energies), we expect the highest sorption to occur at lowest temperatures. Here we see that 77 K temperature is required to maximize sorption in this material, emphasizing the need to develop materials with higher sorption enthalpies, so that high gravimetric densities can be achieved at higher temperatures.

In Figure 2, we present isotherms that outline the dependence of surface excess saturation value on surface area, in carbon aerogels that were synthesized as "baseline" materials for subsequent work. Here the range of surface area scales from 330 to 2,000 m²/g. Higher Bruner-Emmett-Teller (BET) surface areas yield higher surface excess gravimetric densities. Consequently, an important goal of work on physisorbents should be the design of materials that

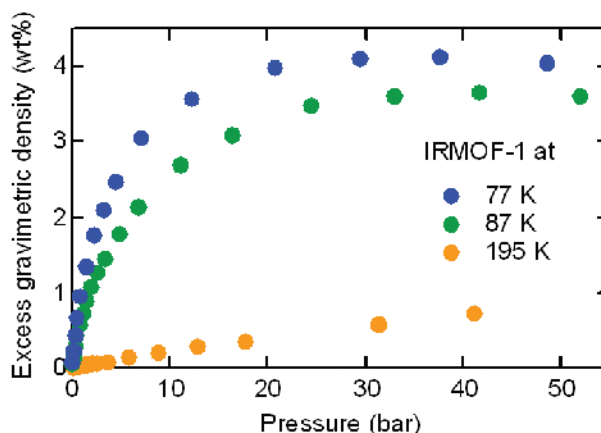


FIGURE 1. Temperature dependence of isotherm behavior in IRMOF 1 at LN₂, liquid Ar and dry ice temperatures. This material has a differential enthalpy of adsorption of 4 kJ/mole.

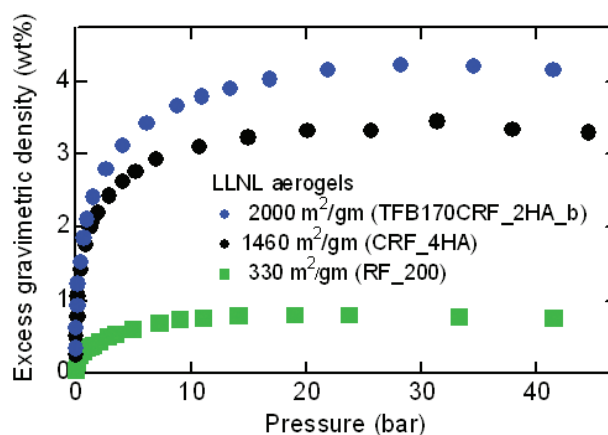


FIGURE 2. Surface area dependence of adsorption isotherms of LLNL aerogels taken at 77 K. Highest surface area aerogel has the highest sorption.

have a combination of high surface area along with high sorption potential sites.

In Figure 3, we show the overall trend with most of the LLNL aerogels that we have analyzed, and added data from the best activated carbons that we have measured. The aerogel data includes data points from samples that have had metal additions either in the form of Co or Ni nanoparticles. The data in the open red circle is from an activated carbon made by Fred Baker of Oak Ridge National Laboratory, while he worked at Mead-Westvaco. This particular activated carbon, had in fact been designed to be optimized for methane storage.

Figure 4 shows the effect of catalytically active Ni particles on the sorption behavior of similar surface area carbon aerogels. While the surface area of these samples was only on the order of 1,000 m²/g, this effect has been seen previously by James Schwarz of Syracuse, and gives us a direction to pursue in the immediate future with our higher surface area samples.

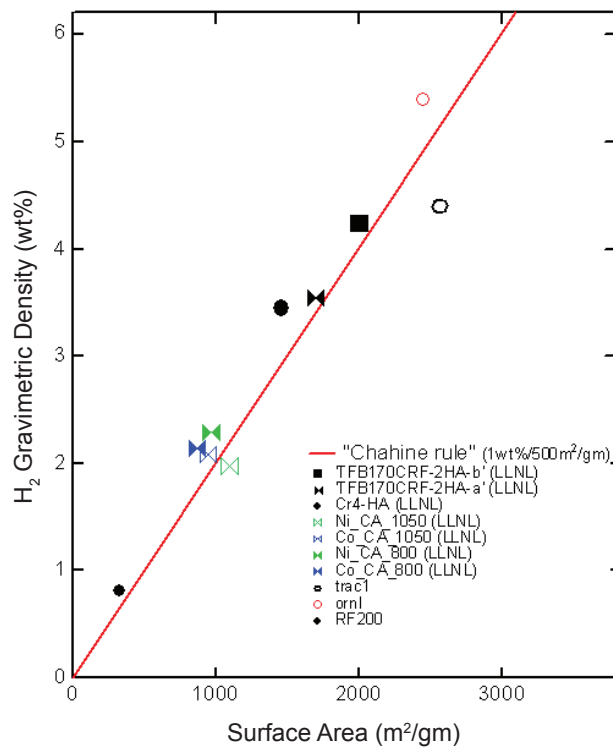


FIGURE 3. Saturation value of the surface excess gravimetric density of LLNL aerogels and activated carbons measured at Caltech.

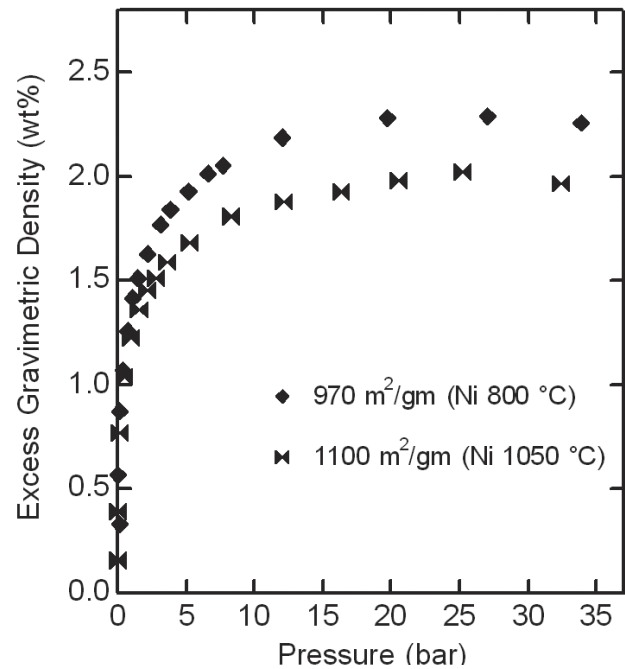


FIGURE 4. Shown are 77 K isotherms of similar surface area Ni aerogels with a catalytically active (diamonds) vs non-catalytically active (bow-ties) material. Temperature indicated in plot is carbonization temperature.

Partner FY 2007 Plans

From our 2006 results, we see that the pursuit of high surface area materials that have high sorption site-potentials should be the aim of our work over the next year. We plan to continue our fruitful collaboration with Ted Baumann of LLNL to look at the intrinsic properties of aerogels, maximizing their surface areas and incorporating additions such as B, in order to alter the sorption potentials of these materials. LLNL recently synthesized a 2,550 m²/g surface area sample and we expect this material to be the basis of further studies, including the tailoring of pore size (to maximize volumetric density), and the addition of Ni catalyst through our own work on Ni salt calcination.

Caltech FY 2006 Publications/Presentations

1. "Saturation of Hydrogen Sorption in Zn Benzenedicarboxylate and Zn Naphthalenedicarboxylate," A. Dailly (GMRD), J. J. Vajo (HRL), and C. C. Ahn (Caltech), *J. Phys. Chem. B Lett.*, **110**, 1099, 2006.
2. "Hydrogen Cryo-adsorption; Comparing Low Pressure and Isothermic Heats", C. C. Ahn (Caltech), invited presentation, American Physical Society Spring Mtg, Baltimore, (March 2006).

3. "Surface Area Dependence of Hydrogen Gravimetric Density in Carbon Aerogels," H. Kabbour(Caltech), A. Saulnier (Caltech), T. F. Baumann (LLNL), J. H. Satcher, Jr. (LLNL) and C. C. Ahn (Caltech), Electrochemical Society Spring Meeting, Denver, (May 2006).

References

1. R. C. Bowman, Jr., C. H. Luo, C. C. Ahn, C. K. Witham, B. Fultz, *J. Alloys Compd.* 217, 185, (1995).
2. "Characterization and Optimization of Adsorbents for Hydrogen Storage," R. Chahine and T.K. Bose, in Hydrogen Energy Prog. XI (3 Vols.), Proc. of the 11th WHEC, Veziroglu, TN, Winter C-J, Baselt JP, Kreysa G., eds. P 1259, Oxford: Pergamon Press, 1996.
3. "Saturation of Hydrogen Sorption in Zn Benzenedicarboxylate and Zn Naphthalenedicarboxylate," A. Dailly, J. J. Vajo, and C. C. Ahn, *J. Phys. Chem. B Lett.*, 110, 1099, 2006.