Enhanced Hydrogen Dipole Physisorption: Henry's Law and isosteric heats in microporous sorbents

Justin Purewal, Nick Stadie and Channing Ahn

Caltech

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Project ID#ST016

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Overview

Timeline

- Project start date:
  October 1, 2004
- Project end date:
  June 30th, 2010
- Percent complete: 100%

On board hydrogen storage Barriers and Targets

(B) Weight and volume of on board hydrogen storage systems

(N) Low temperatures that sorbent-based systems typically need to work in order to store high hydrogen densities.

Budget

- Total project funding
  - DOE share $1M (5 yrs)
  - Contractor share $250k (5 yrs)
- Funding for FY07
  - DOE share $175k
  - Contractor share $43.5k
- Funding for FY08
  - DOE share $175k
  - Contractor share $43.5k

Partners

Interactions/collaborations:

J. J. Vajo, HRL Laboratories
J. Reiter, J. Zan, Jet Propulsion Lab.
T. Baumann, LLNL.
Craig Brown, Dan Neumann, NIST
Carter Kittrell, J. Tour, Rice University
T. Gennett, L. Simpson, NREL

Objectives

- Kinetics of molecular H_2 physisorption relatively fast but adsorption enthalpies typically close to thermal energies requiring low temperatures.
- Past work concentrated on synthesizing and evaluating maximal surface area sorbents (maximizing number of sorption sites), necessary for high gravimetric molecular H_2 storage.
  - Activated carbons, aerogels and metal organic frameworks effective, if not optimized, candidate materials as they presently work best at 77K temperature and pressures of 30 to 40 bar with sorption enthalpies of ~4-8 kJ/mole (from our work, presently at 5.4 wt% surface excess at 77K for a 2447m^2/gm surface area activated carbon, if total including free volume taken into account, gravimetric density closer to 10 wt%).
- Typical sorbents a combination of micro (<2 nm) and mesoporous (2 to 50 nm) microstructures. Enhancement of microporosity in addition to surface area necessary in order to maximize volumetric density. Typical physisorbent volumetric densities presently ~38 gm/liter at 77K).
  - Also expect enhancement of sorption enthalpy with appropriate pore size.

Approach

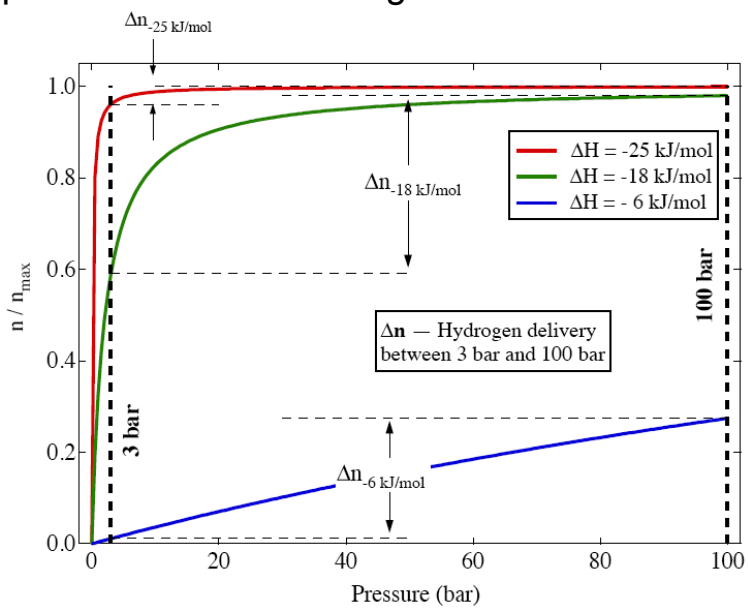
- Synthesis of framework structures via normal solvo-thermal routes.
- Evaluation of aerogel properties in collaboration with LLNL.
- Evaluation of microporous activated carbon properties.
- Adsorption/desorption evaluation with volumetric Sieverts apparatus capable of measurements of samples at 77, 87, 195, and 298K temperatures.
- Thermodynamic evaluation of sorption enthalpies via Henry's law region of isotherm and/or isosteric enthalpy of adsorption.
- Neutron scattering (diffraction and inelastic) of promising systems in collaboration with NIST.

Technical Accomplishments: High, constant isosteric enthalpy of adsorption

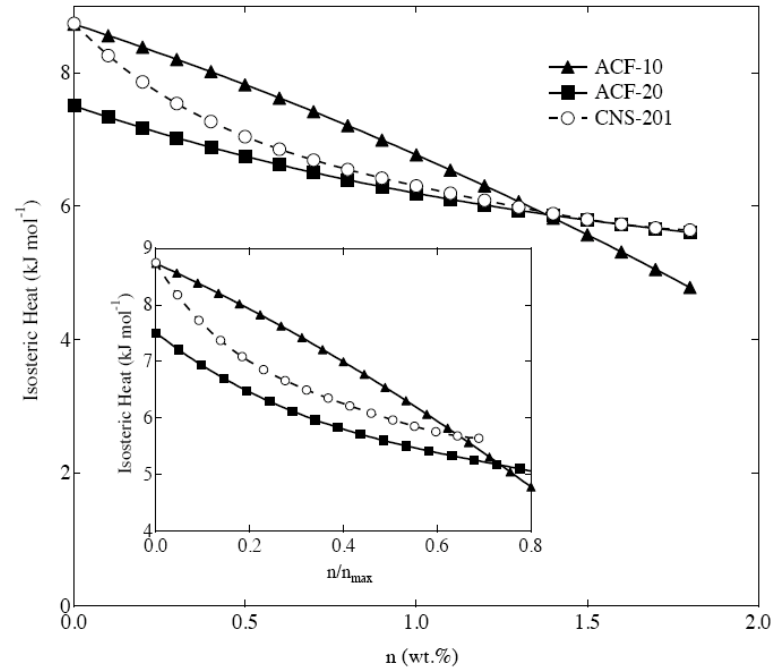
Background:

In virtually all carbons, we can expect a decay in the isosteric enthalpy of adsorption, resulting from isotherm behavior. From our previous work on microporous carbons, we can see at the right the the sorption enthalpy decays, yielding weaker H_2 surface interactions with loading.

A constant isosteric would simplify the engineering requirements for tank design as shown below



Langmuir isotherms for three different adsorption enthalpies (ΔH). Hydrogen delivery (Δn) for each isotherm is indicated by the vertical distance between the adsorption amounts at 3 bar and 100 bar.

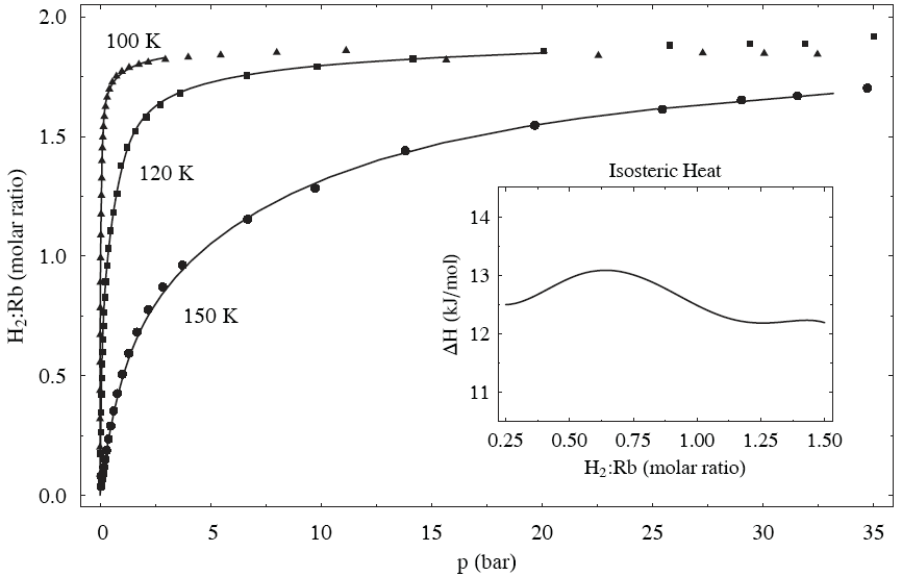


But the H_2 isosteric enthalpy of adsorption as shown above for typical carbons ACF-10, ACF-20, and CNS-201 as a function of surface excess adsorption show that a decrease in isosteric heat is typical. Inset: The isosteric heat is plotted as a function of the fractional amount of adsorption (excess adsorption divided by the saturation adsorption amount at 77 K).

Technical Accomplishments: High isosteric enthalpy of adsorption (cont'd)

Our work on Stage 2 intercalated graphites offers a practical system for assessing the role of constant isosteric heat. Measurements were performed on a Sieverts instrument at NCNR (NIST). Temperature control achieved via closed-cycle helium refrigeration unit, which enabled data to be collected at temperatures different than the standard 77K and 87 K. The collection time for each isotherm point 15 min, regardless of whether equilibrium was reached within that duration.

In the case of RbC_{24} shown to the right, the result of having a nearly constant isosteric heat of over 12kJ/mole H_2 shows that <u>higher than 77K temperature adsorption is possible</u> and given high enough pressure, the 100 K uptake limit can be reached at 150 K.

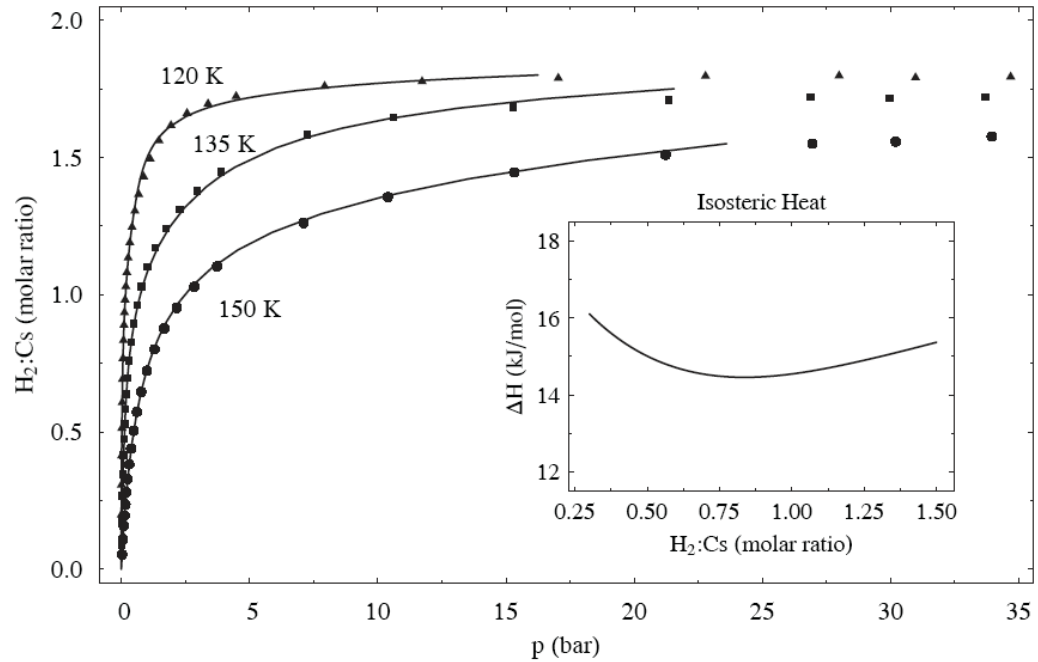


Adsorption isotherms of RbC_{24} at 100 K, 120 K, and 150K fitted to a virial-type thermal equation. Inset: Isosteric heat as a function of adsorption amount.

Technical Accomplishments: Constant isosteric enthalpy of adsorption (cont'd)

Similarly for our work on CsC_{24} Stage 2 intercalated graphite an isosteric heat of over 14 kJ/mole results in the capability of higher temperature adsorption reaching the lower temperature value, given high enough pressure. Again, measurements were performed on a Sieverts instrument at NCNR (NIST).

In the case of CsC_{24} shown to the right, the result of having a nearly constant isosteric heat of over 14kJ/mole H_2 shows that higher temperature adsorption is possible and given high enough pressure, the 120 K uptake limit can be reached at 150 K.

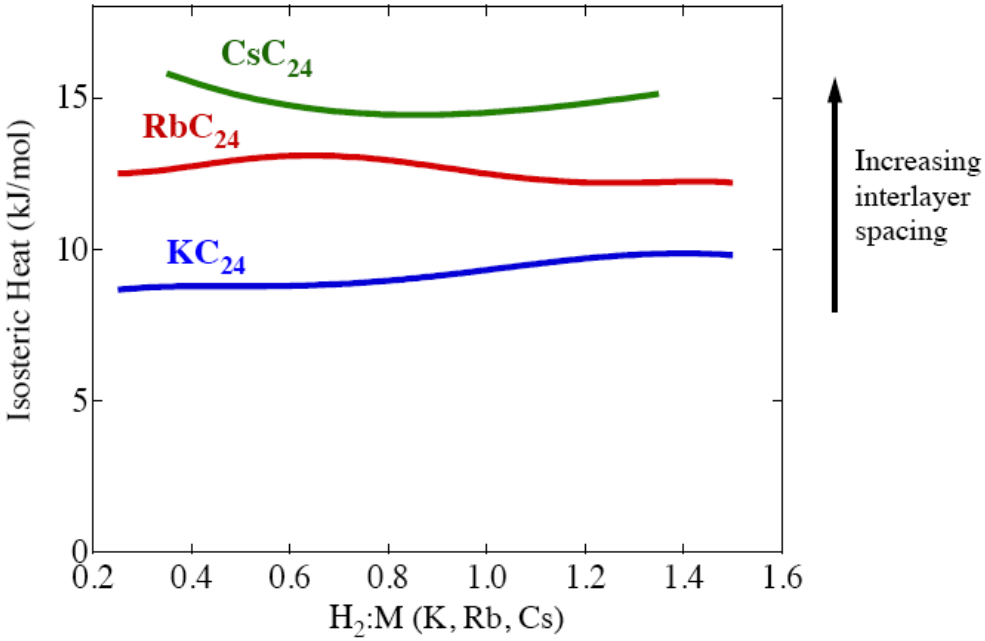


Adsorption isotherms of CsC_{24} at 120 K, 135 K, and 150K fitted to a virial-type thermal equation. Inset: Isosteric heat as a function of adsorption amount.

Technical Accomplishments: Isosteric enthalpy of adsorption for three Stage 2 intercalated graphites

To the right is a summary of isosteric heats for the stage 2 alkali metal intercalated compounds that we have evaluated in this program. The consistency of the values arises presumably from the combination of electron back-donation of the alkali metal to the graphitic layers, and to the narrow "slit-pore" geometries that run from ~5.3 to ~5.8 Å.

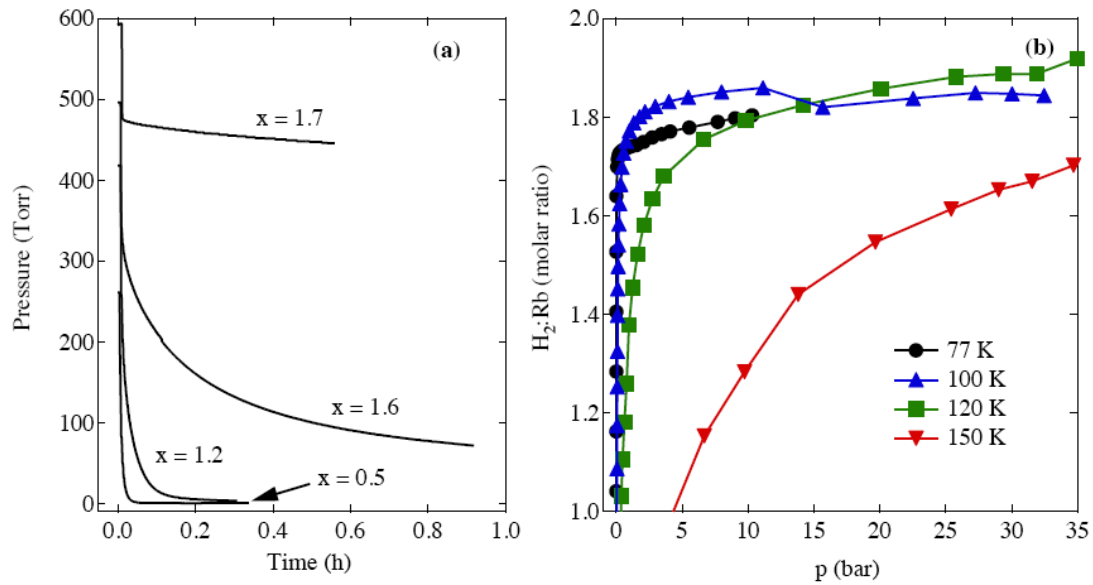
While the gravimetric uptake is on the order of 1wt% for stage 2 intercalation compounds, few materials show consistently high isosteric heats over the sorption range. These materials show that higher temperature adsorption is possible given high enough adsorption enthalpies, over the entire sorption range.



Comparison of hydrogen adsorption enthalpies for KC_{24}, RbC_{24} and CsC_{24}, plotted as a function of composition.

Technical Accomplishments: Uptake kinetics in the RbC_{24} system

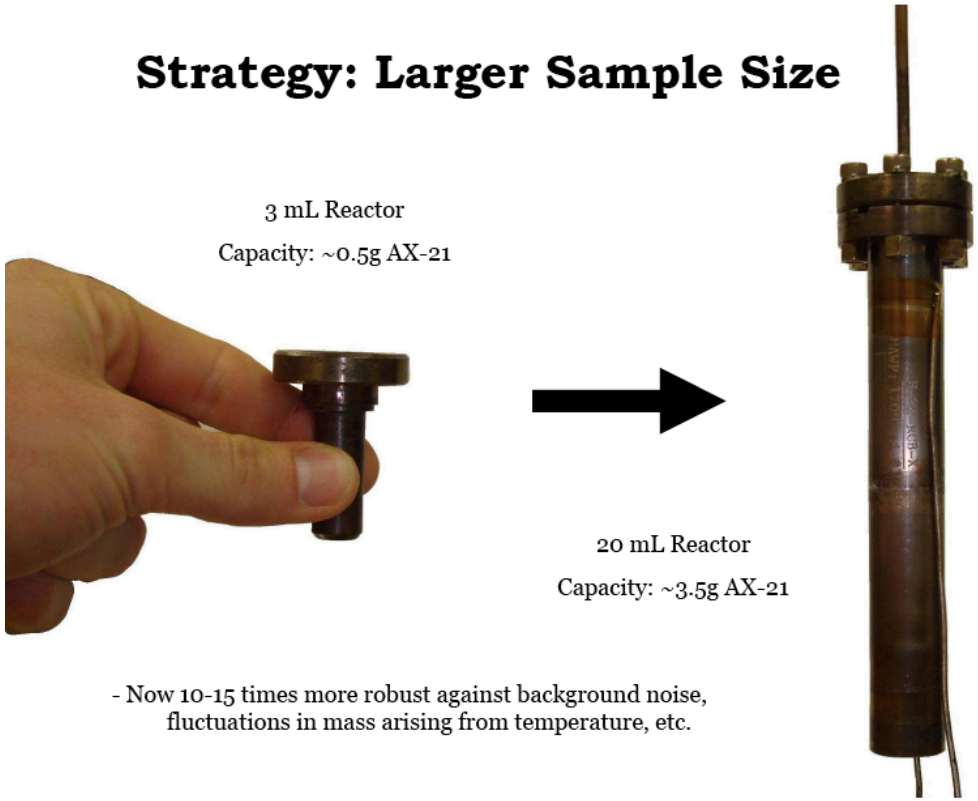
Kinetic limitations of adsorption appear significant in KC_{24} (as well as in RbC_{24} and CsC_{24}) at hydrogen compositions greater than x = 1:5. Few vacant adsorption sites for the H_2 to diffuse through, leading to site-blocking and correlation effects. Combined with the small jump attempt frequency which exists at these low temperatures, result is a reduction in the transport-diffusivity of the adsorbed hydrogen. Adsorption kinetics were measured for RbC_{24} at 77K at various hydrogen compositions, as shown at right. The manifold pressure plotted versus time for several different final compositions. At low H_2 compositions (e.g., x = 0:5) adsorption rapid, and equilibrium reached within minutes. At higher H_2 compositions (e.g., x = 1:6) adsorption extremely sluggish and equilibrium still not reached after an hour. Diffusion-limited adsorption more significant at low temperatures due to the lower jump attempt frequency.



Hydrogen adsorption kinetics of RbC_{24}. (a) Manifold pressure is plotted versus time for several compositions at 77 K. Traces are identied by their final composition $RbC_{24}(H_2)_x$. Pressure decreases versus time due to adsorption. (b) Plateau regions of the H_2 adsorption isotherms of RbC_{24} at 77 K, 100 K, 120 K, and 150 K.

Technical Accomplishments: Pt on C spillover analysis

One year spent in attempting to duplicate spillover results that show that H_2 uptake in Pt modified carbon[1] enhanced by nearly a factor of 2. Our initial work had problems with instrument/background noise so we prepared a large mass of sample according to the synthesis of reference (1).



- 30 samples were prepared by incipient wetness impregnation
- For each sample, 200mg of dried MSC-30 was dispersed in acetone magnetically stirred for 30 min at room temperature. 2mL solution of 50 mg of H_2PtCl_6 in acetone added drop-wise to the MSC-30 solution over 5min.
- Slurry removed and placed in an ultrasonic bath (50 W, 42 kHz, 1.9 L capacity) (60 min), magnetically stirred at RT for 24h.
- Acetone evaporated by heating sample at 333 K for 12h.
- Dry mixture transferred to ceramic boat and placed in He flow inside a horizontal quartz tube furnace to prevent moisture uptake.
- The furnace was preheated to 393 K and held for 2h under constant He flow.
- For reduction, gas flow switched to H_2 and furnace heated to 573 K and held for 2h.
- The flow again returned to He, and furnace allowed to cool to RT over 30 min.
- Each sample (~0.2g) was sealed in a glass vial in Ar atmosphere and
- stored in glovebox.
- Large number of 0.2g Pt-MSC-30 samples (~40) were prepared and then combined to achieve sample sizes up to 3.2g.

[1]Li, Y.; Yang, R. T. *J. Phys. Chem. C* **2007**, 111, 11086-11094

Technical Accomplishments: Pt on C spillover analysis: materials analyzed previously

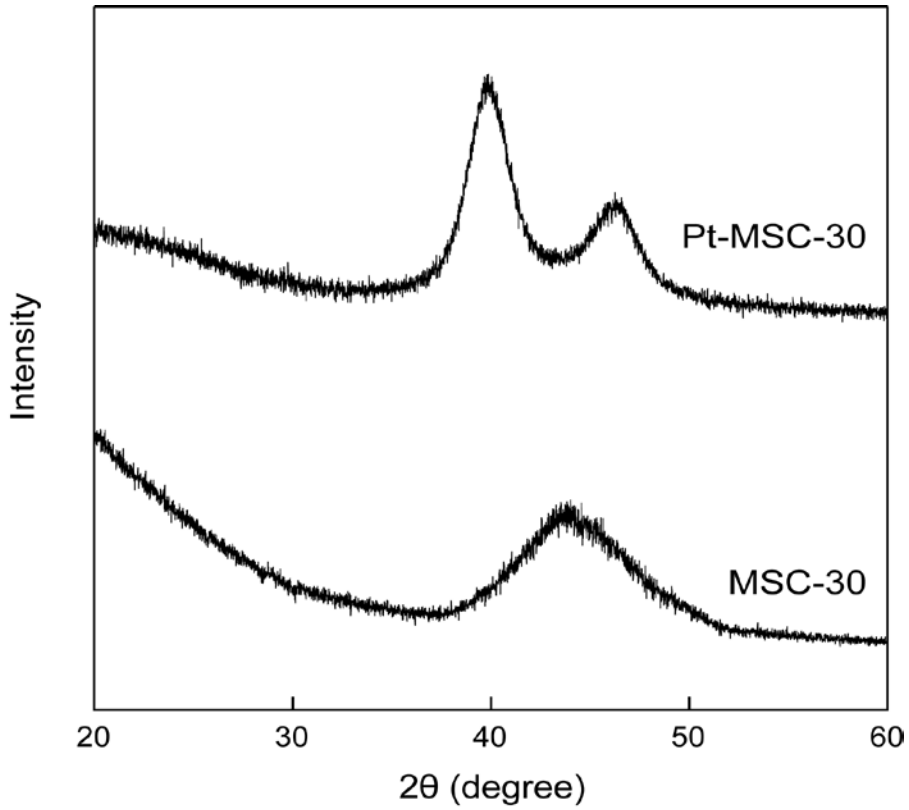
Material	BET SA† (m^2g^{-1})	H_2 Uptake‡ (wt%)
MSC-30 [1]	2680	0.56
MSC-30 [2]	3250	0.6
MSC-30 [3]	3000	0.54
MSC-30 *	3420	0.64
Pt-MSC-30 *	2810	0.59
AX-21 [4]	2880	0.5
Pt/AX-21 [4]	2518	0.9

BET surface areas (SA) and hydrogen uptake capacities reported for MSC-30, Pt-MSC-30, a similarly prepared Pt doped superactivated carbon, Pt/AX-21, and its precursor, AX-21.

* From this study. † Measured using N_2 at 77 K between 0.004-0.03 MPa. ‡ measured using H_2 at 300 K and 7 MPa.

[1]Nishihara, H.; Hou, P. X.; Li, L. X.; Ito, M.; Uchiyama, M.; Kaburagi, T.; Ikura, A.; Katamura, J.; Kawarada, T.; Mizuuchi, K.; Kyotani, T. *J. Phys. Chem. C* 2009, 113, 3189-3196.
[2]Kojima, Y.; Kawai, Y.; Koiwai, A.; Suzuki, N.; Haga, T.; Hioki, T.; Tange, K. *J. Alloys Compd.* 2006, 421, 204-208.
[3]Kiyobayashi, T.; Takeshita, H. T.; Tanaka, H; Takeichi, N.; Zuettel, A.; Schlapbach, L.; Kuriyama, N. *J. Alloys Compd.* **2002**, 330-332, 666-669.
[4]Li, Y.; Yang, R. T. *J. Phys. Chem. C* **2007**, 111, 11086-11094.

Technical Accomplishments: X-ray diffraction



XRD patterns of Pt-MSC-30 and unmodified MSC-30

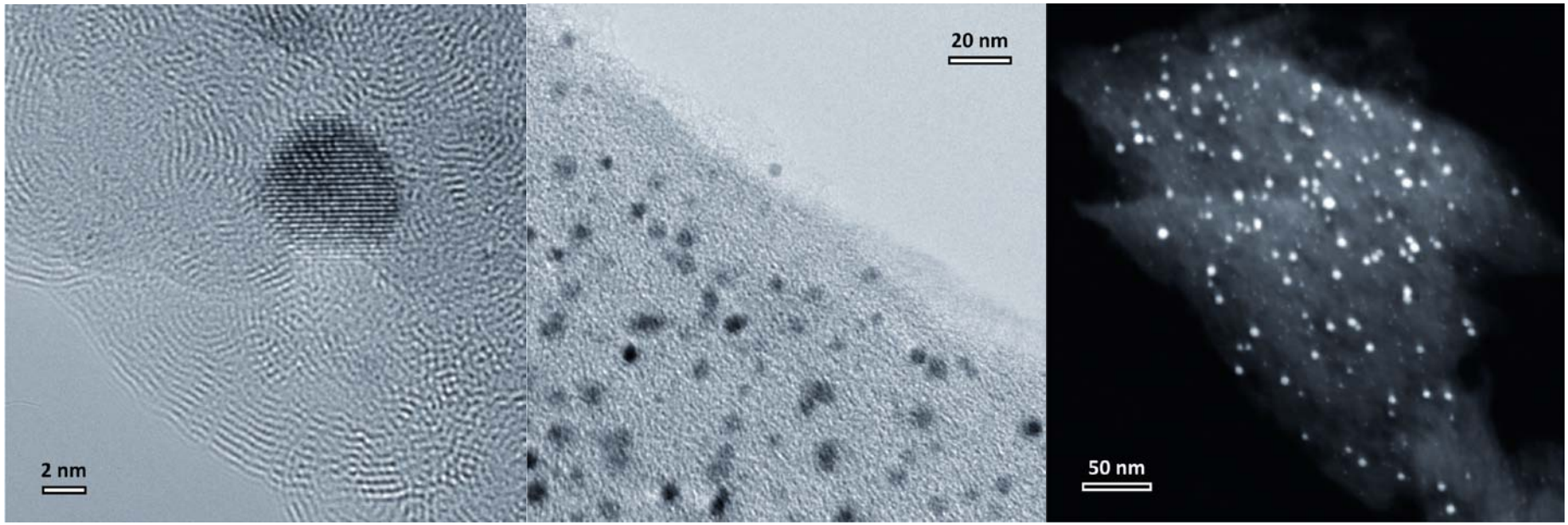
Broad peak centered at 2θ = 43° in the pattern for pure MSC-30 consistent with that reported for AX-21.

The dominant peaks in Pt-MSC-30 pattern at 2θ = 39.9° and 46.4° correspond to the (111) and (200) reflections characteristic of the cubic platinum crystal structure.

No platinum oxide phase peaks detected, suggesting fully reduced Pt metal nanoparticles in the sample.

From the widths of the diffraction peaks, mean crystallite diameter was calculated to be 7 nm using the Scherrer equation (using the constant 0.94 for spherical particles).

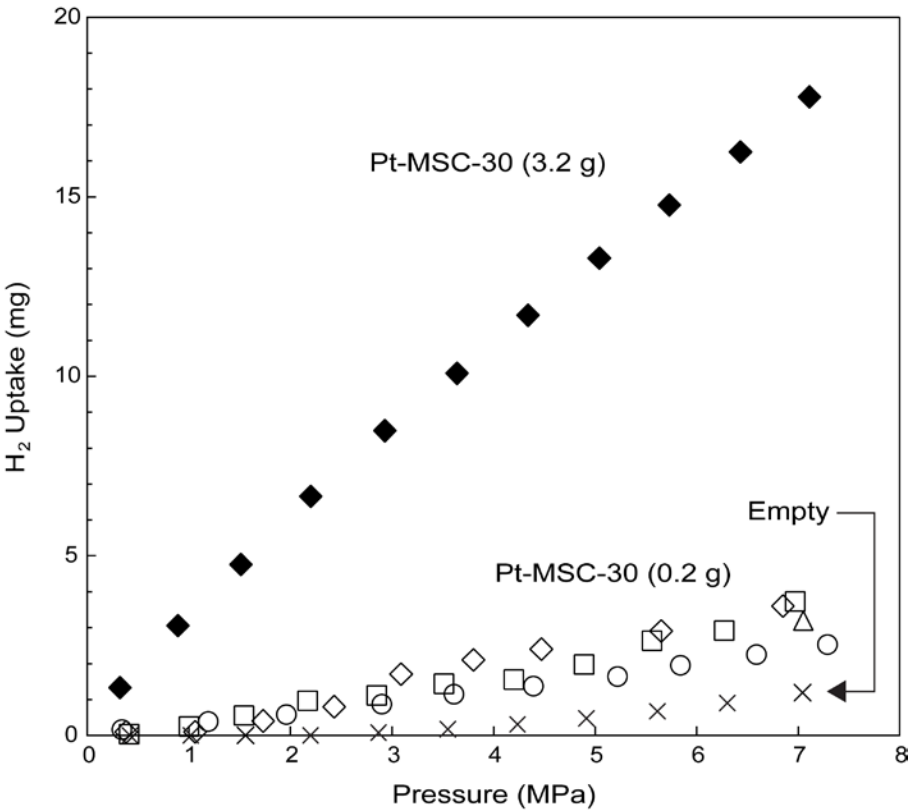
Technical Accomplishments: TEM



TEM images of Pt-MSC-30.

STEM image obtained using a HAADF detector verifies successful dispersion of Pt nanoparticles throughout sample and shows the size distribution of particles expected from this type of processing.

Technical Accomplishments: Mass dependent uptake



Isotherms collected for MSC-30 and Pt-MSC-30 at RT, varying sample size from 0.2-3.2 g.

Similar isotherm measurements for aluminum blanks of comparable volume to 0.2-3.2 g samples (0.1-1.5 mL) collected as control.

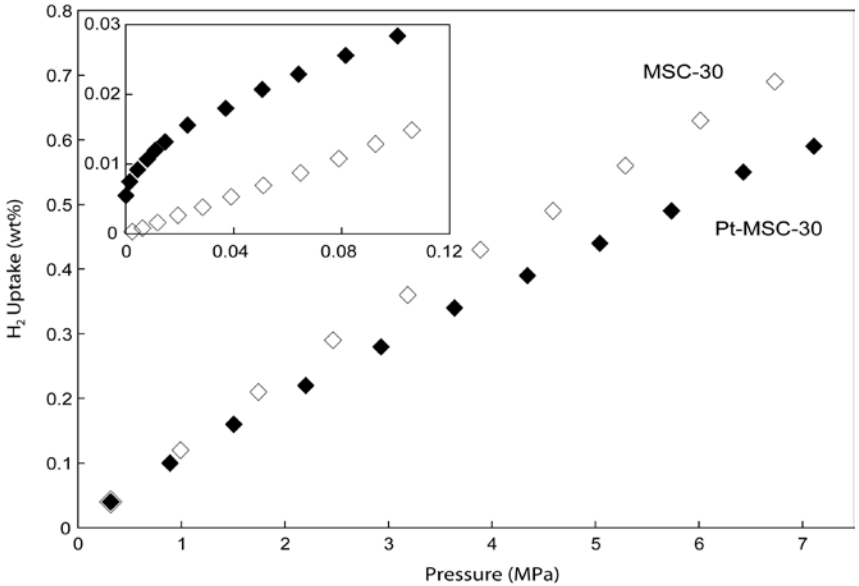
Comparison of measured hydrogen uptake (in mg H_2) as a function of pressure is shown for Pt-MSC-30 and the empty sample holder at left.

In small sample (0.2 g) experiments, adsorption equilibrium difficult to determine as RT fluctuations continued to slowly change pressure readings even after 60 minutes.

Therefore, equilibration step durations between 0.5-24 h were explored and compared. Increasing with the number of data points collected and the duration of time between steps, the room temperature isotherm data for small samples of Pt-MSC-30 showed uptake varying from 2.4-3.8 mg H_2 at 7 MPa.

Temperature changes of even 1°C over the course of an isotherm step were highly correlated with large apparent uptake during that step.

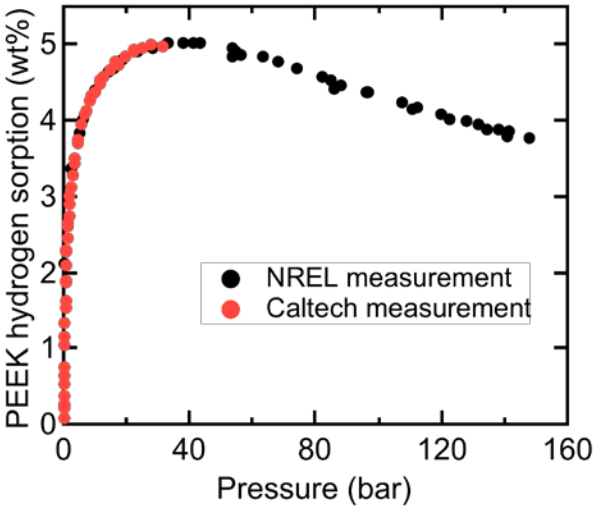
Technical Accomplishments: Isotherm from 3 gm sample

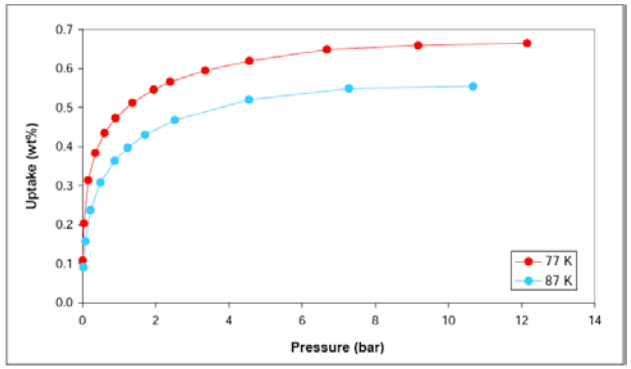


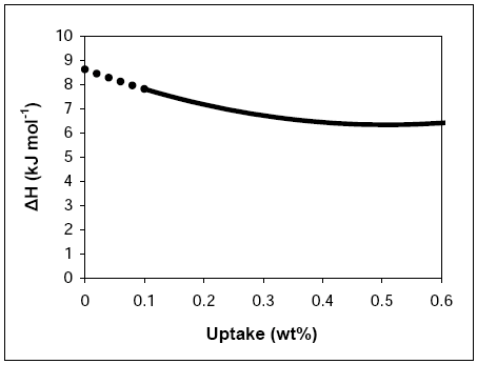
Hydrogen uptake isotherms for large samples (>3 g) of Pt-MSC-30 and unmodified MSC-30 at room temperature, corrected for empty sample holder adsorption, are shown at left. Equilibrium was reached in less than 60 min between each isotherm step and was easily distinguished from adsorption.

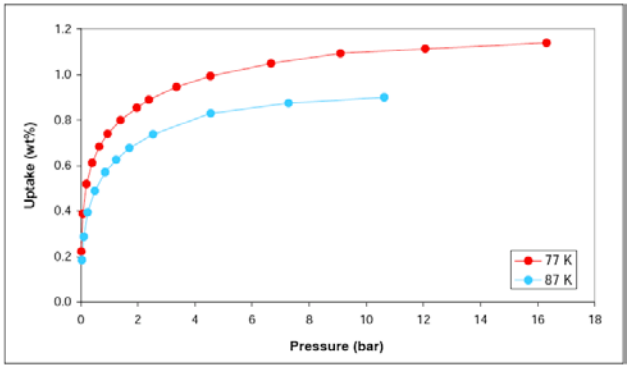
In pure MSC-30, the isotherm showed constant uptake as a function of pressure between 0-2 MPa. At pressures above 2 MPa, the slope decreased as uptake appeared to approach a plateau. At 6.7 MPa, hydrogen uptake in MSC-30 was 0.64 wt%, consistent with reported values for MSC-30 to within 0.06 wt%. In Pt-MSC-30, low pressure data showed a steep initial uptake of hydrogen between 0-0.01 MPa and then a similar constant slope region to MSC-30 between 0.04-2 MPa. The slope of the isotherm in Pt-MSC-30 also decreased slowly at pressures above 2 MPa. Hydrogen uptake at 7.1 MPa was 0.59 wt% in the Pt containing sample, slightly lower than for the unmodified MSC-30.

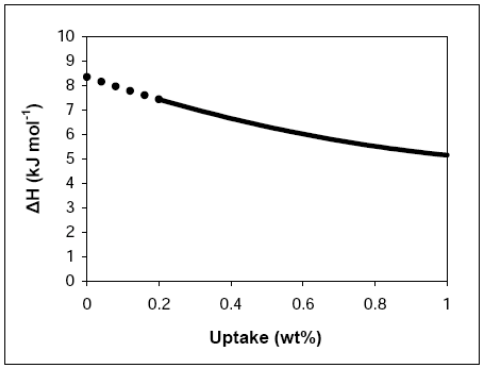
Technical Accomplishments: Collaborations with Duke and Rice Universities and NREL on 77K isotherm measurements

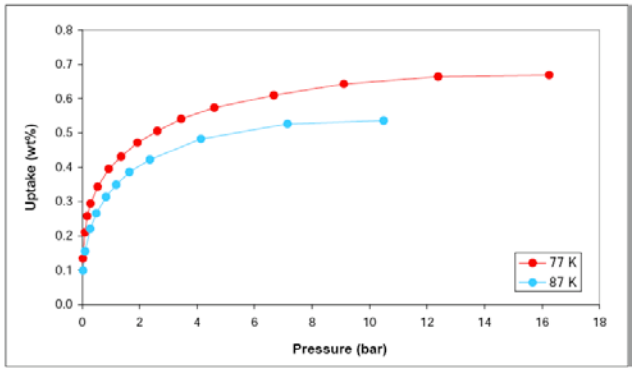


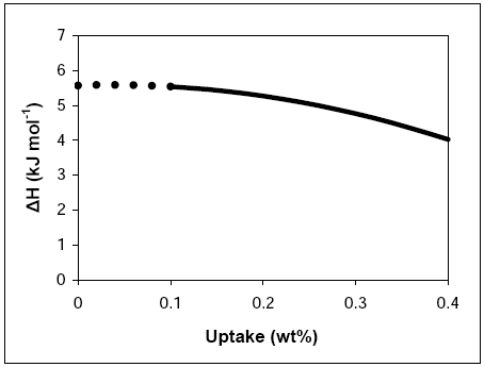








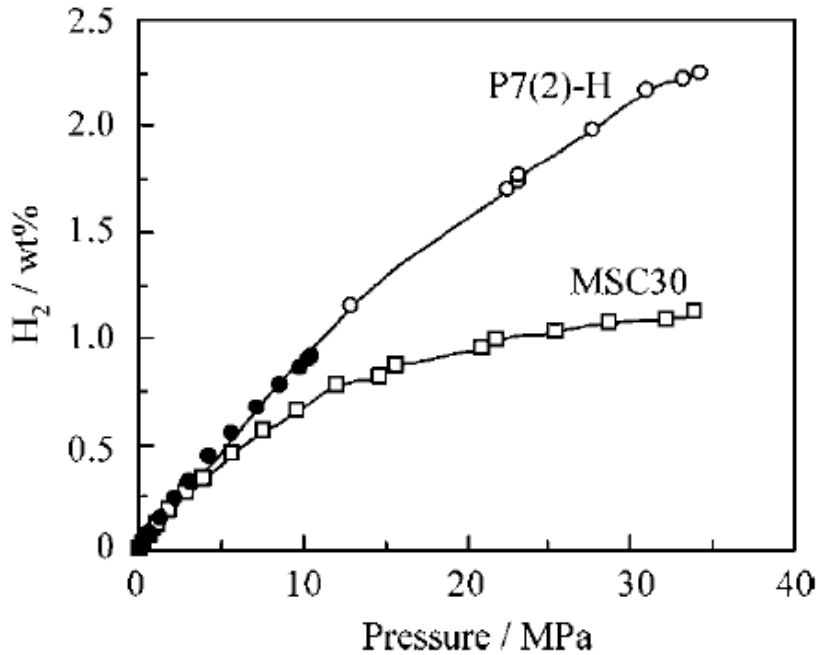


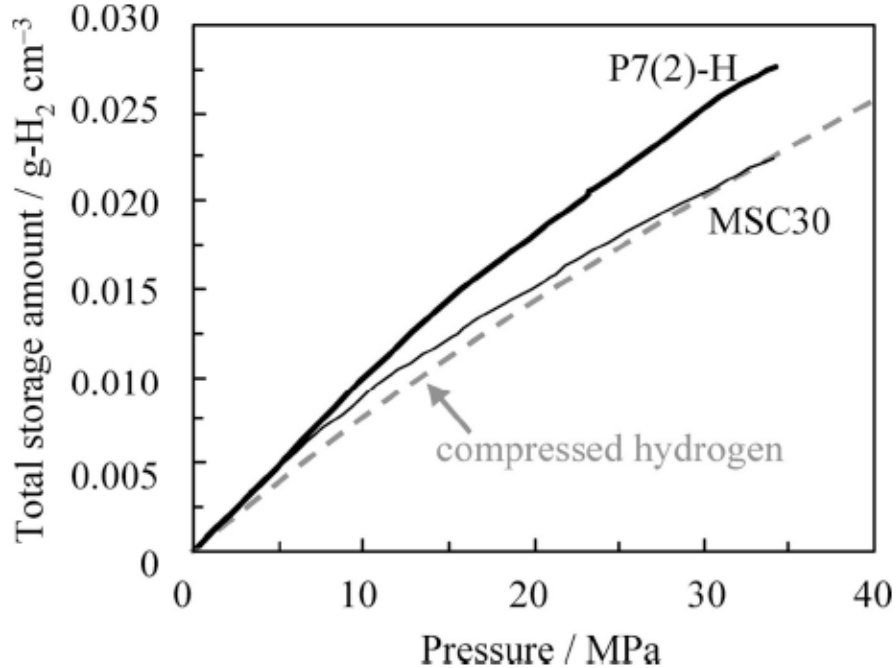


Verification of high hydrogen uptake at high pressure shown above for Duke U. -2-9-80 sample. Caltech and NREL measurements on sample show essentially identical results: 5.0 wt% from Caltech and 5.1 wt% from NREL.

Data in middle column show 77 and 87 K isotherms from B, P and N doped carbons from Rice University. The isosteric heats for these samples are shown in the right column. The isosteric enthalpies of adsorption are similar to those of unmodified microporous carbons.

Continuing work: Motivated by zeolite-templated carbon studies



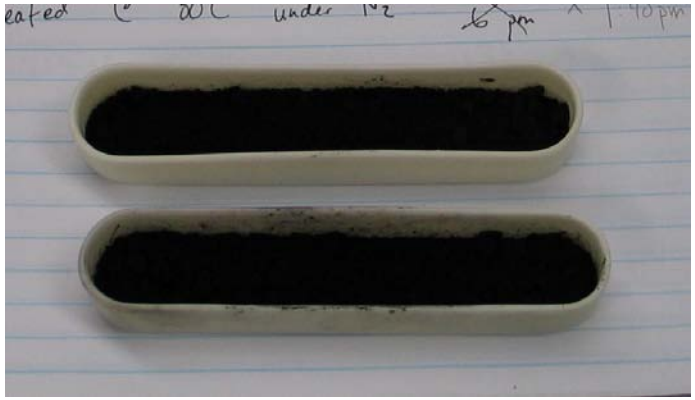


30°C isotherms from (1) show that a zeolite templated carbon could have twice the gravimetric uptake of the superactivated carbon MSC-30. The volumetric uptake is also improved over that of MSC-30. Such a material might prove to be compatible with existing high-pressure tank technology and provide a convenient intermediate solution to higher density hydrogen storage.

(1) "High-Pressure Hydrogen Storage in Zeolite-Templated Carbon," H. Nishihara, P-X. Hou, L-X. Li, M. Ito, M. Uchiyama, T. Kaburagi, A. Ikura, J. Katamura, T. Kawarada, K. Mizuuchi and T. Kyotani, *J. Phys. Chem. C 2009, 113, 3189–3196*

Technical Accomplishments: Progress on ZTC synthesis

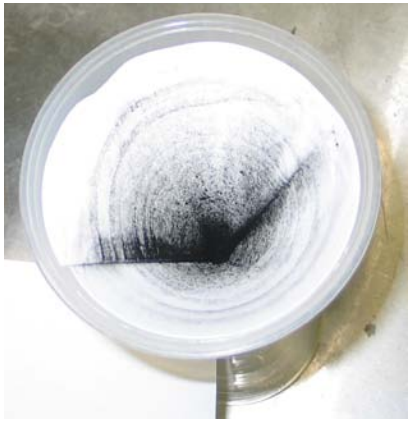
700 °C



- Mix dried zeolite (NaY) + furfuryl alcohol (FA) by stirring at 25 °C

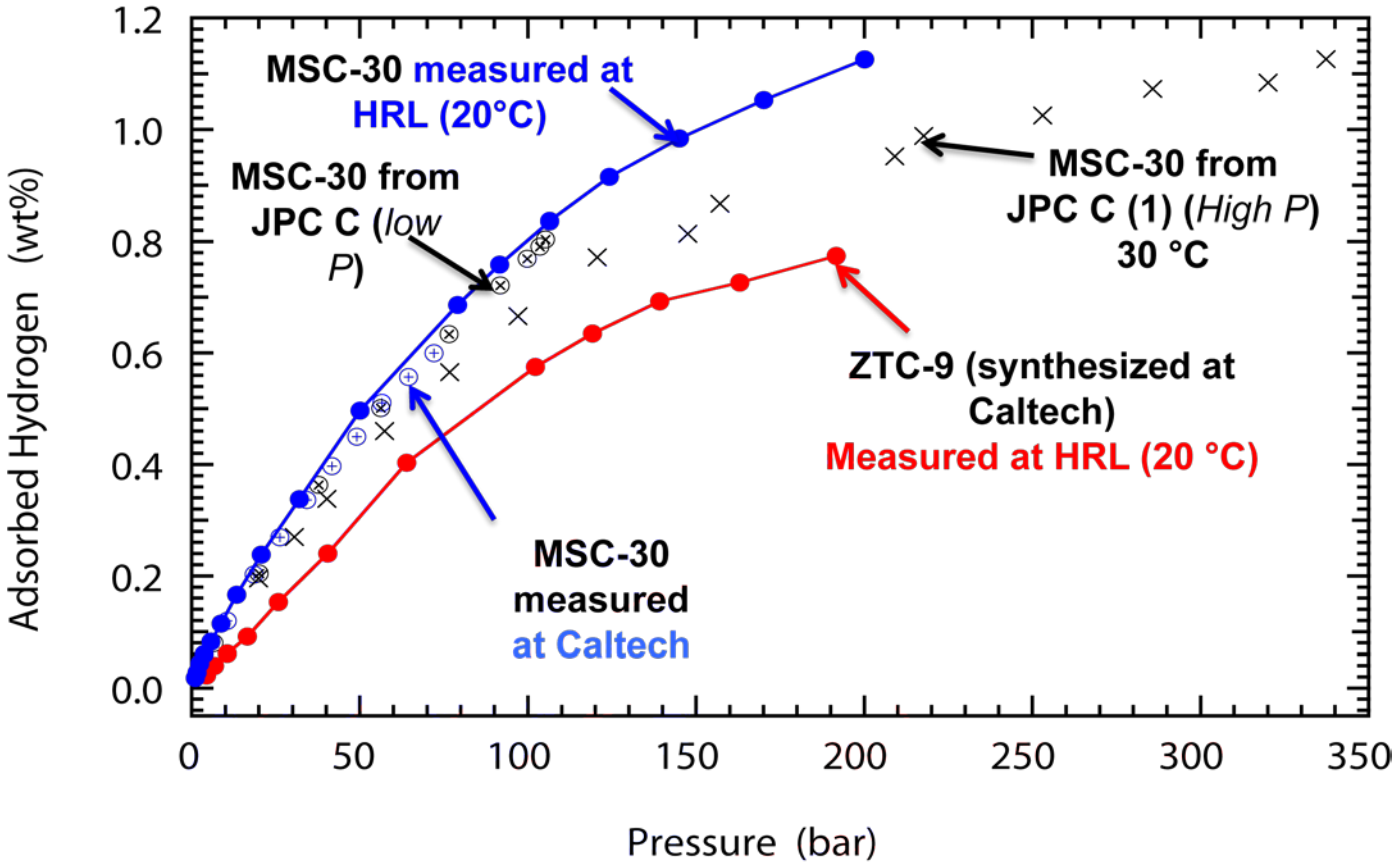
-Capture alcohol impregnated zeolite by vacuum filtration → FA-NaY. Can now use glass frits

Also, CVD using 7% propylene in N_2 at 900°C to fill in the pores completely.



At present: 2 gm yields,
BET Surface Area: 2965 m^2/g
Micropore Area: 1848 m^2/g

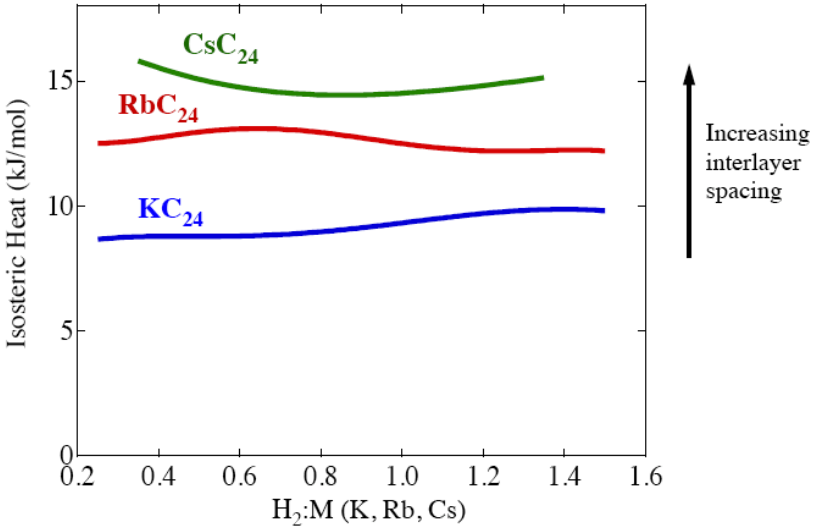
Technical Accomplishments: Ambient temperature, isotherm analysis of ZTC



ZTC material we have synthesized to date at Caltech are not as good as superactivated carbon but further optimization in progress to improve surface area and micropore volume.

(1) "High-Pressure Hydrogen Storage in Zeolite-Templated Carbon," H. Nishihara, P-X. Hou, L-X. Li, M. Ito, M. Uchiyama, T. Kaburagi, A. Ikura, J. Katamura, T. Kawarada, K. Mizuuchi and T. Kyotani, *J. Phys. Chem. C 2009, 113, 3189–3196*

Conclusions:



- Reasonably constant isosteric heat will help in higher temperature adsorption (typical 77 K uptakes can be reached at 150 K). Work to date on specialized stage 2 intercalated graphites advantageous due to combination of "slit pore" geometry and electron back donation from alkali metal.

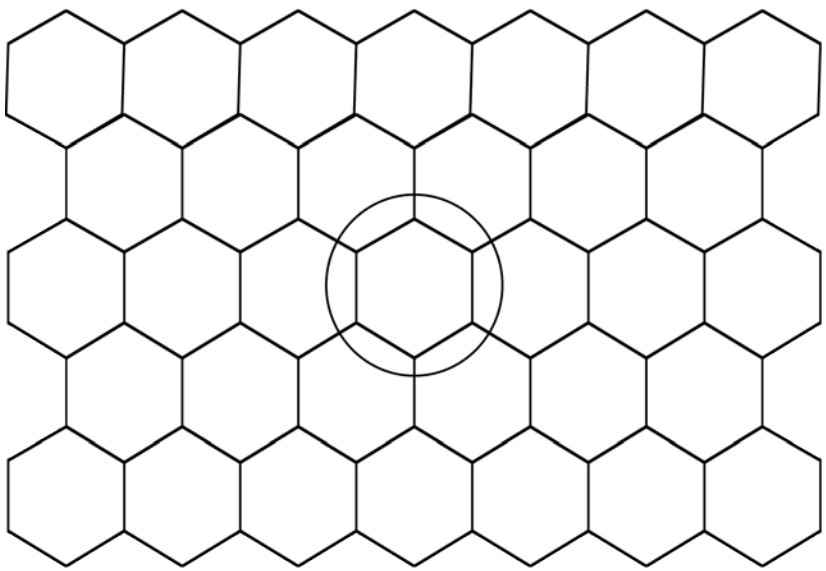
- Factor of two improvement in uptake <u>not</u> seen in Pt modified activated carbon, when large sample masses are prepared and measured according to literature recipes. From our work, gravimetric uptake decreases in Pt modified material.

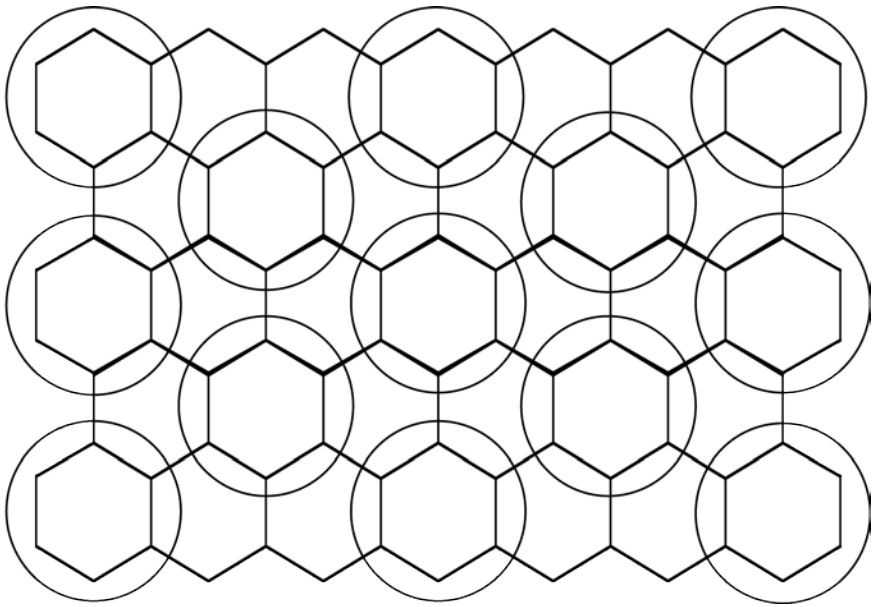
- Work underway to improve synthesis of zeolite templated carbons. High surface areas of nearly 3000m^2/gm accomplished but improvements to micro-pore density still needed.

Additional Slides

Henry's law and isosteric heats

Thermodynamically, strict definitions of engineering value

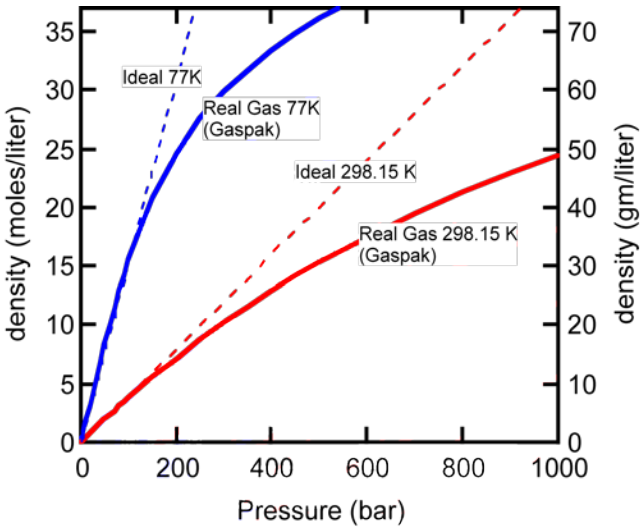


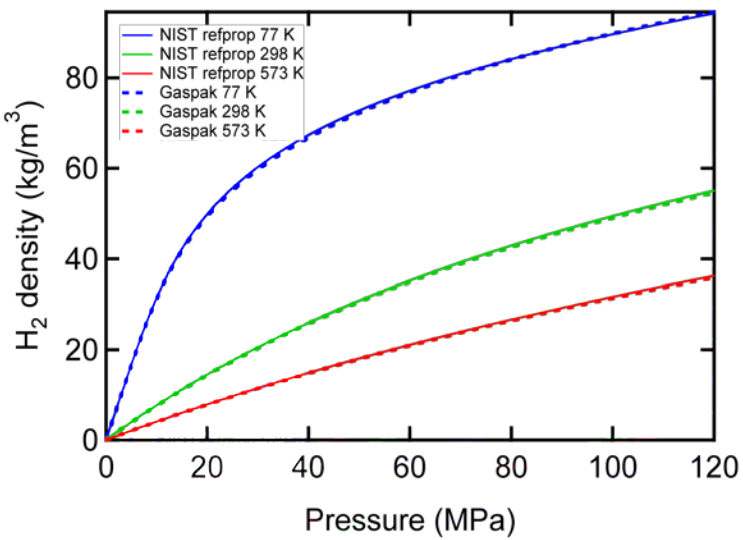


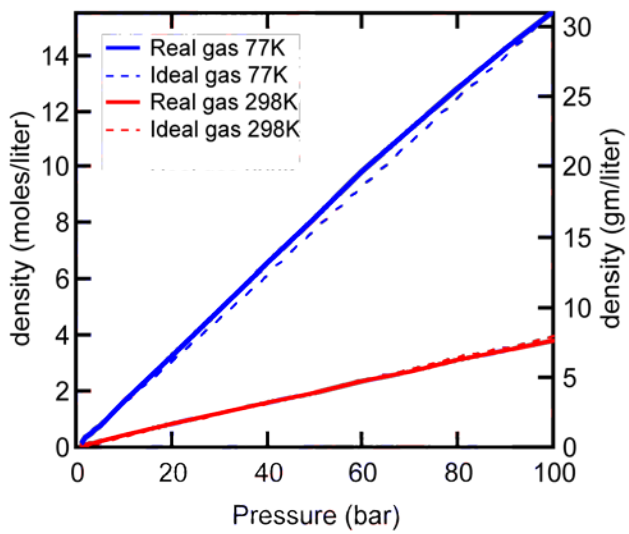
Henry's law region dictated by low coverage, "differential enthalpy of adsorption at zero coverage" so we can assume adsorbate molecules act independently.

Isosteric heat or, "isosteric enthalpy of adsorption" better reflects change in heat vs coverage.

Real vs Ideal gas behavior at 77, 298 and 573K







Comparison of Gaspak and Refprop at top.
Comparison of Gaspak and Refprop at top.

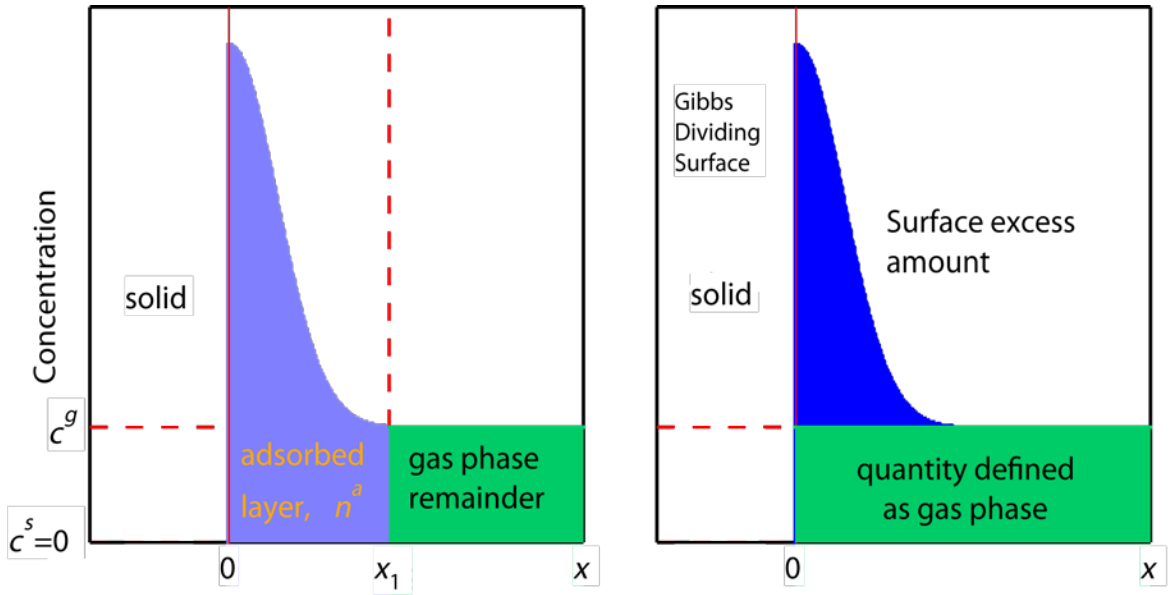
Gaspak equations here updated from hydrogen properties from NBS Technical Monograph 168, February 1981, (R. D. McCarty, J. Hord and H. M. Roder). Equation of state valid from triple point to 5000 K, pressures to 1200 bar.

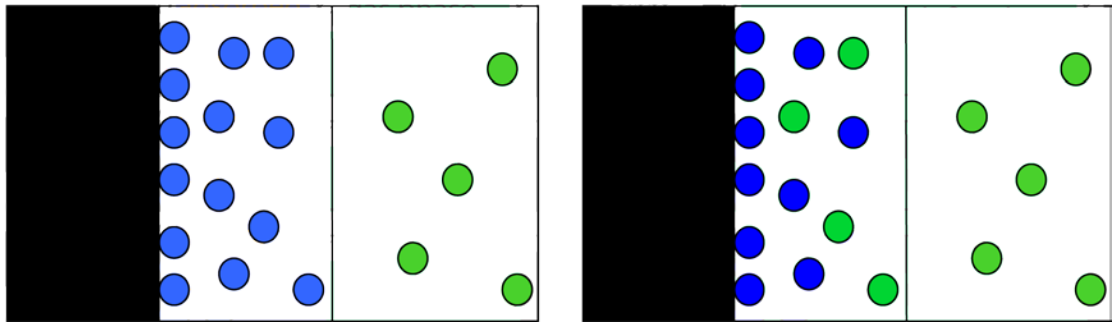
At pressures to 100 bar, real and ideal gas behavior similar for both 77K and RT

Volumetric density analysis, surface excess adsorption assumptions

Adsorbed gas concentration difficult to quantify. Data typically presented as "surface excess quantity" and given thermodynamic meaning by use of Gibbs dividing surface. Need to make assumptions regarding the concentration of surface excess amount.

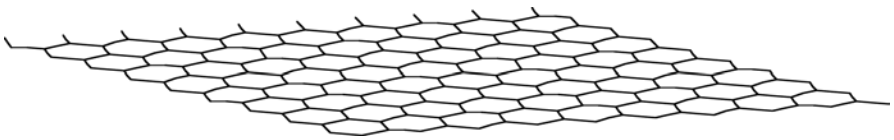
LH_2 > surface density > gas law density

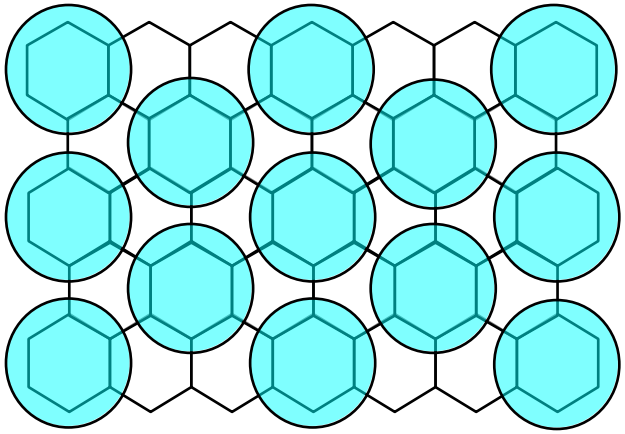




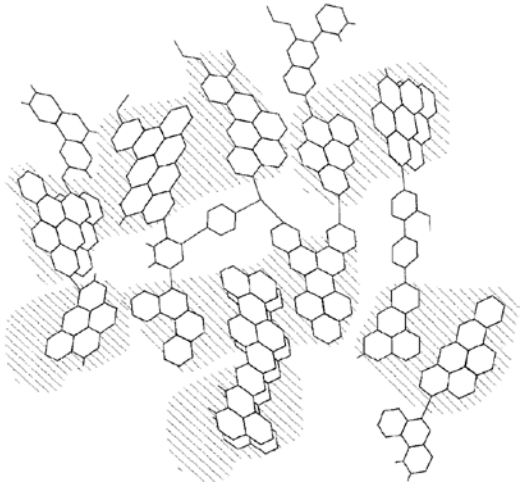
Range of graphitic structures

Theoretical surface area of a graphene sheet is 2630 m^2/gm.

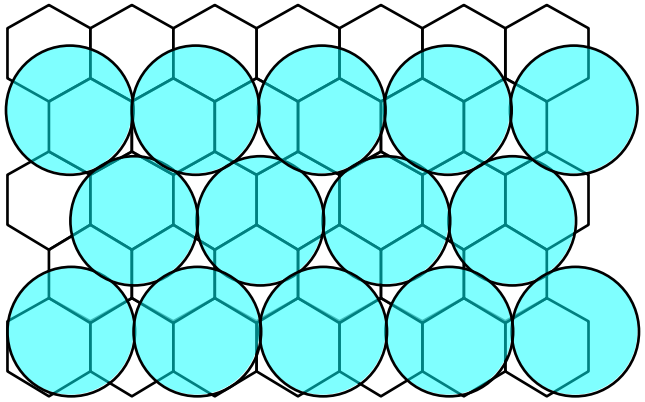




Activated carbons can have higher surface areas of >3100m^2/gm, edge components important.



Commensurate √3 structure (LiC_6) or HC_3 => 2.7 wt% (5.4 wt%)



Incommensurate solid H_2 on graphite => 3.85 wt% (7.7 wt%).