

IV.C.11 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 DOE targets for gravimetric and volumetric capacity are targeted on a system's basis of 5.5 wt% (1.8 kWh/kg) and 0.040 kg/L (1.3 kWh/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

- Completions of synthesis of MOF-177 for neutron scattering studies (that are still in progress).
- Synthesis of intercalated graphites for isosteric heat analysis. These systems are one of the few examples of materials that maintain constant isosteric heat, an important material parameter for designing an engineering system. The isosteric heat in KC24, RbC24 and CsC24 are 9, 11, and 13 kJ/mole H₂ respectively, and unlike most other physisorbents where the heats decay as a function of loading, the values from intercalated graphites are generally constant as a function of loading.
- Improvement to fits of empirical data through modeling of virial equations, yielding improved isosteric heat analysis.
- Synthesis and analysis of a 3 gm batch of Pt loaded super-activated carbon for spillover analysis. All of our previous attempts at determining the extent spillover in carbon systems yielded inconsistent data. We have now concluded that as measured via normal Sieverts volumetric techniques, that any possible enhancement of uptake that might occur through dissociation reactions, is minimal compared to the amount of catalyst weight that is required to initiate dissociation.



Introduction

High surface area-based physisorbents are a class of materials that are closer to engineering viability for high gravimetric density reversible onboard storage applications, than other onboard reversible candidate materials, 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. An important parameter in gauging material properties that will be necessary for consideration for engineering systems is the isosteric heat, or the heat produced during the hydrogenation process. Any material system in which the isosteric heat decays with hydrogen loading, offers poor viability for engineering applications as initially high heats of adsorption result in hydrogen that is difficult to extract unless storage tanks are designed for excursions in both pressure and temperature.

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) that 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.

Recently reported work has also addressed the possibility of di-hydrogen dissociation in the presence of Group VIII catalysts, leading to the possibility that the resulting atomic hydrogen might also be a suitable means of sorbing hydrogen onto high surface area carbons. We have put considerable effort into probing the extent to which this phenomenon exists in a way that is practical to the DOE Hydrogen Program effort.

Approach

We have continued to focus our efforts over the past year in determining the behavior of unmodified carbons and the optimal microporous size distributions necessary for maximizing volumetric densities. In addition, we have considered the prospective requirements of the Engineering Center in designing a system that is capable of handling the appropriate heat transfer conduits associated with the exothermic heat of hydrogenation. Given that a concomitant goal of this project is to assess exothermic properties associated with hydrogen sorption (refueling), we continue to expend effort in determining sorption enthalpies associated with narrow pore size distributions, and in improving the fitting functions used in interpolating data points acquired from our Sieverts apparatus. We continue to perform our isosteric heat analysis through the use of 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. We have also performed experiments at dry ice temperatures (195 K) where appropriate.

We have also re-examined work on material systems that are capable of displaying constant isosteric heat in the hopes that the physical principles behind such systems can be applied to improve sorbent design.

A large fraction of our work this past year has also been expended in spillover system synthesis and analysis. Because of the problems associated with low absolute molar quantities being measured by other research groups, we have invested heavily into producing large quantities of candidate spillover material in order to be sure that our data is free of errors associated with pressure measurements at the resolution limits of our baratron gauges.

Results

Figure 1 shows an updated version of the isosteric heat behavior of ACF10, ACF20 and a microporous CNS-201 activated carbon from Carbone Canada. The result from ACF10 is particularly important as we had believed previously that the near mono-sized pore size in this sample had a constant isosteric heat as reported last year. Subsequent analysis on our part using updated fitting algorithms shows that the isosteric heat in this sample decreases, as in all other unmodified carbons of which we are aware. In typical porous carbons, we expect the sorption enthalpy at near maximum hydrogen coverage to end up at around 5 kJ/mole. This result suggests that geometry alone will not suffice in designing an appropriate sorbent with constant enthalpy, and that some chemical modification of the surface, in addition to an appropriate slit pore geometry, will be necessary in order to maintain a constant isosteric heat.

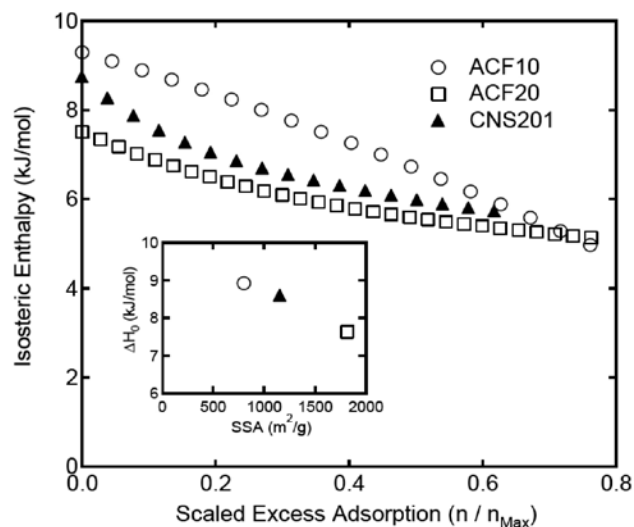


FIGURE 1. The H_2 isosteric enthalpy of adsorption for ACF10, ACF20 and CNS201 as a function of excess adsorption. Inset: the isosteric heat is plotted as a function of the fractional amount of adsorption (excess adsorption divided by the saturation adsorption amount at 77 K).

Figure 2a shows 77 and 87 K isotherm traces from the most important of our baseline systems that we have analyzed as it is a system that demonstrates that constant isosteric heat is possible. The slit pore geometry of the Stage 2 KC24 intercalated graphite shows that some systems are indeed capable of retaining constant sorption enthalpy as a function of loading as denoted in Figure 2b, showing a nearly straight enthalpy.

Figure 3a shows how an enhanced and constant isosteric heat can perhaps obviate some of the low operating temperature concerns of physisorbents. In the case of CsC24, which has a constant 13 kJ/mole isosteric heat, nearly 2/3 of the 77 or 87 K maximum capacity of the sorbent can be achieved at 195 K as shown in Figure 3b, albeit at modest pressures of 60 bar. We believe that this is the first empirical example of a high/constant isosteric heat material that demonstrates that higher temperature sorption is possible with a high constant isosteric heat.

Figure 4 shows low and high-pressure data ranges taken from two different sample masses that were prepared for “spillover” analysis. The difficulty encountered with the measurement of small sample masses for the 1% gravimetric uptake that is typical of such systems is that the absolute molar quantities of hydrogen that are measured are at the noise limit of

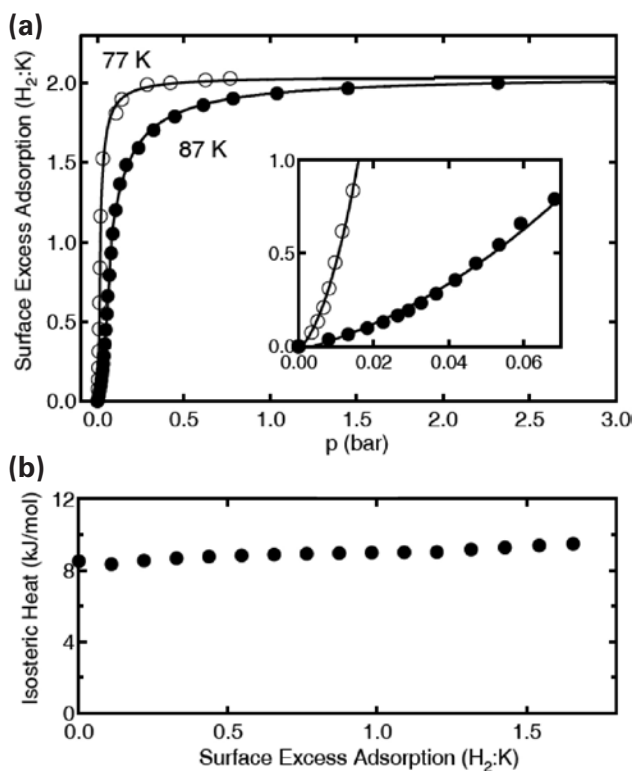


FIGURE 2. (a) Shows 77 and 87 K isotherms with a blowup of the low-pressure regime in the inset. (b) Beneath the isotherms shows a plot of the isosteric enthalpy of adsorption and shows nearly constant sorption enthalpy values with loading.

typical Sieverts instruments. We have synthesized and taken measurements from roughly 0.2 and 3 gm size samples that have Pt additions and we note the extent of the error bars when the small quantities of material are measured. We have concluded from this work and other data that the overall extent of spillover is negligibly small in comparison to the absolute value of hydrogen that can be sorbed in an unmodified carbon.

Figure 5 shows a comparison of a super-activated carbon that we have analyzed for ambient temperature uptake. The sample was also measured at National Institute of Standards and Technology and that data is shown in red.

Conclusions and Future Directions

Having established the surface area dependence in carbon aerogels in previous work, we have assessed the thermodynamic effects of pore sizes in the micropore regime by probing the 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

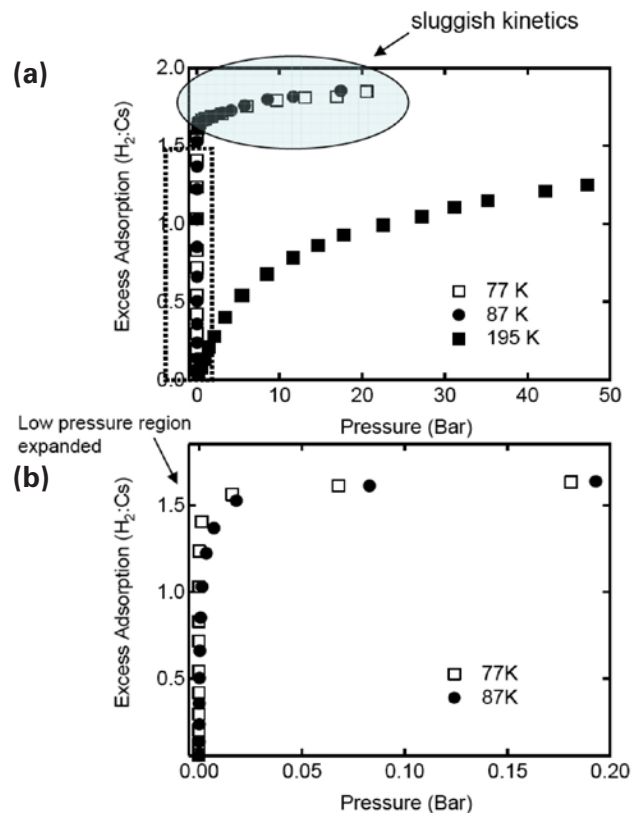


FIGURE 3. (a) Shows isotherms from CsC24, a 13 kJ/mole sorption enthalpy system and shows the important 195 K isotherm, that retains a high percentage of the 77 and 87 K maximum loading value. Typical carbons would have data half of this value. (b) The lower plot shows a blow-up of the low-pressure regime.

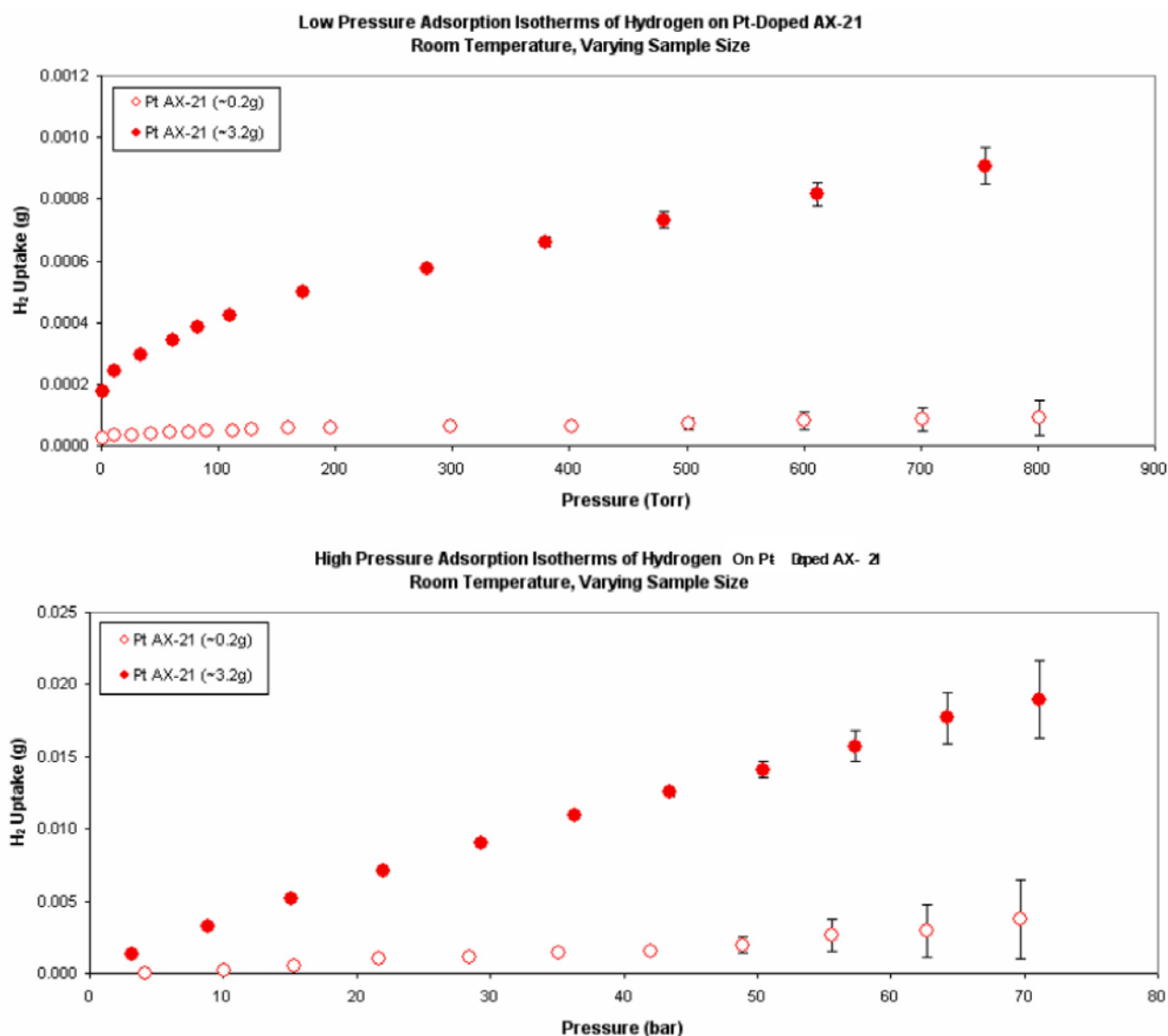


FIGURE 4. Isotherms from spillover samples using 0.2 gm and 3.2 gm sample sizes. Our work concludes that errors in measurement and analysis from using small sample sizes can result, yielding large error bars. We have been unable to detect for the presence of the spillover effect when using large sample quantities, in any of our work.

work has seen isosteric enthalpies of adsorption at zero coverage that range from 8.5 to 5 kJ/mole. We expect these values to be typical of carbon-only-based sorbents.

Because chemical modification of carbons will be necessary to maintain a constant isosteric heat, we have looked at Stage 2 alkali metal intercalated carbons and have found that these do retain constant isosteric heat values as a function of hydrogen loading. Most importantly, in a CsC24 system, this constant isosteric heat of 13 kJ/mole results in high loading fractions over that of unmodified carbons at higher than 77 K temperatures. This system can achieve >60% of the 77 K hydrogen capacity, at 195 K.

We plan to spend the last year of this project in the synthesis and analysis of BC3 templated carbons. While the study of framework structures has been a part of our work effort over the past several years, we feel that BC3 may offer better possibilities for sorbing hydrogen given a zeolite based open structure that we intend to synthesize.

FY 2009 Publications/Presentations

1. J.J. Purewal, J.B. Keith, C.C. Ahn, B. Fultz, C.M. Brown and M. Tyagi, PRB 79, 054305 (2009).
2. Justin Purewal, Bulletin of the American Physical Society, Volume 54, Number 1 (2009).

High Pressure Adsorption Isotherms of Hydrogen on Maxsorb MSC-30 Room Temperature

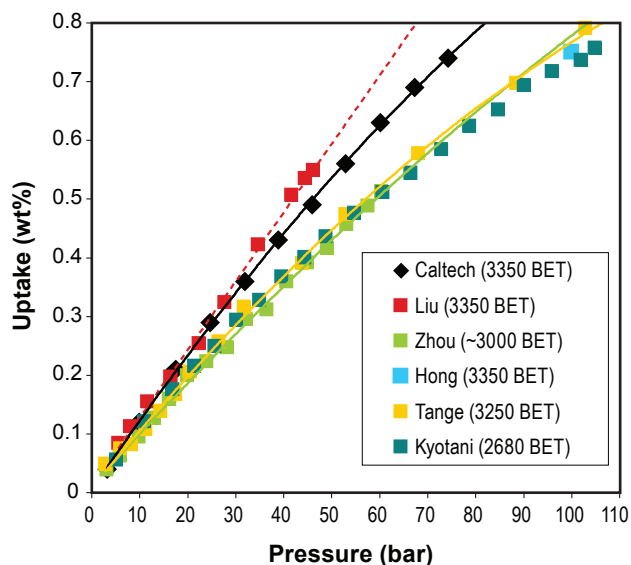


FIGURE 5. Comparison of Caltech and NIST (red and black data points), with that of published values of otherwise unmodified super-activated carbon hydrogen uptake at ambient temperature as a function of pressure.

3. J.J. Purewal, H. Kabbour, J.J. Vajo, C.C. Ahn and B. Fultz, *Nanotechnology* 20, 204012 (2009).

4. “Hydrogen Spillover in Platinum Doped Superactivated Carbon.” presented at the “Summer School on Methods and Applications of Neutron Spectroscopy” at the NIST Center for Neutron Research (2009).

5. “Vehicular Hydrogen Storage with Ad(b)sorbent Materials,” C. Ahn, APS Energy Research Workshop Program and Hydrogen Focus Topic Symposium chair, *American Physical Society, March 2009, Natl. Meeting, Pittsburgh.*