



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

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Caltech

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Project ID #ST23

Overview

Timeline

- Project start date:
October 1, 2004
- Project end date:
January 31, 2010
- Percent complete: 60%

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
R. C. Bowman, Jr., Jet Propulsion Lab.
T. Baumann, J. Satcher, Jr., J. Herberg,
Lawrence Livermore Natl. Lab.
Yun Liu, Craig Brown, Dan Neumann,
NIST

Objectives

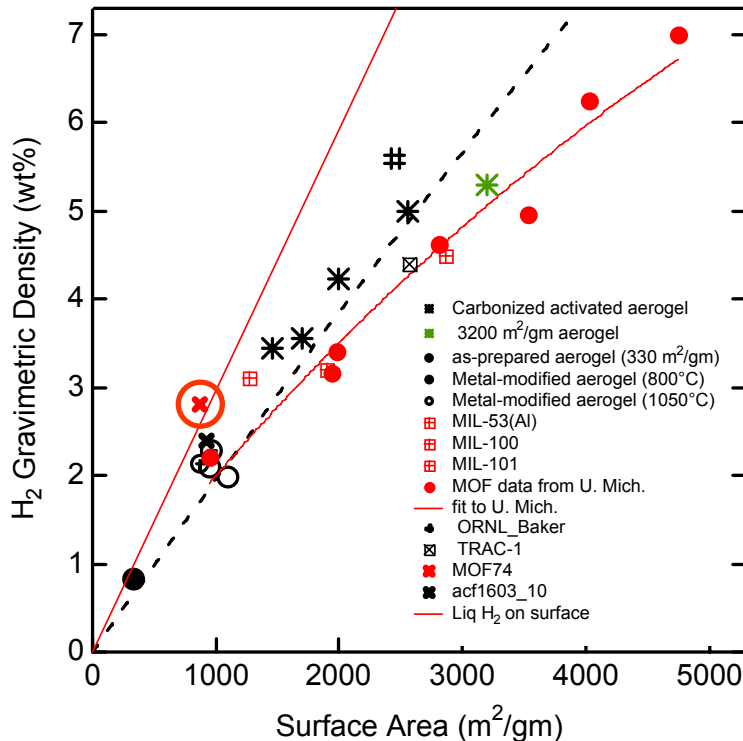
- Kinetics of molecular H₂ physisorption relatively fast but adsorption enthalpies typically close to thermal energies requiring low temperatures.
- Past work concentrated on synthesizing and evaluating maximal surface area sorbents (maximizing number of sorption sites), necessary for high gravimetric molecular H₂ 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 2447m²/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: micropore/slit pore (< 2 nm) geometry critical for volumetric optimization

Previous work established gravimetric surface area dependence in aerogels*

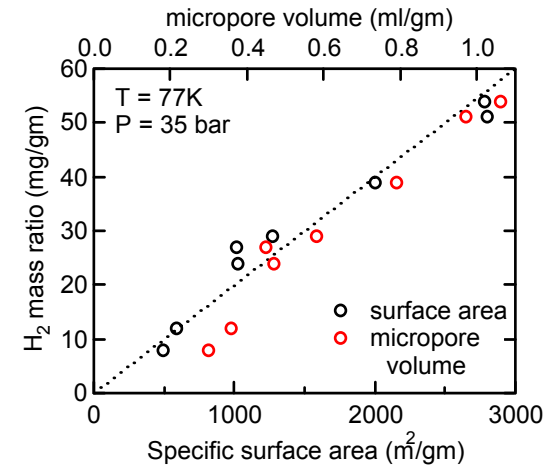


Left trace = density of LH₂ on graphene. This density can be exceeded in MOF-74.

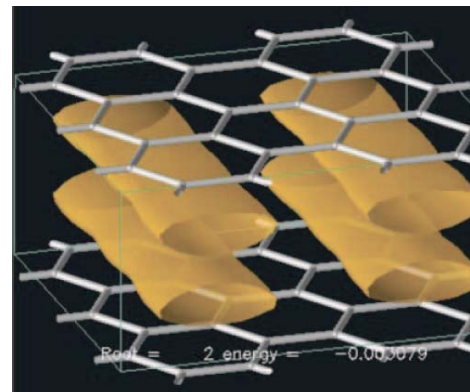
*"Toward New Candidates for Hydrogen Storage: High-Surface-Area Carbon Aerogels," H. Kabbour, T. F. Baumann, J. H. Satcher, Jr., A. Saulnier and C. C. Ahn, Chem Mater, 18, (2006).

Details of micropore/slit pore geometry critical for volumetric optimization

"Characterization and optimization of adsorbents for hydrogen storage," R. Chahine, T. K. Bose, In 11th WHEC, 1996; Pergamon Press: Oxford, U.K., 1996.

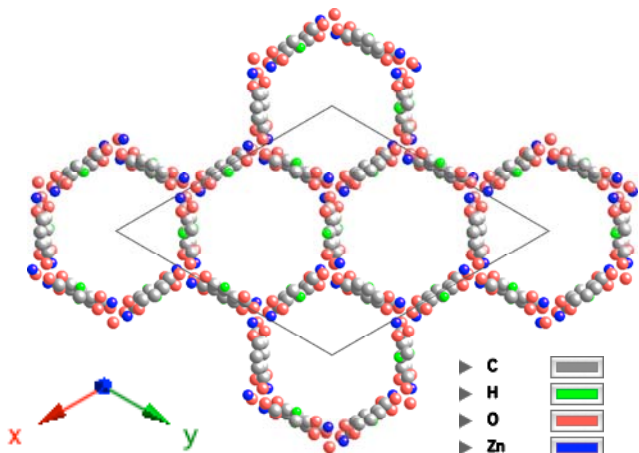


"Molecular simulation of hydrogen adsorption in single-walled carbon nanotubes and idealized carbon slit pores," Q. Wang and J. K. Johnson, J. Chem Phys. 110,(1) (1999).

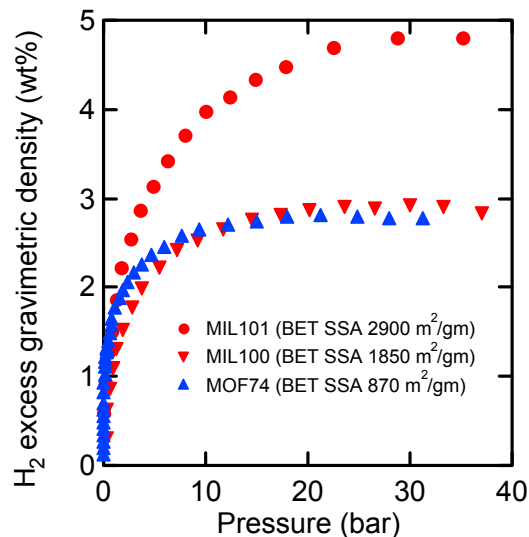


"Graphene nanostructures as tunable storage media for molecular hydrogen" S. Patchkovskii, J. S. Tse, S. N. Yurchenko, L. Zhechkov, T. Heine, and G. Seifert, PNAS, 102(30), 10439, 2005.

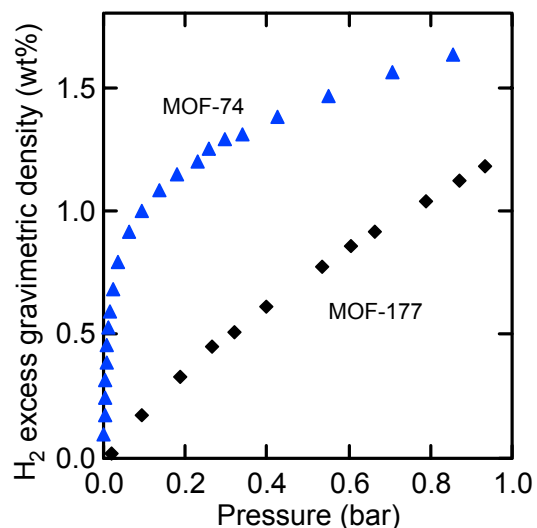
Technical Accomplishments: Increasing molecular hydrogen density via a microporous framework structure, MOF-74



MOF-74 as shown above, one of the few examples of a microporous metal organic framework. R-3 space group $a=25.9 \text{ \AA}$ and $c=6.8 \text{ \AA}$. Zinc octahedra (ZnO_6) share edges and form long chains parallel to c -axis. Organic units link chains leading to channeled structure with small hexagonal windows of $\sim 11 \text{ \AA}$ diameter. Chains provide high density of exposed metallic sites. Bulk density of 1.2 gm/cc . Synthesis of 2 gms required 2 months.

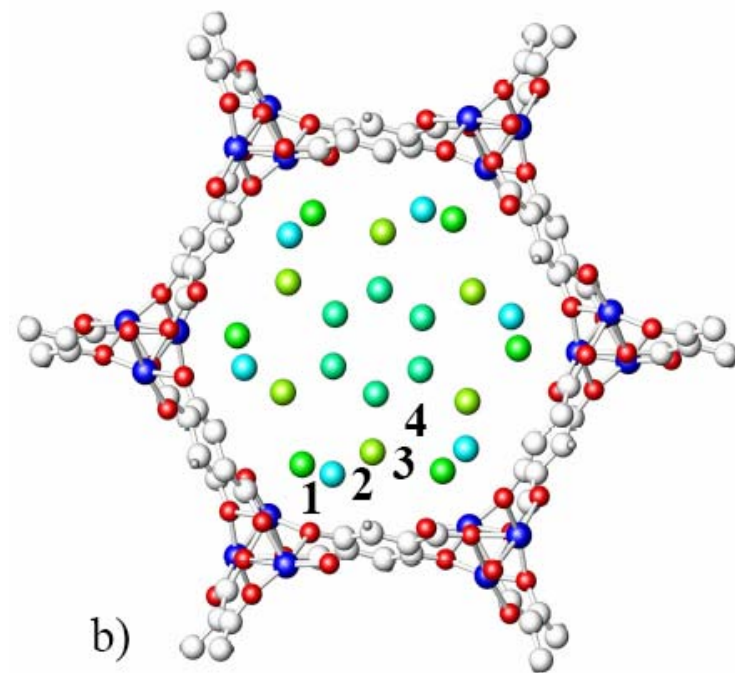
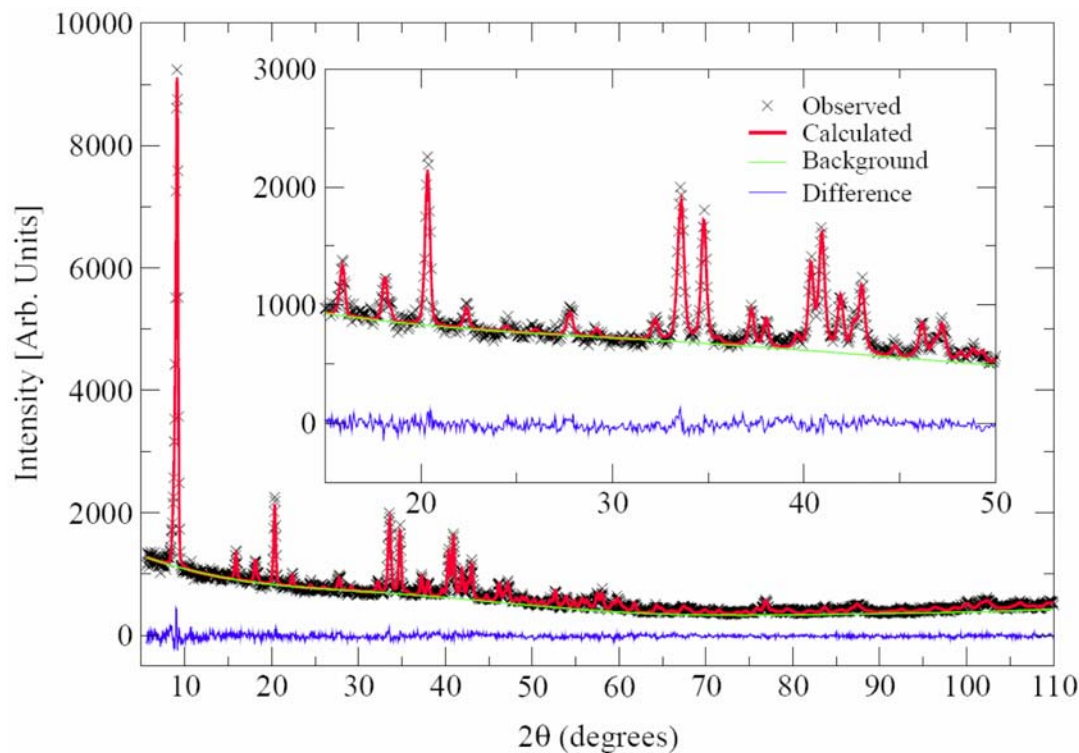


Isotherm at left shows that MOF 74 with SSA of $870 \text{ m}^2/\text{gm}$ has surface excess sorption comparable to a typical $1850 \text{ m}^2/\text{gm}$ sorbent (here compared with MIL100 and MIL101). Attributed to high surface density of molecular hydrogen. Volumetric density of 33 kg/m^3 .



Sharper initial isotherm seen at left indicates higher sorption enthalpy in Henry's law region.

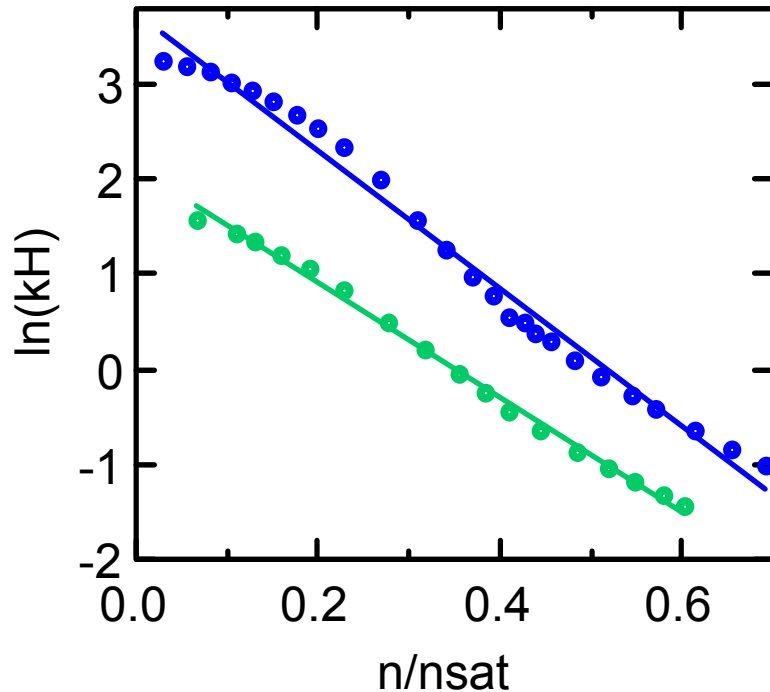
Technical Accomplishments: closest hydrogen near neighbor distances in MOF 74 as determined at NIST



Rietveld refinement and neutron powder diffraction data for a loading at 3.0 D_2 :Zn (model showing loading positions at right). Cross, red line, green line, and blue line represent the experimental diffraction pattern, calculated pattern, calculated background, and the difference between experiment and calculated patterns. Data were collected using 2.0787 Å wavelength neutrons.

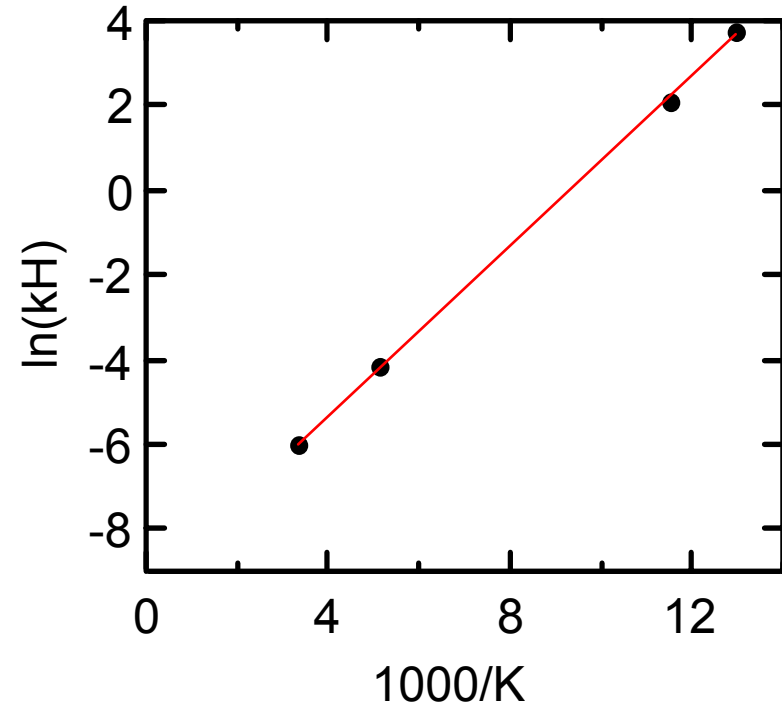
“Increasing the density of adsorbed hydrogen with coordinatively unsaturated metal centers in metal-organic frameworks,” Yun Liu, Houria Kabbour, Craig M. Brown, Dan A. Neumann, Channing C. Ahn, Langmuir published online March 27, 2008, 10.1021/la703864a

Technical Accomplishments: Henry's law heat for MOF-74



Henry's law region (differential enthalpy of adsorption at zero coverage) the heat of initial H₂ molecule adsorbed onto surface. Non-linearity of semi-log fit an indication of heterogeneity in sorption site.

Seen at both 77 and 87K.

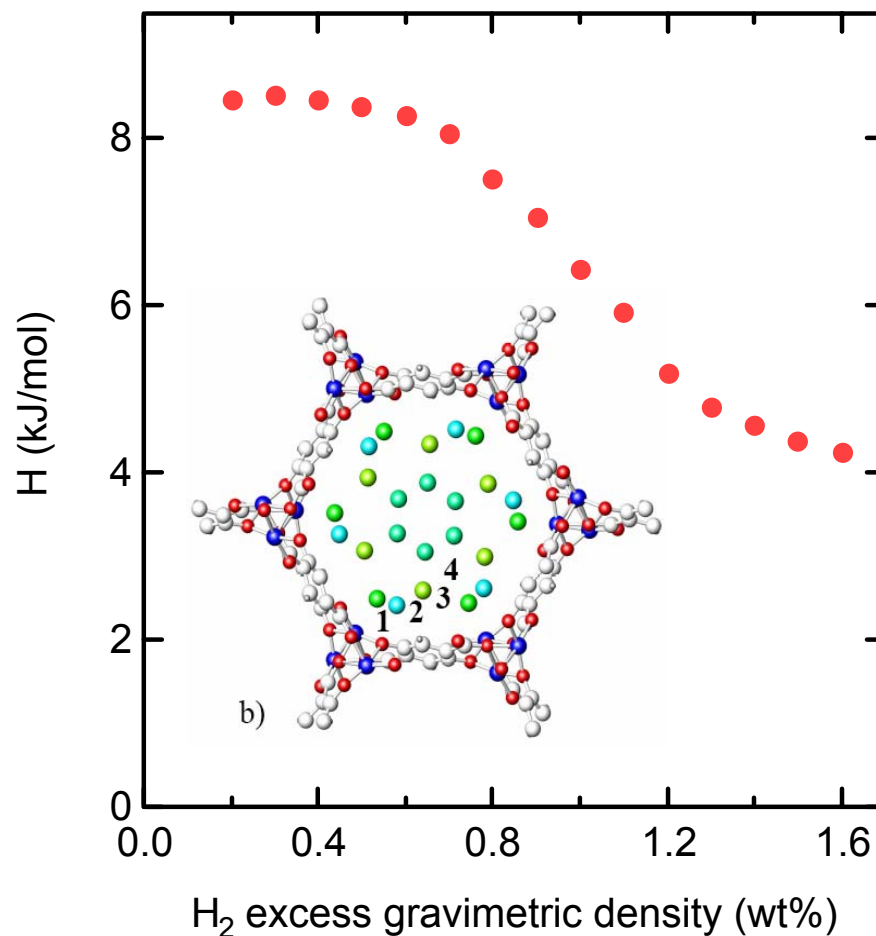


Henry's law fit indicates -9.4 kJ/mole differential enthalpy of adsorption at zero coverage.

$$\left(\frac{\partial H}{\partial n}\right) = RT^2 \frac{\partial(\ln k_H)}{\partial T}$$

Technical Accomplishments: H₂ site occupancy and isosteric heat in MOF 74

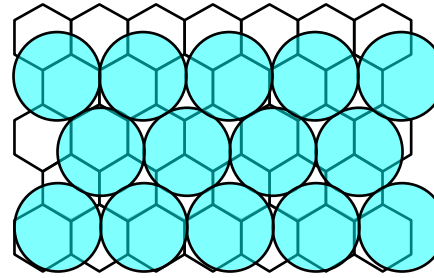
- Isosteric enthalpy of adsorption tracks enthalpy vs coverage. Initially loaded site above coordinatively unsaturated Zn as determined by neutron diffraction (NIST).
- Near neighbor 2.85 Å D₂-D₂ spacing (site 1 to site 3) helps explain high surface packing density (range from 2.85 to 4.2 Å). 2.85 Å the closest packing of D₂ seen under these conditions! Normally 3.4 Å on graphitic carbon (~3.6 Å in liq H₂).
- Isosteric enthalpy of adsorption shows drop by nearly a factor of 2 as a function of loading. Site heterogeneity an issue.



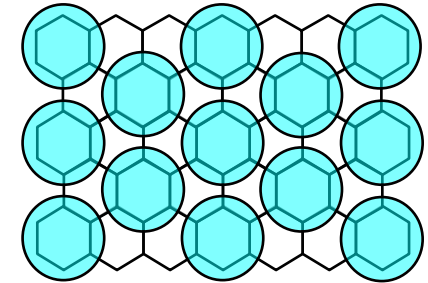
Technical Accomplishments: Higher surface packing density

We want to maximize adsorbed density of H_2 molecules, to maximize gravimetric and volumetric densities. No metric previously defined to quantify this so “surface packing density” (surface excess mass fraction)/(BET specific surface area) used and this value the highest for MOF 74 as shown in lower left.

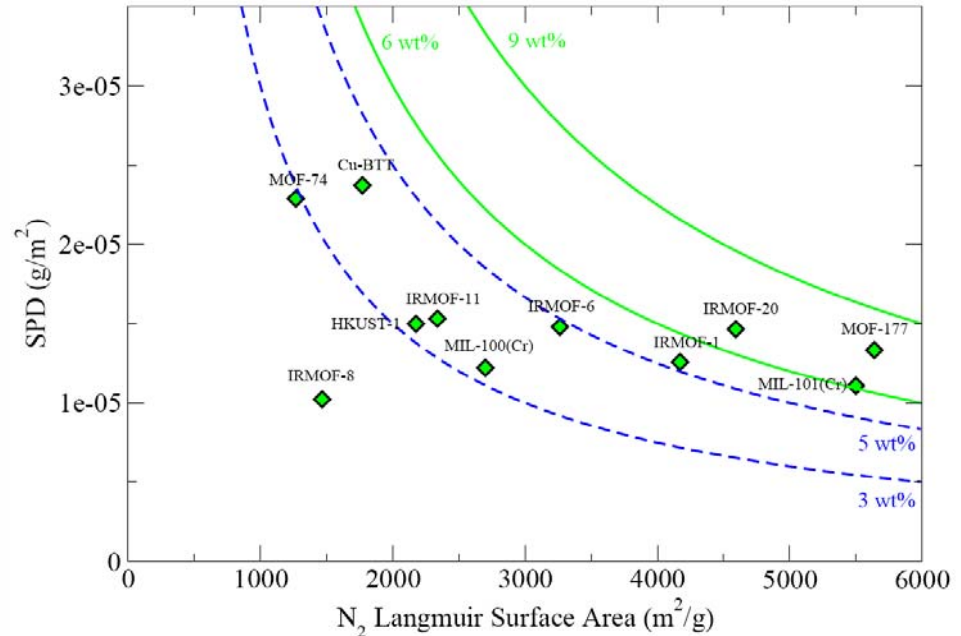
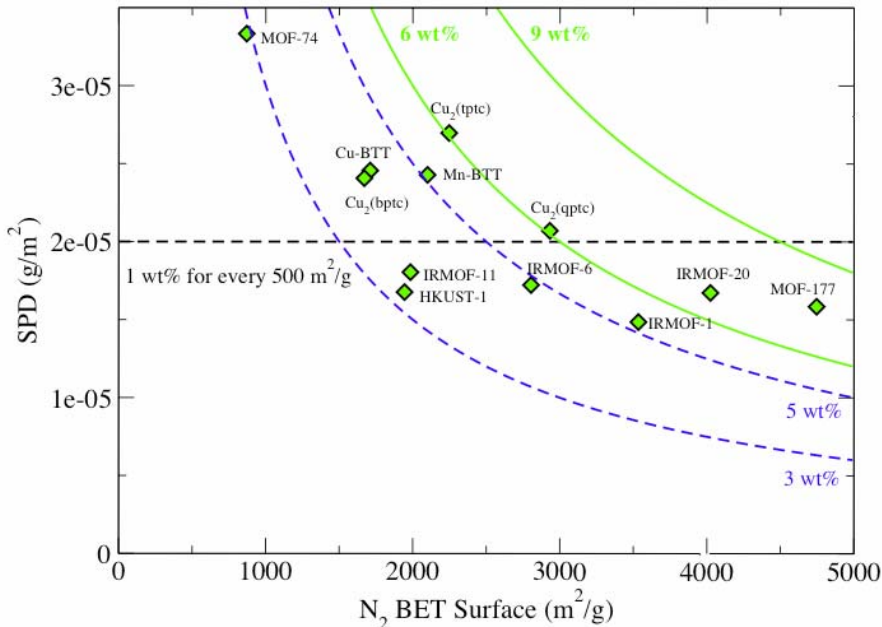
Also high if Langmuir surface area used as shown in lower right.



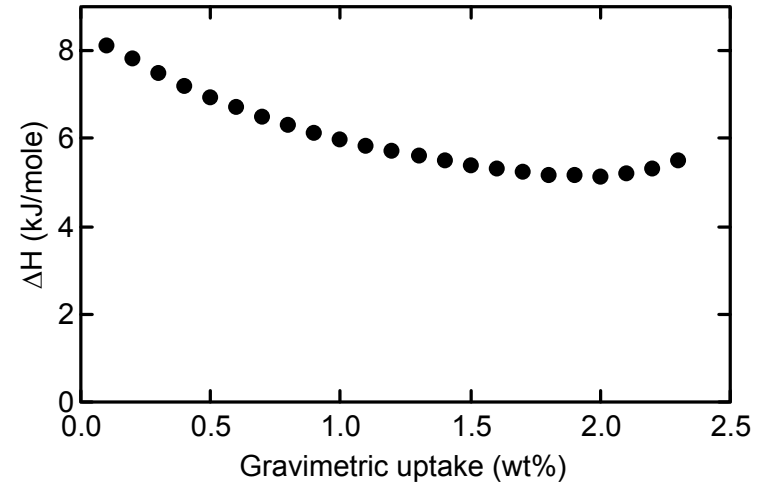
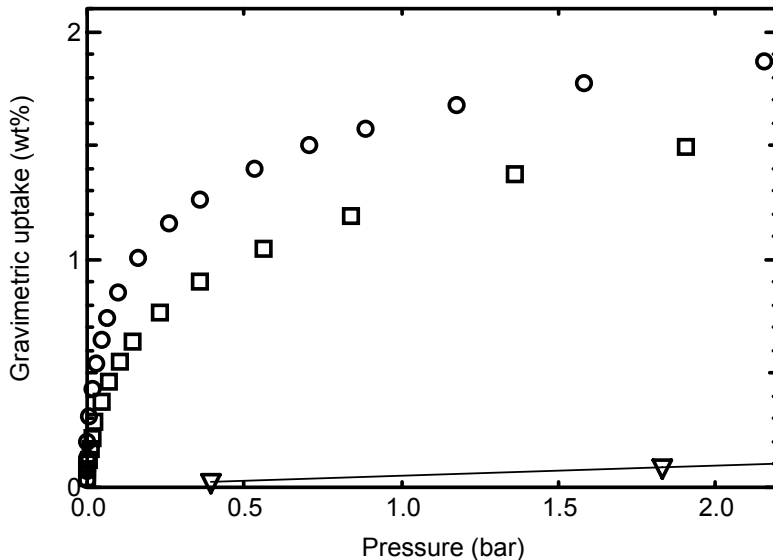
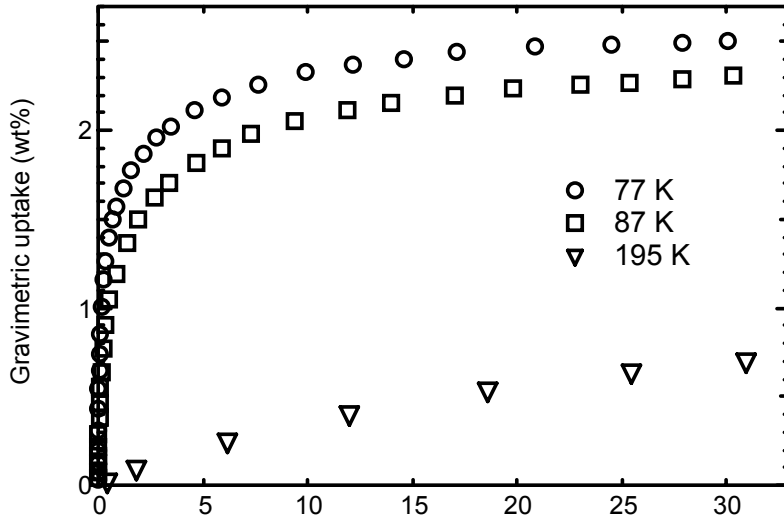
Preferred packing density above



Lower packing density

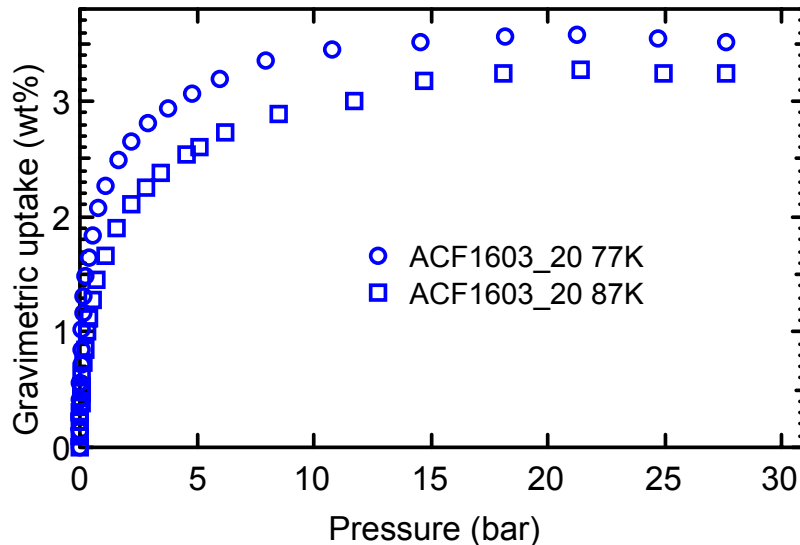
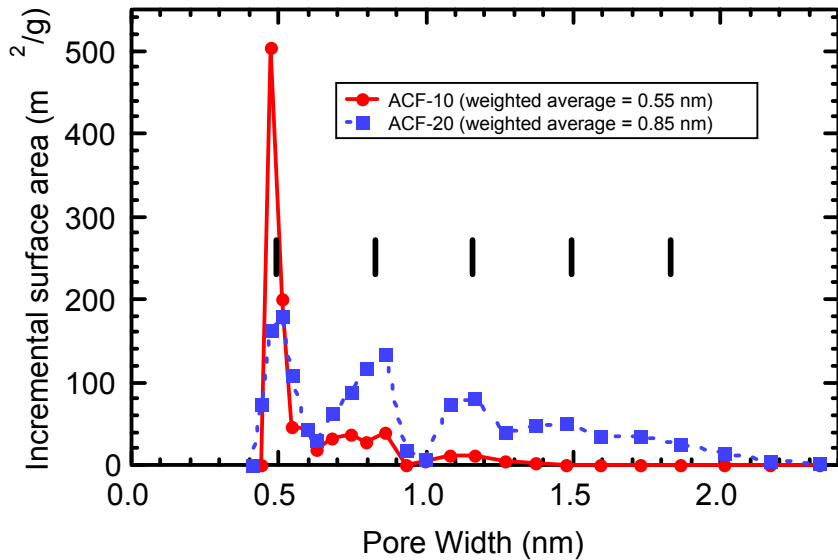


Technical Accomplishments: Enthalpy analysis of microporous activated carbons, CNS-201 (coconut-based) and Kynol ACF1603-10/20 (phenol-aldehyde)



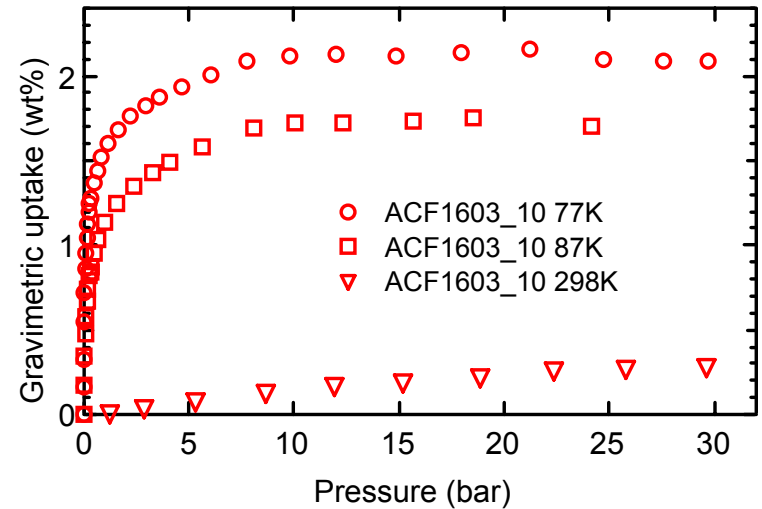
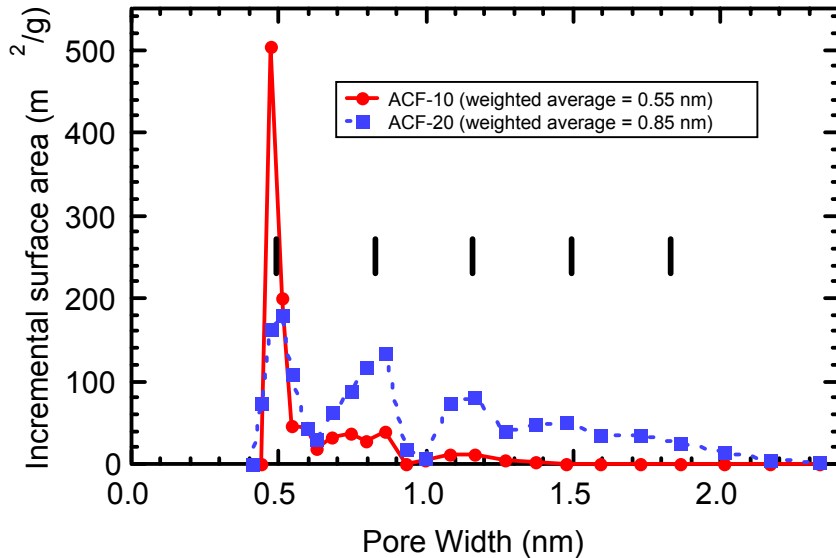
- Pore optimization presently being done at LLNL, so commercial microporous carbons being studied to determine optimum sizes.
- At left, 77 and 87 K isotherms from CNS-201, a microporous activated carbon with pore size centered at 1.1 nm. BET surface area $\sim 1100 \text{ m}^2/\text{gm}$. Maximum surface excess at between 30 and 35 bar pressure.
- Henry's law analysis indicates an 8.5 kJ/mole heat.
- The isosteric heat from this carbon is shown above and shows a range of 8.5 to ~ 5 kJ/mole as a function of loading.
 - a) The steep slope from the high sorption enthalpy at 77K results in $\sim 28\%$ of the maximum surface excess available above 2 bar pressure.
 - b) At 87K this value is $\sim 35\%$ of the maximum surface excess.

Technical Accomplishments: Enthalpy analysis in microporous activated carbons Kynol ACF1603-10/20

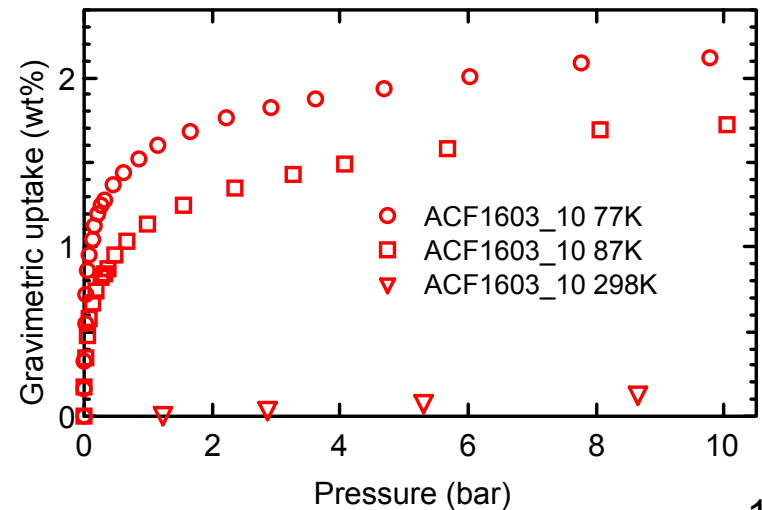


- ACF 1603-10, a well-defined, narrow pore size distribution activated carbon with 917 m²/gm surface area (red), pore distribution peaks at 0.55 nm.
- ACF 1603-20 with 2140 m²/gm surface area (blue) with broader distributions but primarily microporous. Lines correspond to graphitic spacings (3.35 Å).
- Isotherm at left shows maximum of surface excess between 20 - 25 bar, lower pressure than typical carbons that contain both micro and macropores (that are typically from 30 to 35 bar).
 - a) At 77K, ~28% of the maximum surface excess available above 2 bar pressure.
 - b) At 87K, ~41% of the maximum surface excess.

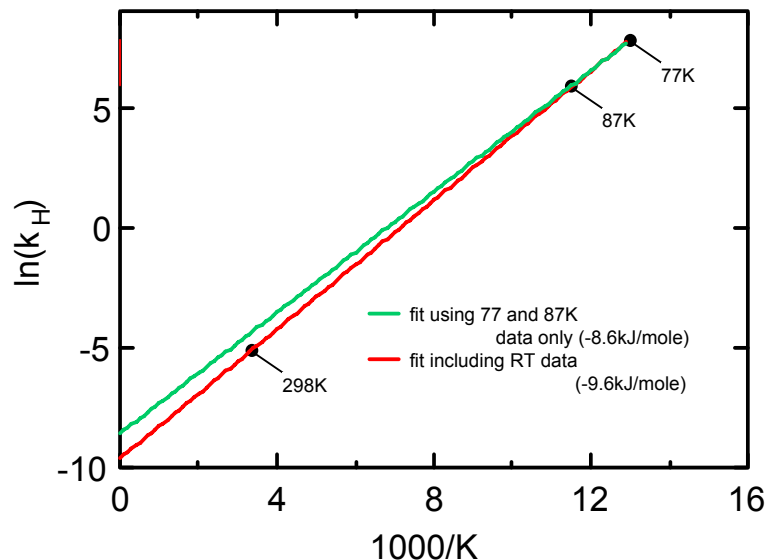
Technical Accomplishments: isotherm analysis in microporous activated carbons, Kynol ACF1603-10/20



- Isotherms from narrow pore distribution, ACF 1603-10 at upper right shows Langmuir type behavior.
- Maximum of surface excess at ~10 bar at both 77 and 87K.
 - a) At 77K ~23% of the maximum surface excess available above 2 bar pressure.
 - b) At 87K this value is ~28% of the maximum surface excess.



Technical Accomplishments: Enthalpy analysis in microporous Kynol

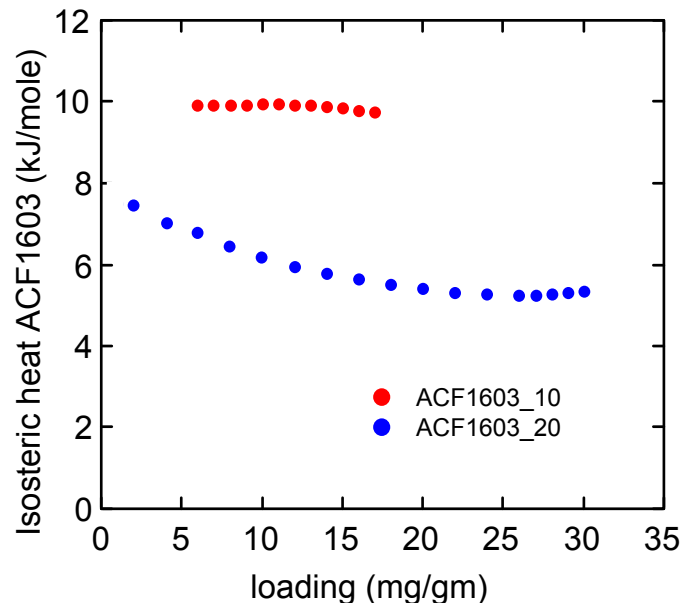


Initial determination of Henry's law heat: semi-log analysis of ACF1603_10 yields linear behavior to 10 bar.

Extrapolation to determine differential enthalpy of adsorption at zero coverage by using only 77 and 87 K data yields value within 1 kJ/mole of actual value.

Enthalpy ~twice that seen in typical activated carbons.

Micropore structure increases Henry's law sorption enthalpy.

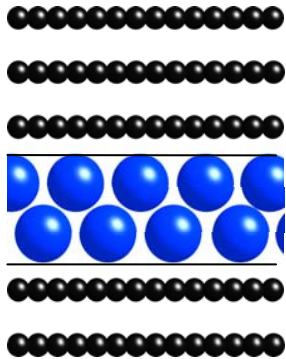


In ACF 1603-10, Henry's law value yields -9.6 kJ/mole.

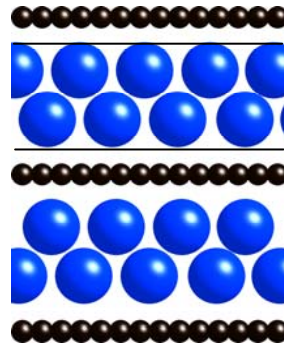
Narrow pore distribution effectively yields high homogeneous site potentials.

In ACF 1603-20, Henry's law value yields -7.6 kJ/mole with decreasing isosteric heat shown due to broad pore size distribution.

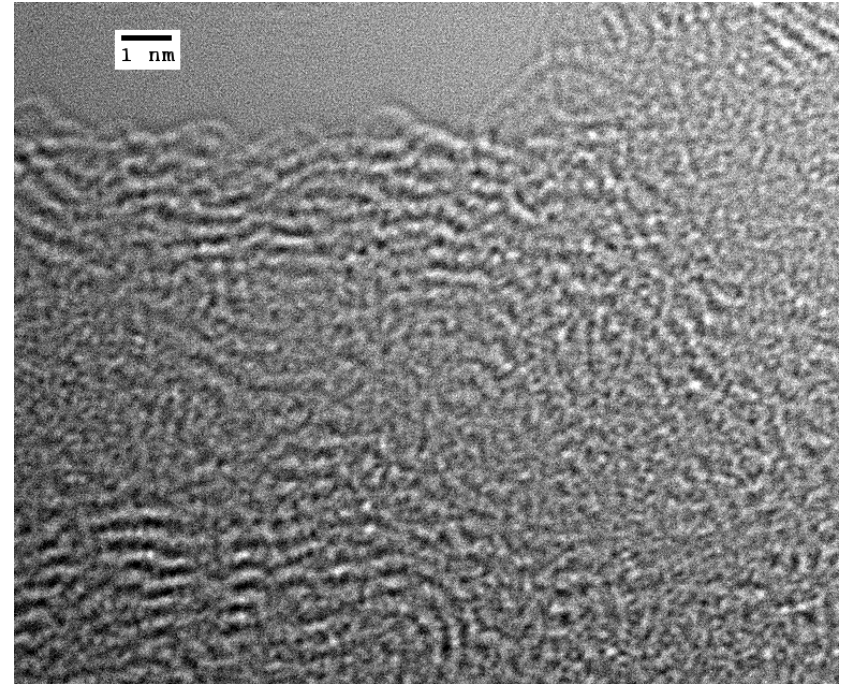
Optimal graphitic spacings



Assumed structure

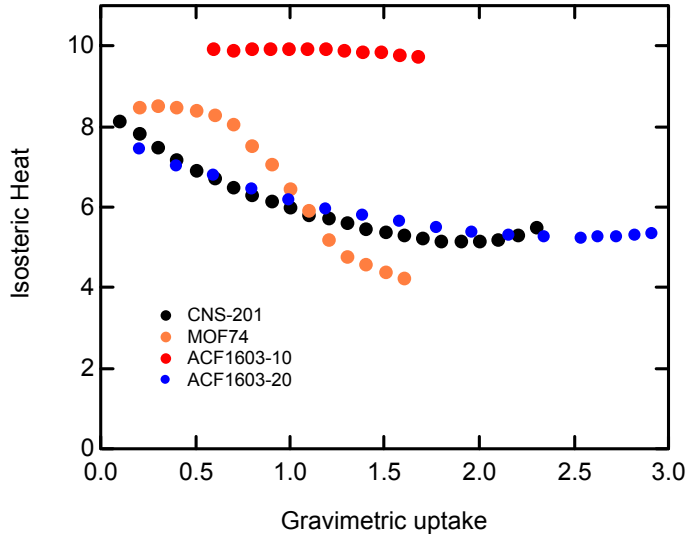


idealized structure



- Slit pores would make the ideal microstructure for maximizing volumetric density.
- A 1.1 nm pore should yield ~7.7 wt% gravimetric and ~44 gm/L volumetric density. Differential enthalpy of adsorption at zero coverage of ~8.5 kJ/mole.
- Actual microstructure, TEM micrograph of Kynol carbon fiber ACF1603-10.
- Not a simple graphitic slit pore structure.

Conclusions:



- Homogeneous enthalpies seen when pore size distribution narrow.
 - Heterogeneous isosteric heats in most microporous materials with enthalpies that drop by $\sim 1/3$ to $\sim 1/2$ of the Henry's law value.
 - Heterogeneity due either to presence of coordinatively unsaturated metal center (MOF) or due to distribution of pore size within microporous regime (< 2 nm).
-
- At 77K, high sorption enthalpy results in majority of sorbed hydrogen to be retained at pressures < 2 bar for pore dimensions that are small.
 - At 87K, larger fraction of hydrogen available > 2 bar.
 - Pore dimensions can be too small but narrow pore size distribution that peaks at 1.1 nm probably the optimal size.

Plans for 2008/2009

- Continued collaboration with LLNL on aerogel analysis including:
 - Further incorporation of catalysts in higher surface area aerogels to improve gravimetric densities over the 5.6 wt% presently achievable.
- Continued synthesis and activation of MOF and MIL (Material Institut Lavoisier) and other high surface area structures to improve gravimetric densities. Pursuit of those systems that display homogeneous sorption enthalpies.
- Optimization of pore size/volume in order to maximize volumetric density. An ideal graphitic structure with a 1.1 nm pore size can accommodate as much as 7.7 wt% gravimetric and, from 44 to 58 gm/liter volumetric density.
- Continuation of evaluation of thermodynamic properties (isosteric enthalpy of adsorption and differential enthalpy of adsorption at zero coverage).

Summary of thermodynamic analysis of microporous sorbents

- Microporous solids will increase volumetric density and sorption enthalpy.
- Active sorption site in MOF-74 at coordinatively unsaturated Zn site responsible for initially high Henry's law heat but decay seen in isosteric enthalpy when active site occupied.
- Differential enthalpy of adsorption at 'zero' coverage different than isosteric enthalpy of adsorption (which will always decrease with increasing coverage, depending on site heterogeneities).
- Homogeneity of isosteric enthalpy of adsorption in graphitic slit pore for narrow pore size distribution.

Sample	Gravimetric	Volumetric	ΔH_h (kJ/mole)	ΔH_i (kJ/mole)
MOF-74	2.8 wt% (3.6 wt% tot)	33 kg/m ³	8.5	8.5 to 4
ACF-1603_10	2.3 wt%	-	9.6	10
ACF-1603_20	3.6 wt%	6.6 kg/m ³	7.6	7.6 to 5
CNS-201	2.4 wt% (4 wt% tot)	16 kg/m ³	8.4	8.5 to 5