

IV.C.1n Enhanced Hydrogen Dipole Physisorption

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Objectives

- Synthesis, analysis, and quantification of surface excess isotherm behavior in high surface area carbon and modified framework structures.
- Establishment of the principle of enhanced dipole physisorption.
- Evaluation of the efficacy of carbon and other high surface area systems as commercially viable hydrogen storage sorbents.
- Overcome specific thermodynamic limitations to hydrogen physisorption, by deepening the potential well for physisorption.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

Data are typically reported as surface excess gravimetric densities that reflect the amount of hydrogen sorbed due to the presence of the sorbent. Gas law

contributions are not considered as part of this analysis as these depend on the surface area and skeletal density of the sorbent. Inclusion of such a number will typically add ~30% to the values noted below. The contribution to the system weights from the tanks and insulation are not considered in our values whereas the 2010 targets for gravimetric and volumetric capacity are targeted on system's basis of 6% and 0.045 kg/L, respectively.

The best materials we have synthesized/studied to date have a specific energy of 1.91 kWh/kg and a volumetric density of 1.28 kWh/L, measured at 77 K.

Accomplishments

- Synthesis of metal organic framework (MOF) 74, an example of a framework structure with a narrow pore size distribution. The isosteric heat we measured ranges from 8.5 to 4 kJ/mole with the initially high value attributable to the coordinatively unsaturated Zn site. In collaboration with the National Institute of Standards and Technology (NIST), we have determined that this material has one of the highest surface packing densities of molecular H₂ and the closest H₂-H₂ distance (2.85 Å) measured at low pressure. If such a packing density were achieved in a high surface area activated carbon or carbon aerogel, ~9 wt% surface excess density could be achieved on a materials basis.
- Because heat transfer associated with the sorption of hydrogen needs to be assessed in order to design an engineering system, we have concentrated on a more complete analysis of this enthalpy or heat by comparing the single sorption value (differential enthalpy of adsorption at zero coverage), to the isosteric enthalpy of adsorption. This is of particular interest as the isosteric enthalpy shows the heat associated with hydrogen loading in the sorbents generally drops. Our work shows that microporous and narrow pore distribution activated carbon fibers and carbons that display high initial isosteric heats are due to wave function overlap of the sorbent surface, making the design of pore size of critical importance.



Introduction

High surface area-based physisorbents are a class of materials that are close to engineering viability for high gravimetric density reversible onboard storage

applications, provided that 77 K is an acceptable temperature at which to store hydrogen. Further optimization of this class of materials will be necessary in order to increase volumetric densities and to offer the possibility of ambient temperature operation. This optimization will require promoting narrow pore distribution in these materials, and modifications to the surface in order to increase the sorption enthalpy.

Typical high surface area carbons such as activated carbons and carbon aerogels generally show great promise for use in storage tanks but the pore distributions in these materials range from microporous (<2 nm) to macroporous (>50 nm) resulting in poor volumetric densities. Framework structures also have a range of free space dimensions that can be in the mesoporous regime (2 to 50 nm) which makes a number of these materials less than ideal for storage applications. Moreover, typical sorption enthalpies of 4 to 6 kJ/mole are close to thermal energies, requiring low temperatures if large quantities of hydrogen are to be sorbed. Our work is focused on addressing both of these areas.

Approach

In our previous annual report, we noted high surface area to be amongst the criteria for high gravimetric density storage [1]. Having determined the validity of this trend for carbon aerogel sorbents, we have focused our efforts over the past year on determining the optimal microporous size distributions necessary for maximizing volumetric densities. Given that a concomitant goal of this project is to assess exothermic properties associated with hydrogen sorption (refueling), we have expended effort in determining sorption enthalpies associated with narrow pore size distributions. We have accomplished this by using an analogue of the Clausius-Clapeyron equation where $\Delta H = R[T_1 T_2 / (T_2 - T_1)] \ln(P_2 / P_1)$ [2] for isotherms taken at 77 and 87 K. The use of temperatures that are close to each other using this analysis is required in order to maximize the range of data (loading) along the x-axis.

We have also worked in collaboration with NIST in order to assess sites associated with initial loading of molecular hydrogen and to assess exothermic properties associated with a narrow pore size and coordinatively unsaturated metal center framework structure MOF-74 [3]. This is especially important as typical framework structures that have high surface areas, also have very low densities, ultimately yielding a low volumetric density sorbent.

Results

Figure 1a shows 77 and 87 and 195 K isotherm traces from a microporous CNS-201 activated carbon from Carbone Canada that had a pore distribution reported in the literature to peak at 1.1 nm. The

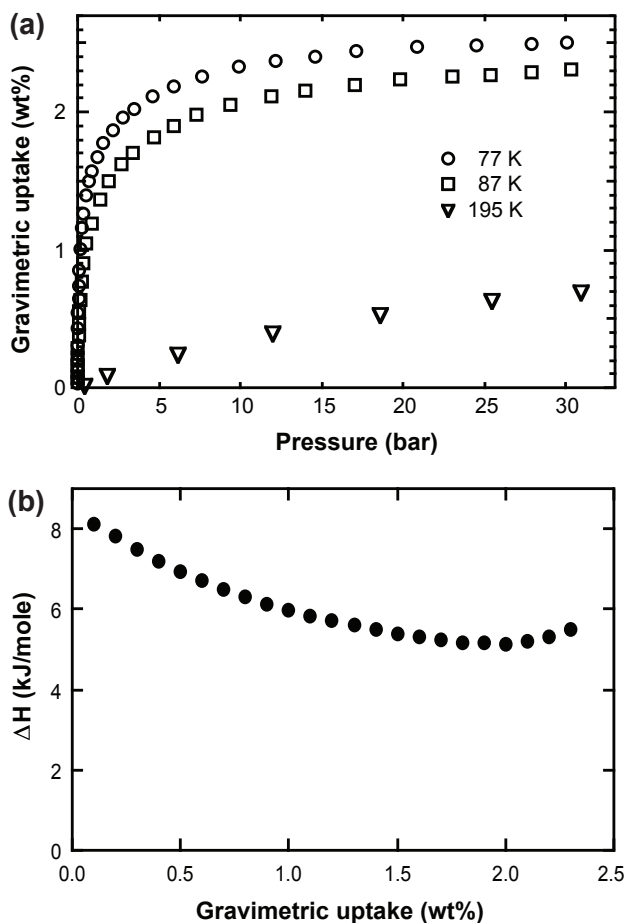


FIGURE 1. (a) Isotherm Traces for a CNS-210 Activated Carbon (b) Isothermic Enthalpy of Adsorption for this Sample using Data Taken at 77 and 87 K

Brunauer-Emmett-Teller (BET) surface area of this material was measured to be $\sim 1,160 \text{ m}^2/\text{gm}$ by Micromeritics in Norcross, Georgia. While this is a modest surface area in comparison to activated carbons and carbon aerogels that can reach surface areas of $>3,300 \text{ m}^2/\text{gm}$, carbons that are microporous (< 2 nm) are particularly valuable in determining the pore size targets for sorbents of this type. Figure 1b shows the isothermic enthalpy of adsorption for CNS-201. The heat starts initially at 8 kJ/mole (8.5 kJ/mole from a Henry's law analysis) but drops to $\sim 5 \text{ kJ/mole}$ as a function of loading. We note that the role of microporosity in this case appears to promote a higher initial sorption enthalpy over the 4 to 6 kJ/mole that is typical of most carbons.

Figure 2a shows 77 and 87 K isotherm traces from a phenol-aldehyde-based carbon fiber, Kynol ACF 1603-20, which has a BET surface area of $\sim 2,140 \text{ m}^2/\text{gm}$. Figure 2b shows 77 and 87 K isotherm traces from a similar fiber, Kynol ACF 1603-10, which has a BET surface area of $\sim 917 \text{ m}^2/\text{gm}$. The hydrogen uptake in these materials scales roughly with BET surface area.

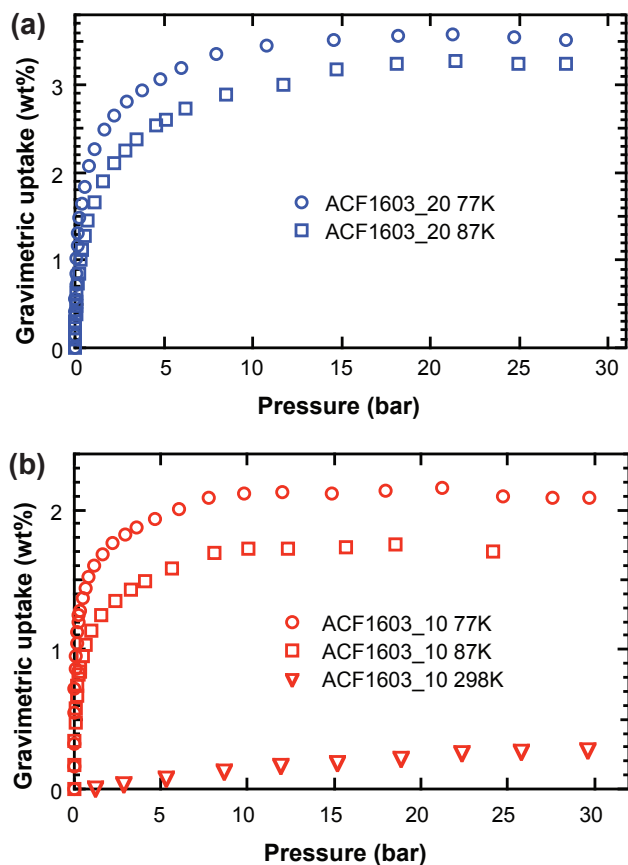


FIGURE 2. (a) Isotherms from a Kynol activated carbon fiber with a surface area of 2,100 m²/gm that is microporous. (b) Isotherm from a similar activated carbon fiber but with a pore size that peaks at ~5.5 Å.

Of note is the fact that the typical maximum of the surface excess sorption in carbons is at usually between 30 and 40 bar pressure. In ACF1630-20, the maximum surface excess value is reached at 20 bar and for ACF1630-10, the maximum is reached at 10 bar.

Figure 3a shows the incremental surface area as a function of pore dimension for CNS-201 and Kynol ACF 1603-20. The pore distributions in each of these materials are similar and appear to peak at ~5 Å. Of interest is the fact that while the CNS-201 sample was generally believed to have a peak distribution at 11 Å, that value appears to be the mean value, with the peak in surface area actually taking place at a much smaller dimension. Figure 3b shows a comparison of ACF 1603-10 and -20. The sharp narrow distribution of pores in ACF 1603-10 is one of the best examples of a material of this type.

Figure 4 shows a summary of isosteric heat behavior in microporous sorbents including MOF-74, CNS-201 and ACF 1603-10 and -20. The narrow distribution ACF1603-10 shows a constant isosteric heat as a function of loading. The broader distribution CNS-201 and ACF1603-20 show initially high isosteric heats that

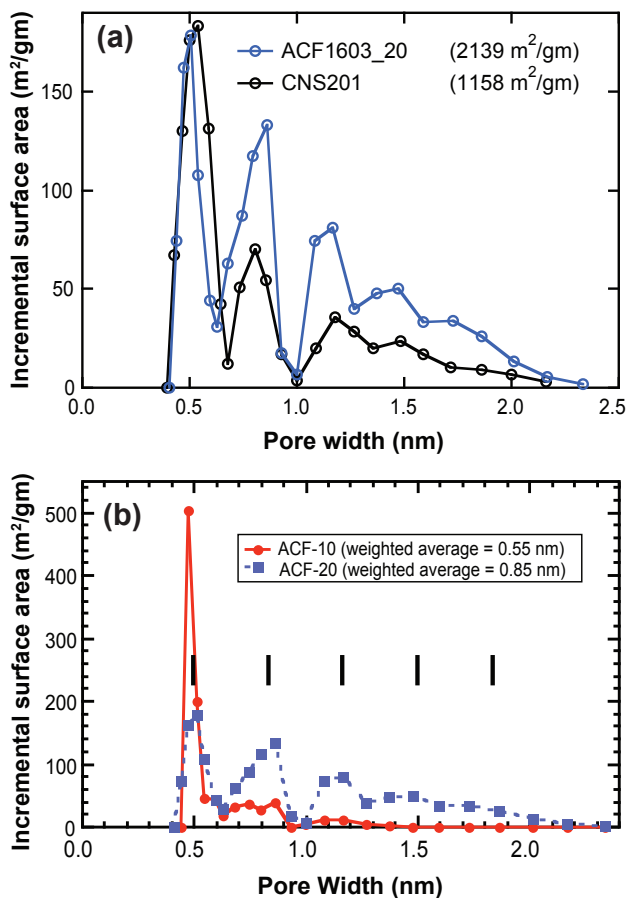


FIGURE 3. (a) Incremental surface area as a function of pore dimension. The integrated areas of the data appropriately scale with surface area. (b) Comparison of the two Kynol activated carbon fibers and show that the sample ACF1603-10 has a narrow pore size distribution.

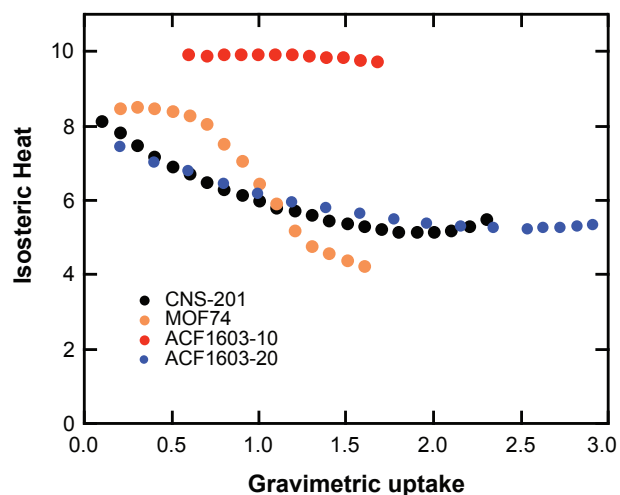


FIGURE 4. Isosteric Enthalpies for the Sorbents that We Studied this Year

start at ~8.5 kJ/mole, but that begin to drop to a typical value of 5 kJ/mole, due presumably to adsorption onto

sites with larger pore sizes that resemble a typical carbon surface. We can compare these with data that were presented in last year's report, in which the MOF-74 isosteric heat drops from ~8.5 to 4 kJ/mole.

Conclusions and Future Directions

Sorbents for non-dissociative hydrogen storage offer higher storage densities than compressed gas storage alone. Having established the surface area dependence in carbon aerogels, we have assessed the effect of pore sizes in the micropore regime in order to improve the volumetric density and we have probed the effect of pore size on isosteric heat. Micropore sorbent geometries will result in higher initially isosteric heats but these values tend to drop to values that are typical of carbon surfaces as a function of loading. Our overall work has seen isosteric enthalpies of adsorption at zero coverage that range from 8.5 to 4 kJ/mole. We expect these values to be typical of carbon-based sorbents.

While pore sizes near 5 Å show some enhancement as a function of surface area, and while this dimension shows advantages from the standpoint of achieving the maximum of surface excess at ~10 bar pressure, a pore dimension of closer to 10 Å will be better optimized for gravimetric and volumetric density.

We anticipate continued collaboration with Lawrence Livermore National Laboratory on aerogel synthesis that aims to promote a high level of microporosity in the 10 Å range. We also intend to synthesize other framework structures that consist of microporous geometries and that offer some prospect of homogeneous isosteric heat behavior. We will also continue to assess the optimal temperature range in sorbents that offers the best compromise in maximizing surface excess sorption.

FY 2008 Publications/Presentations

1. "Increasing the density of adsorbed hydrogen with coordinatively unsaturated metal centers in metal-organic frameworks," Yun Liu, Houria Kabbour, Craig M. Brown, Dan A. Neumann, Channing C. Ahn, Langmuir, published online March 27, 2008, 10.1021/la703864a.
2. "Henry's Law and Isosteric Heats in Physisorbents," Channing Ahn and Houria Kabbour, invited presentation: International Symposium on Materials Issues in a Hydrogen Economy, November 12-15, 2007, Richmond, Virginia.
3. "Impact of coordinatively unsaturated metal sites on hydrogen affinity and surface packing density," Craig M. Brown, Yun Liu, Houria Kabbour, Dan A. Neumann, and Channing Ahn, American Chemical Society, Spring 2008 Natl. Mtg. New Orleans.

References

1. "Toward New Candidates for Hydrogen Storage: High-Surface-Area Carbon Aerogels," Houria Kabbour, Theodore F. Baumann, Joe H. Satcher, Jr., Angélique Saulnier and Channing C. Ahn, Chem. Mater. 18 (26), 6085 (Dec. 2006).
2. see for instance, Adsorption by powders and porous solids, F. Rouquerol, J. Rouquerol and K. Sing, 1999, Academic Press.
3. "Increasing the density of adsorbed hydrogen with coordinatively unsaturated metal centers in metal-organic frameworks," Yun Liu, Houria Kabbour, Craig M. Brown, Dan A. Neumann, Channing C. Ahn, Langmuir, published online March 27, 2008, 10.1021/la703864a.