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Hydrogen Storage through Nanostructured Polymeric Materials

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DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Arlington VA

May 21, 2009

Project ID ST_27_Liu

Overview

Timeline

- Project start: July 2007
- Project end: June 2012
- % complete: 40%

Barriers

- Barriers addressed
  - A. System Weight and Volume
  - B. System cost
  - C. Efficiency
  - D. Durability/Operability

Budget

- Total project funding: $2 Million
  - DOE share: $1.88 Million
  - Contractor share: $120 K
- Funding received in FY08
  - $ 516 K (operation)
  - $100 K (equipment)
- Funding for FY09
  - $ 800 K

Partners

- Interactions/collaborations
  - Argonne National Laboratory (Lead)
  - U of Chicago (Subcontractor)
  - HSCoE Members
    - *U of N. Carolina (^{1}H NMR)*
    - *NIST (Neutron)*
    - *Air Products (Sample exchange)*

Objective

- **To design, synthesize, and evaluate nanostructured polymeric materials (NPM) as new hydrogen storage adsorbents for transportation applications**
- **To support polymer materials development with modeling/simulation and advanced structural characterizations**

Potential Advantages of Polymeric H_2 Adsorbent & Their Impacts to Technology Barriers

- **System Weight and Volume** – Polymers are light weight and can be converted to high volumetric density by engineering process such as compression, pelletizing, etc.
- **System Cost** – Polymer can be scaled-up for industrial production with the existing infrastructure at competitive cost.
- **Efficiency** – Polymeric adsorbent is based on physi-adsorption/desorption principle with minimum parasitic energy consumption.
- **Durability/Operability** – Polymeric materials are stable under the temperature and humidity conditions required for hydrogen storage application.

Milestones

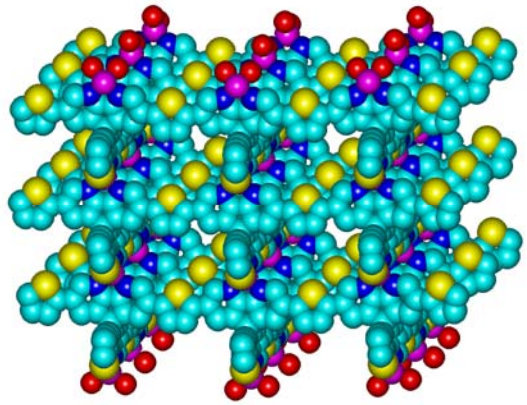
Month/ Year	Milestones	Status Update
05/08	Complete the surface property and hydrogen storage capacity measurement of the benchmark materials	**Completed**. Several published materials including MOF and polymers were duplicated and tested.
08/08	Initiate theoretical simulation of the interactions between hydrogen and model polymer systems	**Completed**. Preliminary modeling on conjugated polymer and metal doped systems were completed at Argonne.
08/08	Complete design and synthesize two or more new porous polymer materials with targeted hydrogen uptake capacity of 3% at 77 K and 1% at 298 K	**Completed**. Three classes of polymers with over *50* different structures and synthesis schemes were prepared and characterized. H_2 updates of 5.1% at 77K and 0.5% at RT were achieved, a major improvement over FY08 results.
05/09	Complete surface area and hydrogen uptake measurements for the first batch of metal-doped porous polymers	**60% completed**. BET, H_2 uptake and ΔH_{ads} studies of the representative samples are completed. Measurement is underway for other samples
08/09	Complete quantum chemical study at MP2/DFT level of hydrogen adsorption on polymer model with transition metal sites	**50% completed**. The modeling on doped metal system is finished. Work on synthesized system will start soon.
09/09	Complete the improvement for the new polymers to reach H_2 adsorption capacity of 1.5 wt.% at the ambient temperature & 100 bars	**20% completed**. Focus is now on polymers with variable pore size, metal and other non-C element incorporation. Other modification methods are under evaluation.

We significantly expanded synthesis effort leading to > 50 new polymers produced with nearly doubled surface area and H_2 storage capacity over last AMR report!

Approach

New Polymer Exploration (UofC/ANL)	Measurement & Optimization (ANL)	Modeling & Characterization (ANL/HSCoE)
■ New polymer synthesis through rational design at molecular level ■ Molecular structure characterization	■ H_2 storage capacity measurement ■ Surface structure characterization ■ Synthesis method improvement	■ H_2-polymer interaction study via *ab initio*, DFTB & MD methods ■ Advanced characterization through NMR, neutron, x-ray, etc.

- Preparing high surface area & narrow/adjustable pore size polymers through rational design and synthesis
- Incorporate "metallic" feature into polymer through conductive backbone or metal doping
- Improve polymer-H_2 interaction by incorporating functional groups with hetero (non-C) elements
- Develop fundamental understanding through modeling and advanced characterization

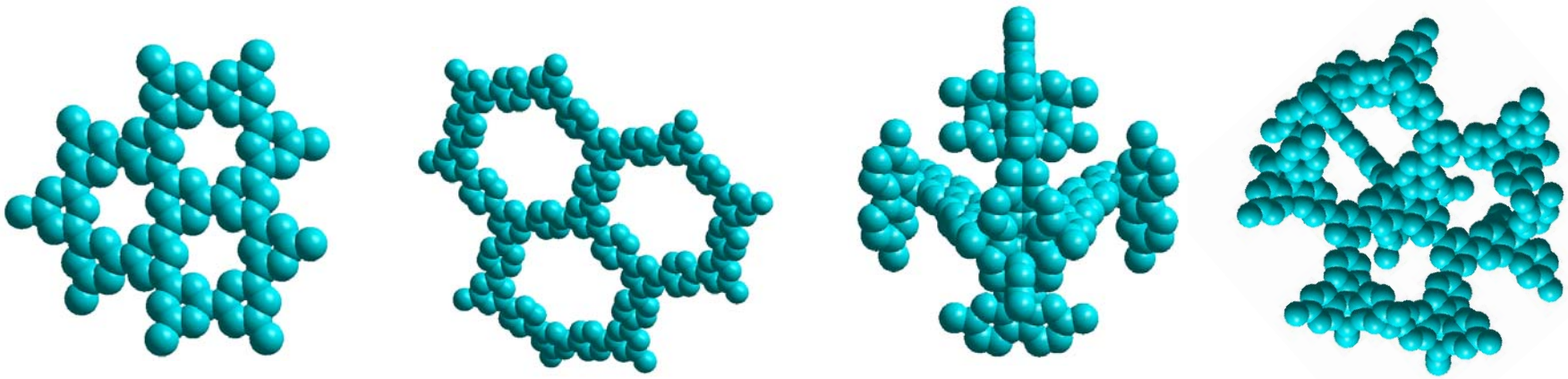


An example of ANL/UofC polymer with conductive backbone incorporated with different elements

Progress Update – Porous Polymers Prepared from Aromatic Monomers

- **A variety of monomers and synthesis methods were used to fine-tune the surface area and porosity, including contorted monomers, Friedel-Crafts reaction, etc.**
- **Over *20* porous polymers with different 3-D structures were prepared with simple aromatic building blocks.**
- **Studies on correlation between surface properties & H_2 adsorption capacity/energy is underway.**

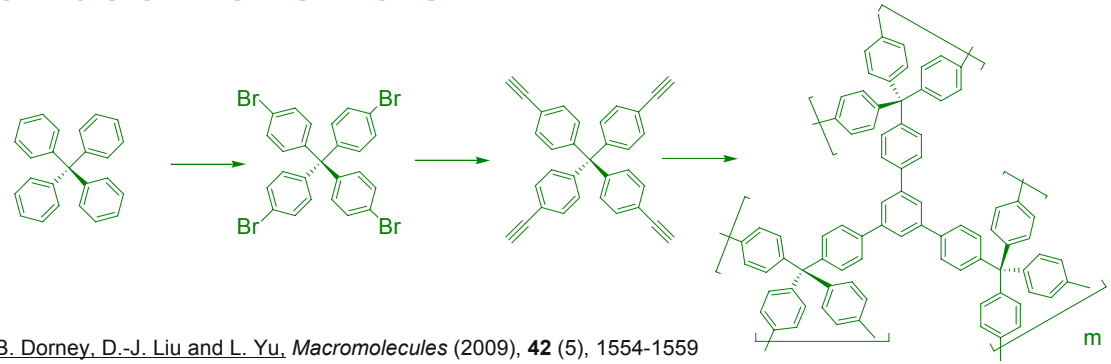
3-D structures of selected aromatic polymers prepared at Argonne and U of Chicago



High surface area (1000 M^2/g ~ 1800 M^2/g) & narrow pore size (6Å to 10Å) were achieved!

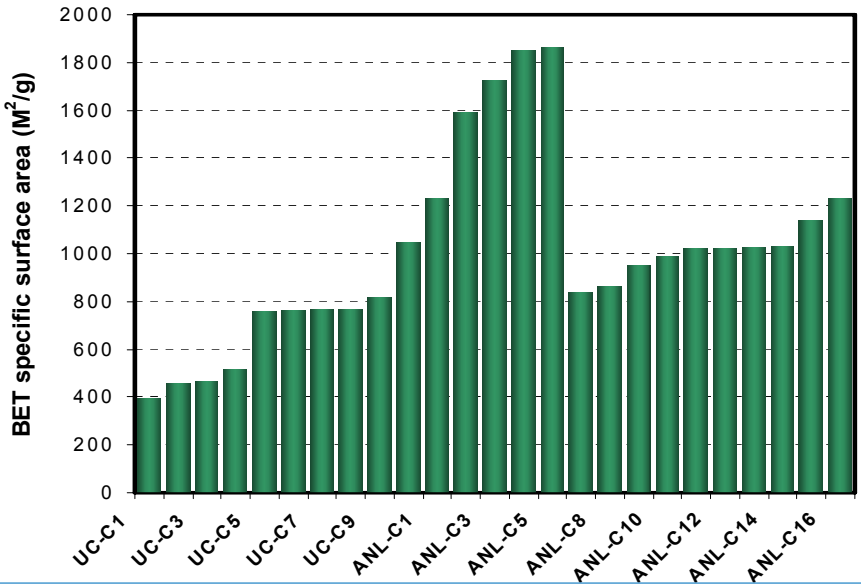
Progress Update – Design, Synthesis & Surface Properties of Porous Polymers from Aromatic Monomers

An example of generating microporosity through contorted monomers

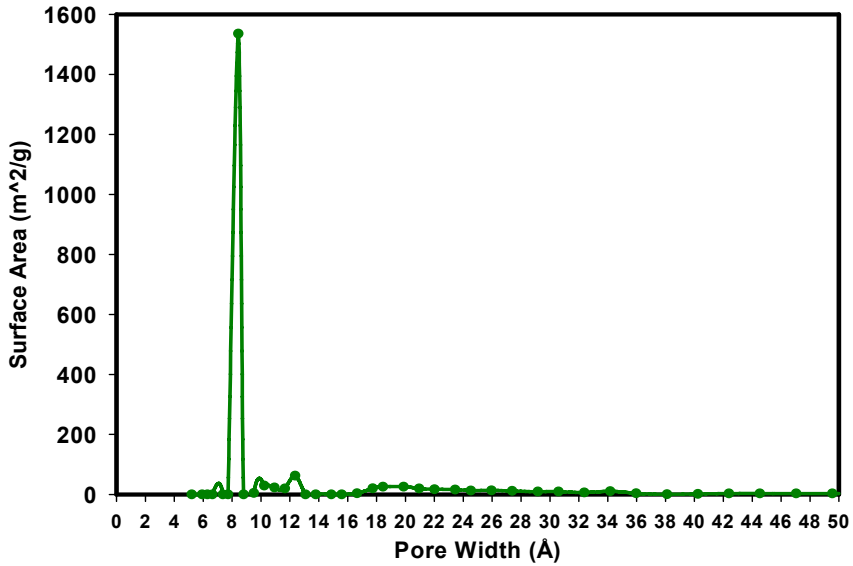


S. Yuan, S. Kirklin, B. Dorney, D.-J. Liu and L. Yu, *Macromolecules* (2009), **42** (5), 1554-1559

BET surface areas of selected polymers



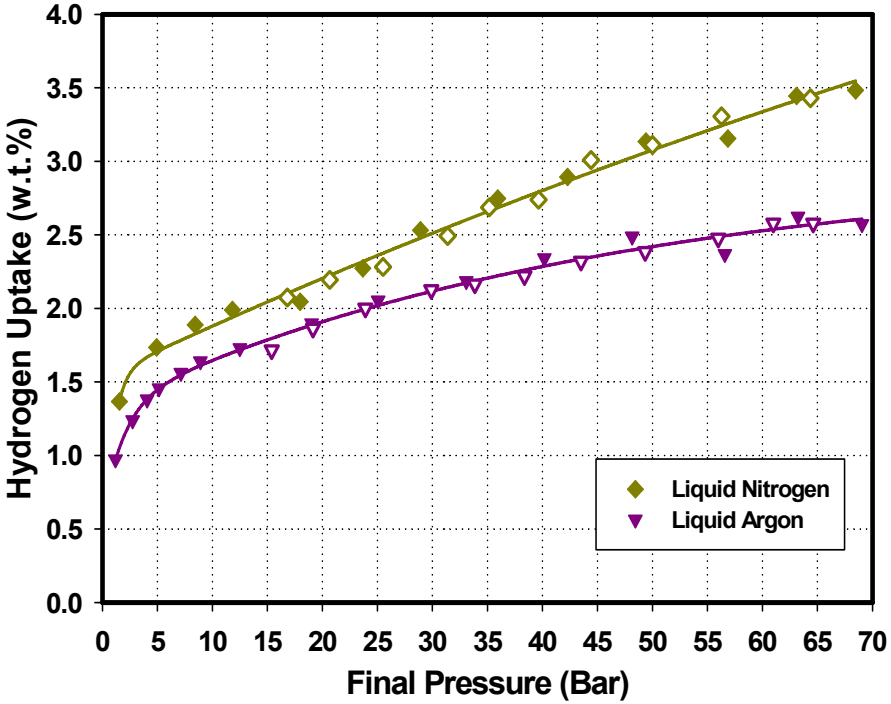
An example of SSA distribution ~ pore size



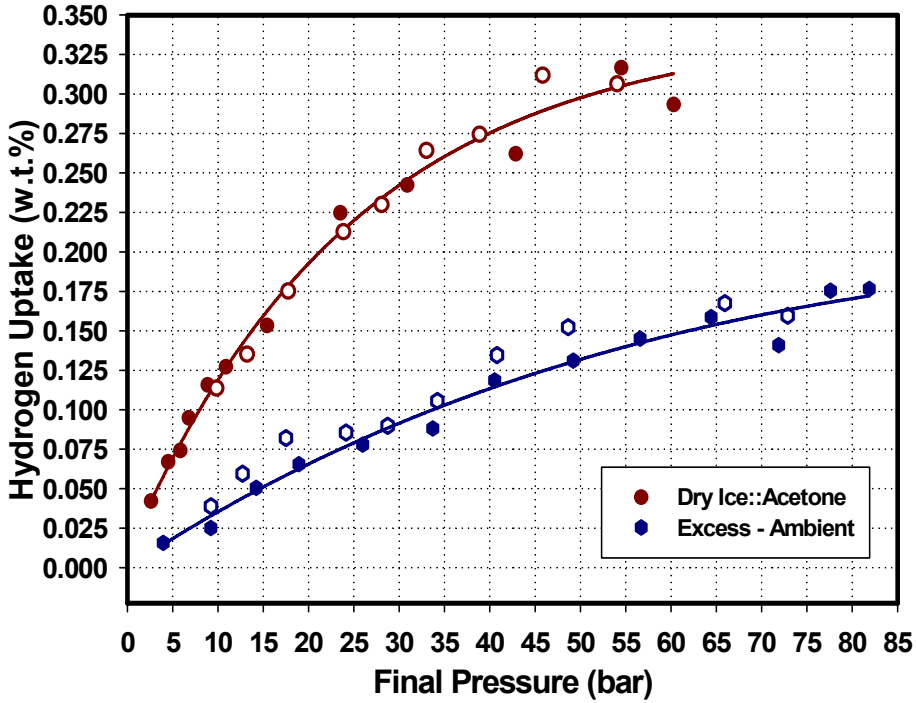
Majority of polymers showed narrow pore size distribution following our design principle. Systematically controlling pore dimension for better H_2 trapping is underway.

Progress Update – H_2 Storage Capacity Measurements

Excess H_2 adsorption measurements at 77K and 87K*



Excess H_2 adsorption measurements at 197K, and 297K*

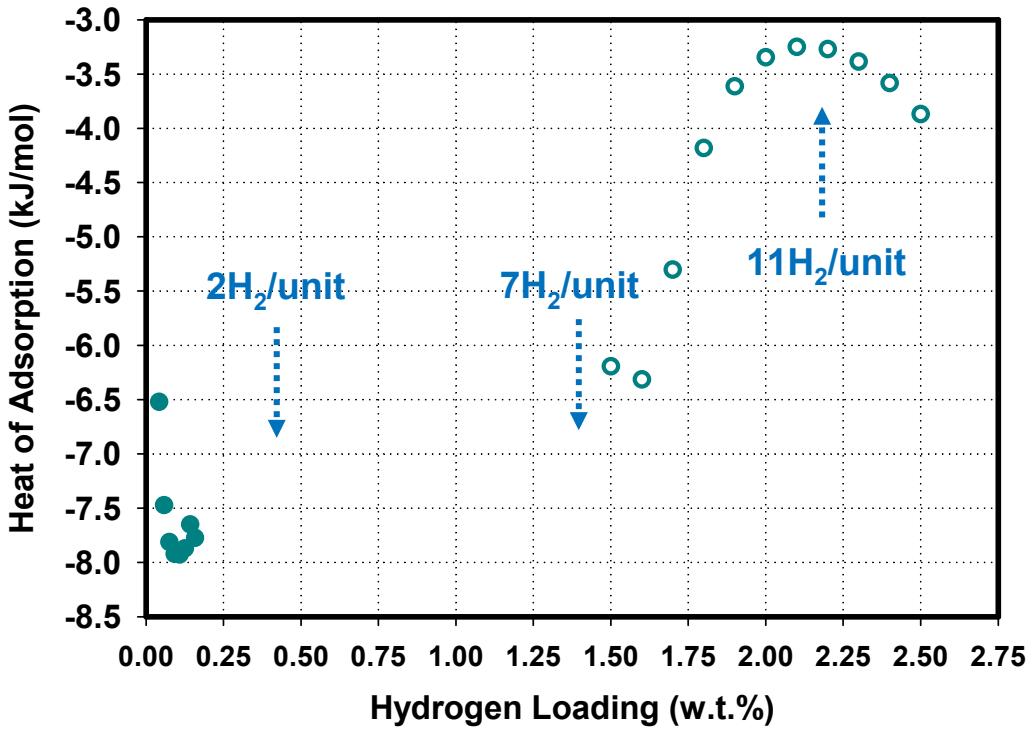


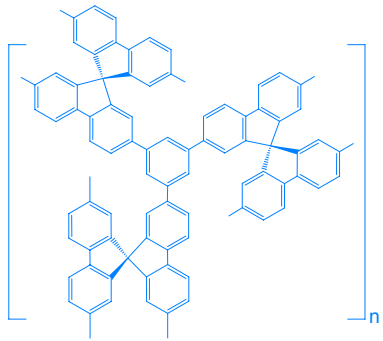
**Solid symbol – adsorption: Hollow symbol – desorption*

- Adsorption reaches saturation at relatively high equilibrium pressure.
- Desorption is completely reversible down to 2 bar.

Progress Update – Isosteric Heat of Adsorption Derived from Experiment & Theory: A Case Study

ΔH_{ads} from experiment





Unit Cell

ΔH_{ads} from theory

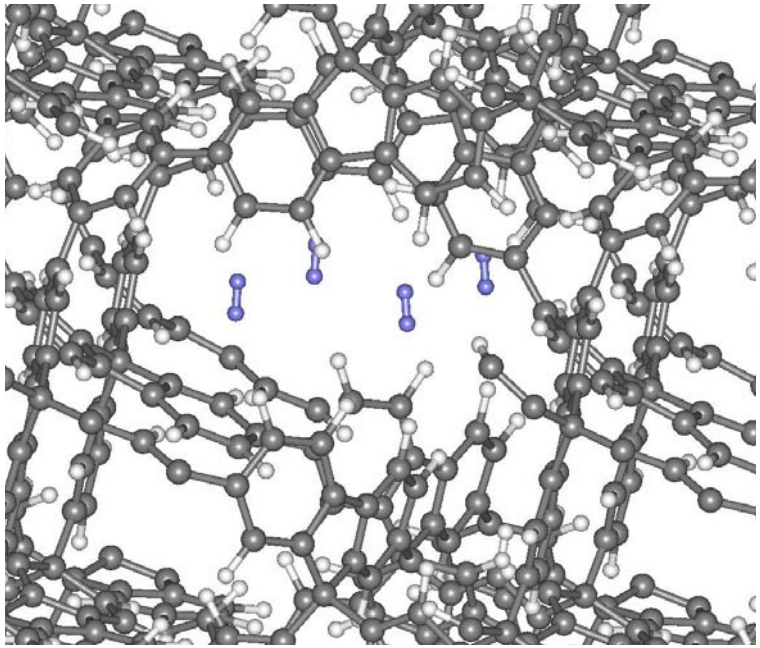
# H_2/unit cell	Gr. uptake (%)	ΔH_{ads} (kJ/mol)
2	0.4	6.77
11	2.2	6.53
21	4.2	5.29

DFT calculations (PW91)

- Experimentally determined ΔH_{ads} demonstrated dependence on H_2 coverage.
- DFT calculation correctly predicted the same trend.

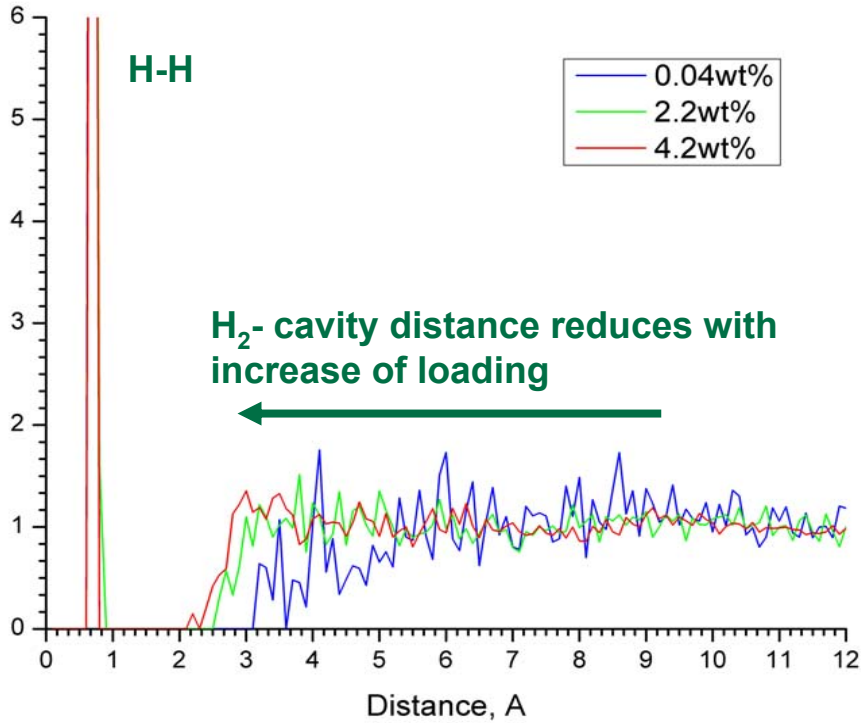
Progress Update – Theoretical Investigation of H_2-Polymer Interaction

Polymer structure optimization and interaction with H_2



H_2 loading = 0.4 wt%

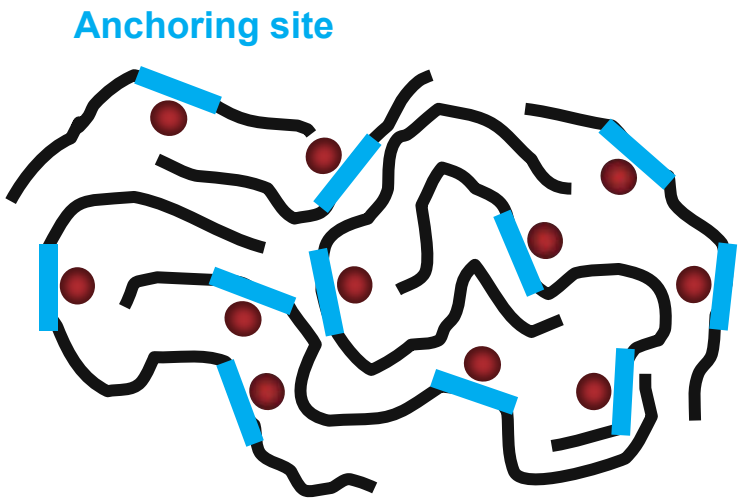
Partial radial distribution function (RDF) of H_2 in adsorbent



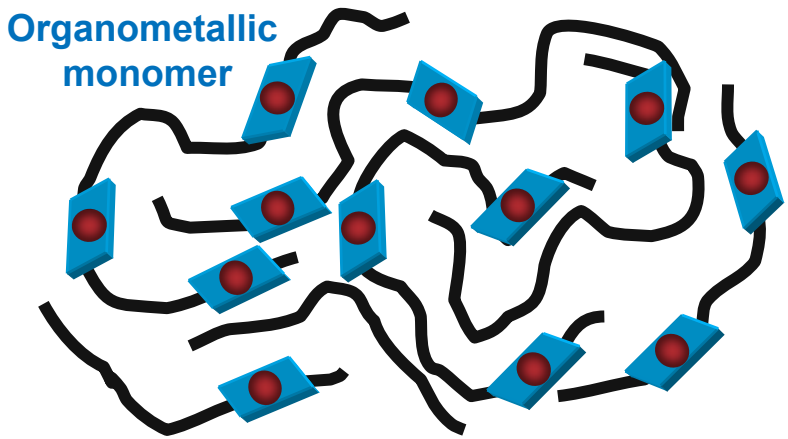
- Optimized 3-D structure through DFT duplicated the experimental pore size.
- RDF calculation revealed the interatomic distance changes between H_2 & adsorbent.
- Further study will include the prediction of H_2 packing limit.

Progress Update – Porous Polymers Containing Transition Metals

- To promote the orbital interaction between H_2 and adsorbent, transition metals were atomically dispersed into nanoporous space within the polymers.
- Fifteen samples were designed and prepared containing transition metals (M = Co, Ni, Fe, Cu, etc).
- Metals were incorporated either through post-doping or direct synthesis.



Adding metal through post-doping

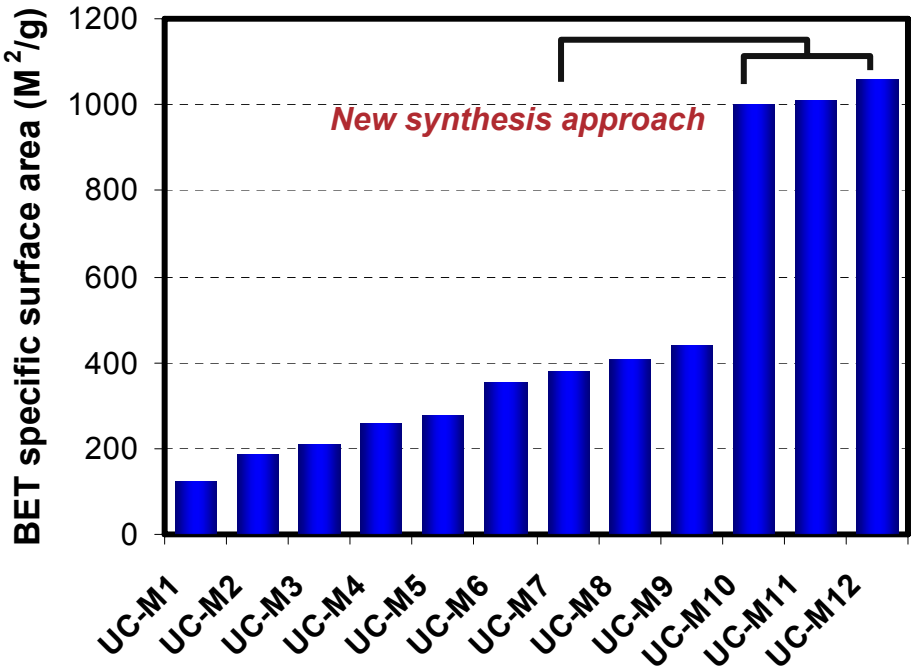


Adding metal through synthesis

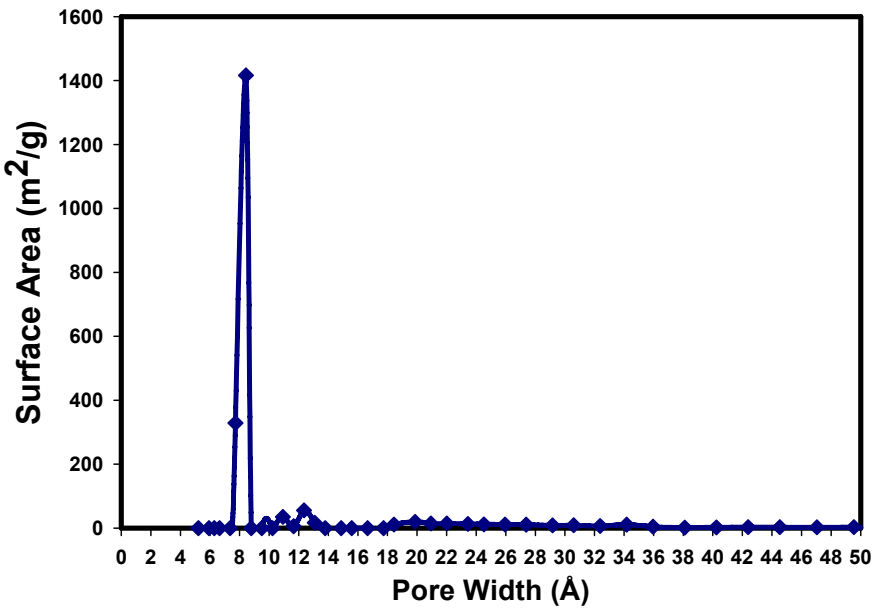
Progress Update – Porous Polymers Containing Transition Metals

- Post-doping: building ligation site on polymer followed by metal addition
- Direct synthesis: Incorporating metal into polymer through cross-linking of organometallic monomers

BET surface areas of selected polymers



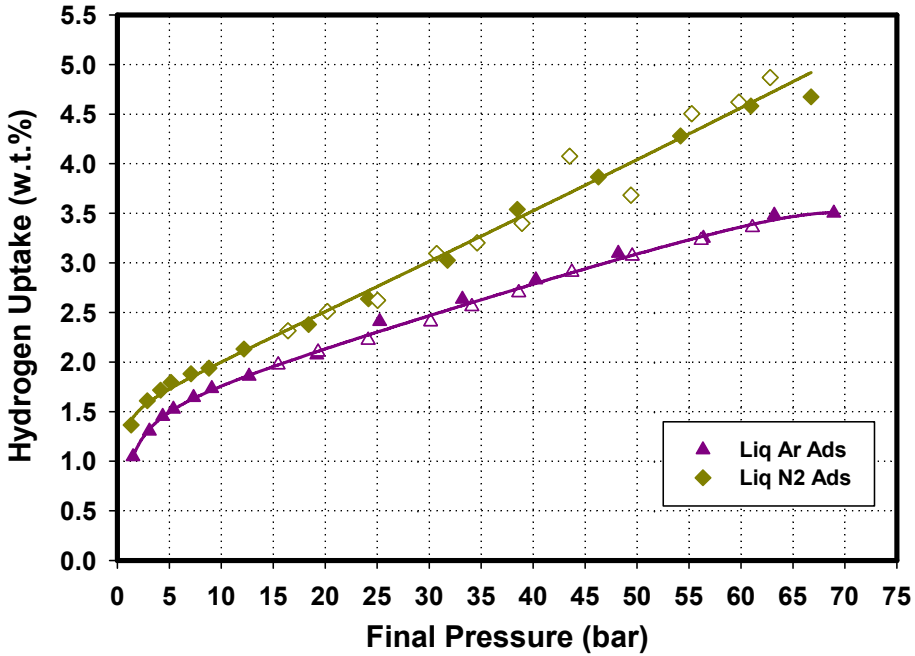
An example of SSA distribution ~ pore size



New cross-linking chemistry of metal-containing monomers resulted in significant enhancement in surface area! Improvement of synthesis is on-going.

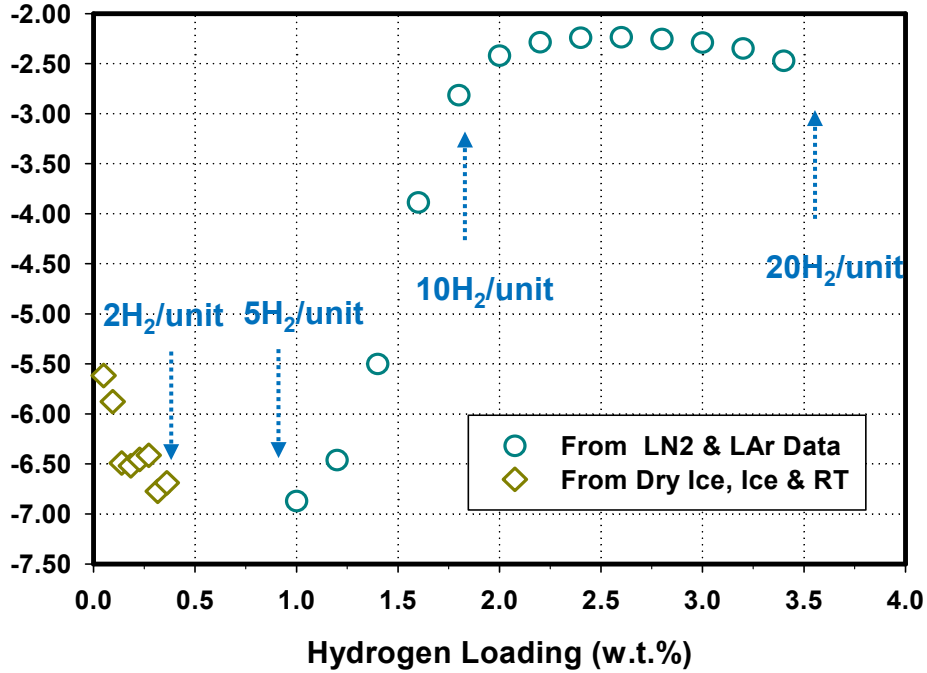
Progress Update – H_2 Uptake Isotherm & Isosteric Heat of Adsorption Measurements for Metal-containing polymer

Excess H_2 adsorption measurements at 77K and 87K*



Solid symbol – adsorption: Hollow symbol – desorption

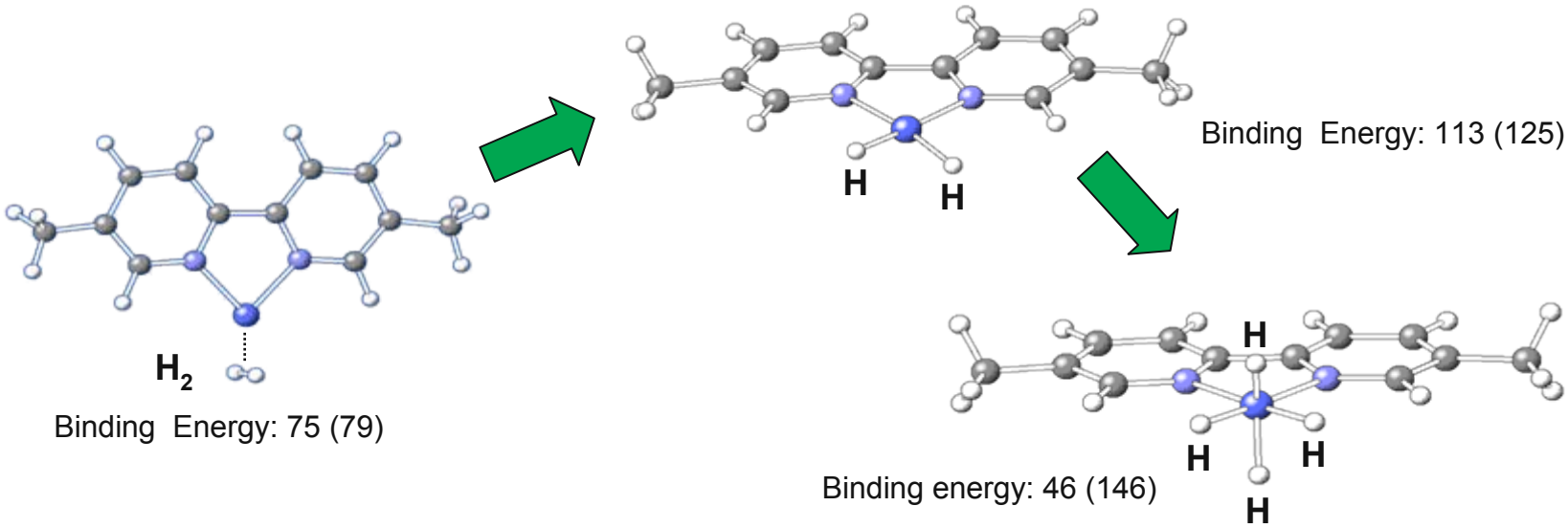
Isosteric heat of adsorption as the function of hydrogen loading



Decreasing heat of adsorption with the increase of storage capacity suggests additional H_2 are spread to the weaker binding sites, possibly away from metal center.

Progress Update – Modeling Effort in Support of Metal Incorporated Polymer Development

Computational modeling of strong binding of H_2 to Co in a polymer unit with atomically substituted cobalt



Binding Energy: 75 (79)

Binding Energy: 113 (125)

Binding energy: 46 (146)

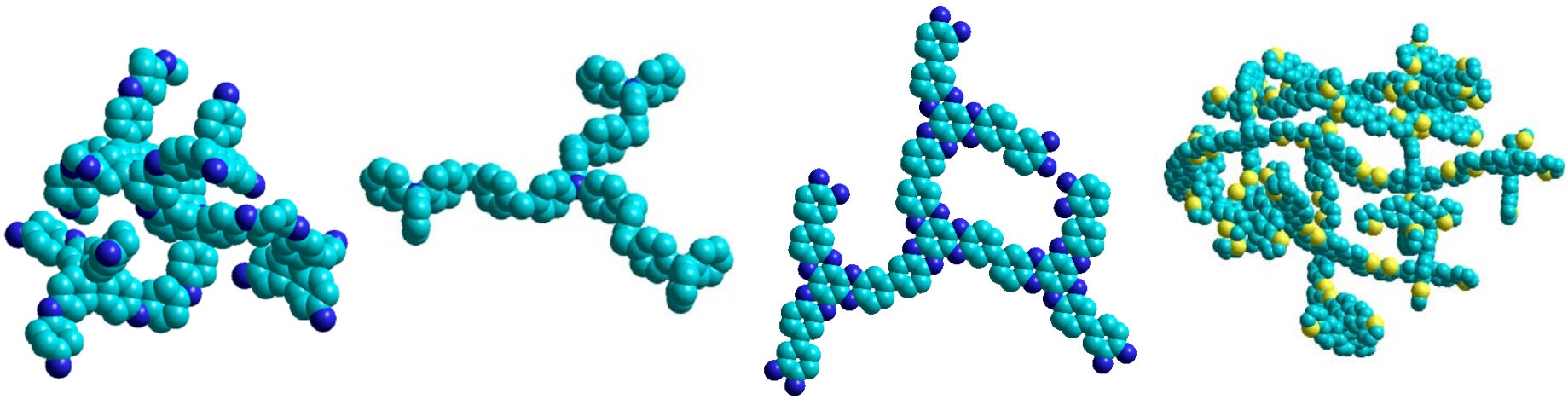
*** Binding energy relative to H_2 in kJ/mol; Theory level: B3LYP/6-31G*//B3LYP/6-31G* (PW91/g4mp2large//B3LYP/6-31G*); g4mp2large is a triple-zeta basis set**

**** Both non-dissociative and dissociative adsorptions of H_2 on PBPY2 are favorable; Dissociation becomes less exothermic with the increase in number of H_2**

Progress Update – Porous Polymers Prepared from Monomers with Non-C Element

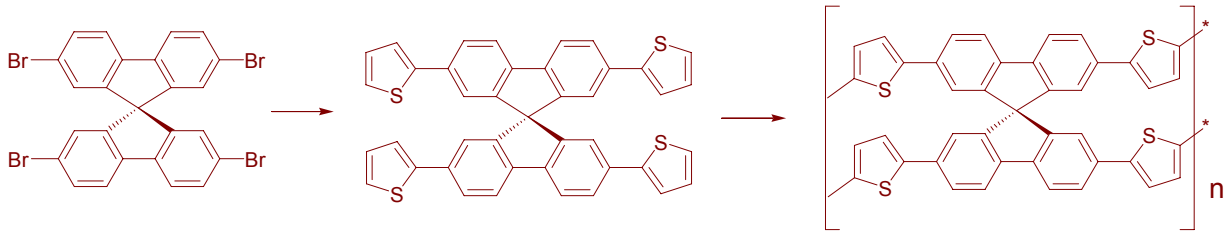
- **To generate "dipole" - "induce dipole" and electronic interactions, non-C element substitution is used to create C-X bonds (X = N, S, B, P, O, ...) within the nano-space of polymers.**
- **Over *20* such porous polymers with different 3-D structures were designed and prepared.**

3-D structures of selected polymers with non-C element prepared at Argonne and U of Chicago

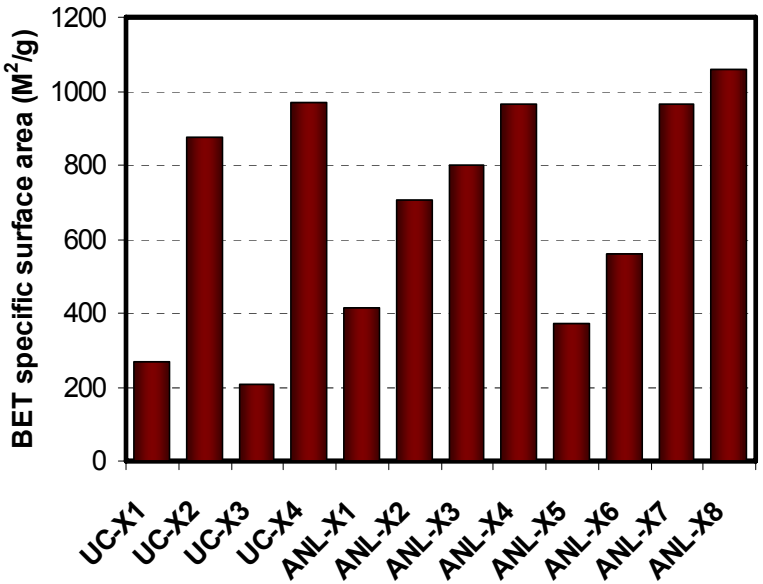


Progress Update – Porous Polymers Prepared from Monomers with Non-C Element

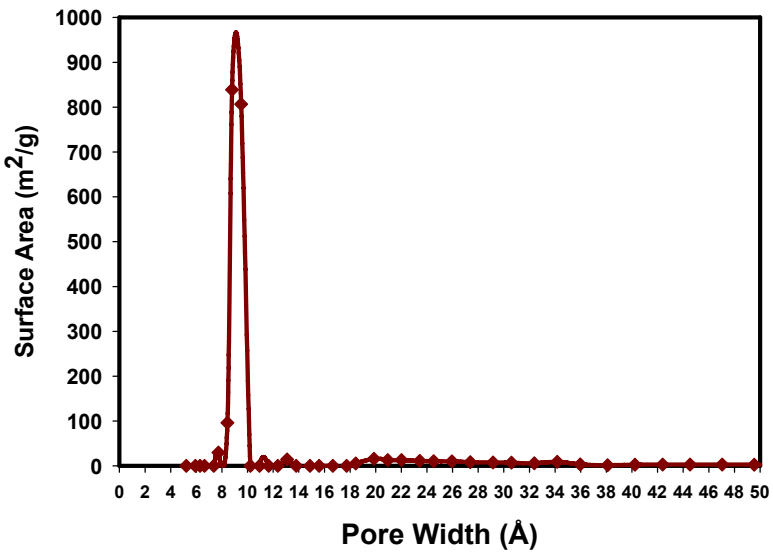
An example of introducing *S* in porous framework



BET surface areas of selected polymers



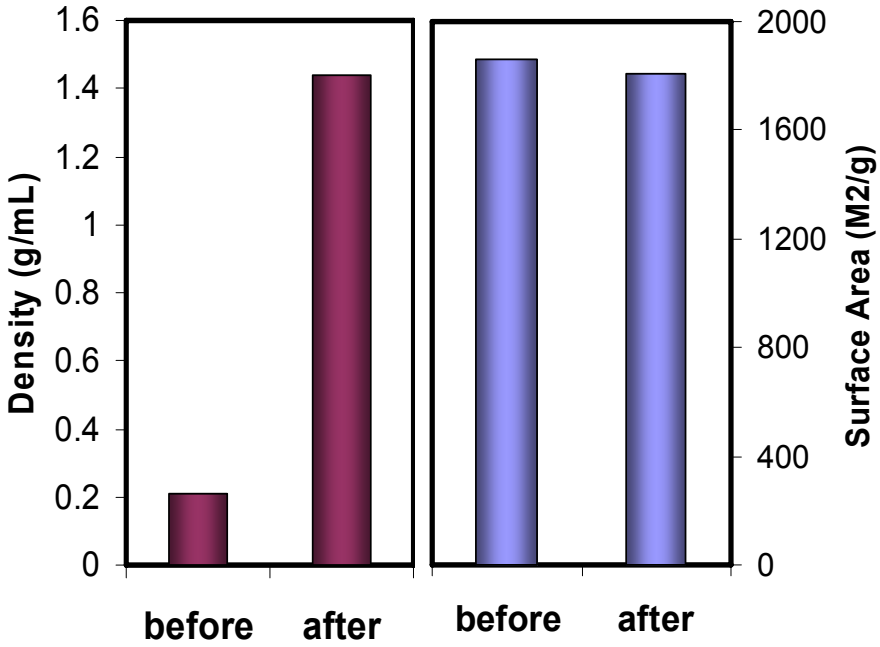
An example of SSA distribution ~ pore size



Contorted core approach enables successful substitution of N, S, etc. while maintaining high surface areas and narrow pore diameters. New approaches include B-substitution.

Progress Update – Volumetric Capacity Study

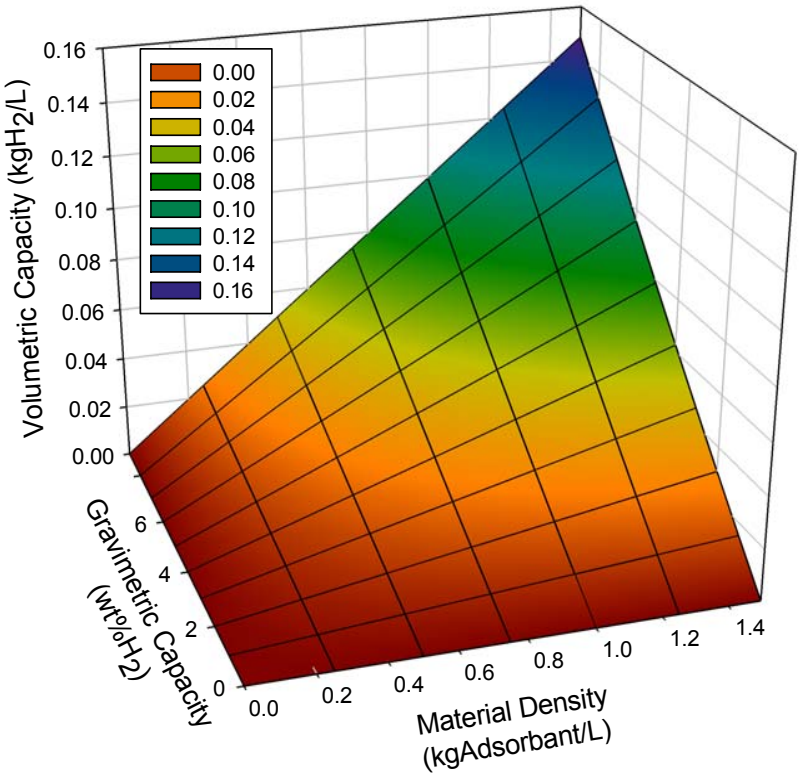
Density ~ SSA changes under compression - a case study, *P = 50,000 lb/in²*



Polymer compression does not cause major changes in microporosity and SSA

	Polymer Sample I		Polymer Sample II	
	Density (g/mL)	Surface Area (M^2/g)	Density (g/mL)	Surface Area (M^2/g)
Before	0.208	1861	0.503	640
After	1.44	1805	1.14	634

Correlations between gravimetric & volumetric capacities vs. adsorbent density



Pelletizing polymer can significantly enhance volumetric capacity!

Collaboration

Partnership with Hydrogen Sorption Center of Excellence

- Team – Argonne National Laboratory (prime) and The University of Chicago (subcontractor)
- Members of DOE HSCoE under the clusters of "Engineered Nanospace" (RC1) and "Substituted Materials" (RC2)
- Collaboration with UNC (HSCoE member) on ^{1}H NMR experiment
- Planned experiment with NIST (HSCoE member) on neutron study
- Sample exchanges with NREL and Air Products (HSCoE members) on measurement validation and benchmark material

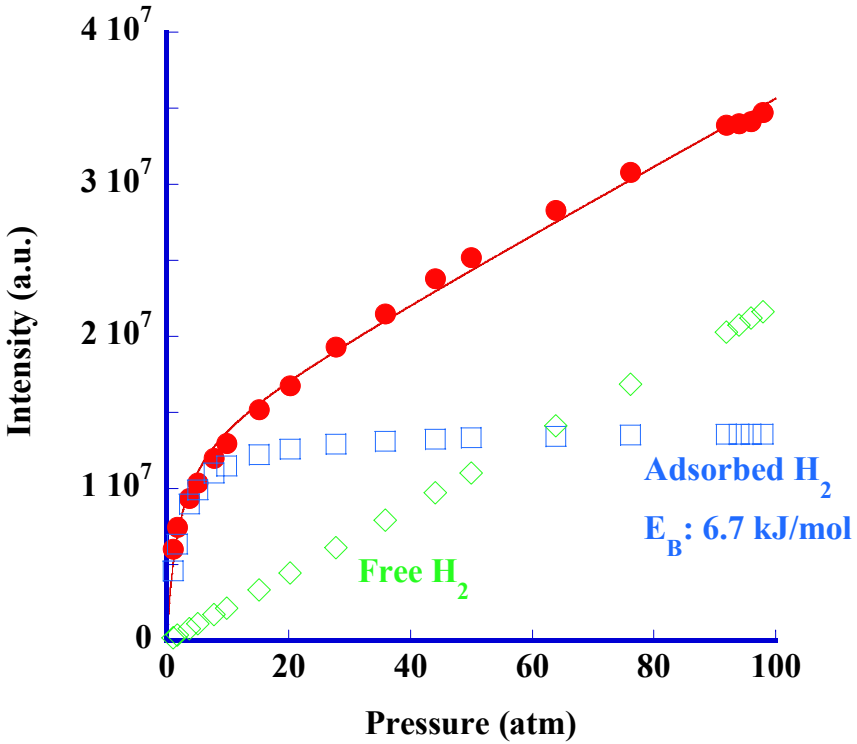
Technology Transfer through HSCoE

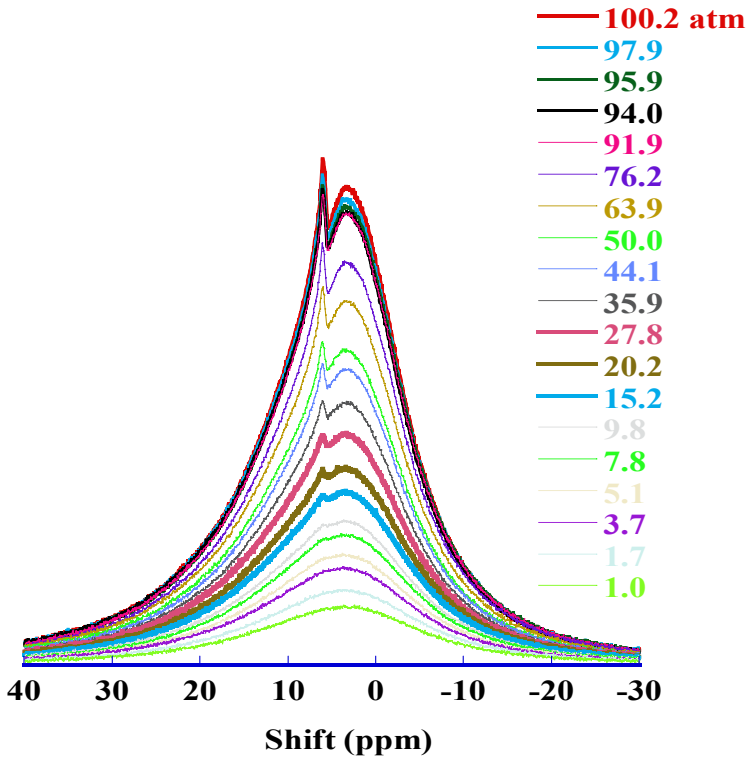
- Valuable inputs on our adsorption apparatus test validation
- New ideas and direction, examples include B and metal doped polymers
- Collaboration opportunities in polymer characterization, examples include NMR & neutron studies
- Up-to-date information on new developments in sorption based materials

Collaboration

High pressure ^{1}H NMR study on ANL-UofC polymer performed by Kleinhammes/Wu (U of North Carolina)

Sample = contorted aromatic polymer, UC-C6
SSA = 760 M^2/g





More collaborations of H_2-polymer interaction studies by NMR & Neutron are underway!

Future Work

FY09

- Improve H_2-adsorbent interaction through pore size control and rational design
- Explore new synthesis methods for metal-containing polymers and to investigate the structure-heat of adsorption correlations
- Refine modeling on H_2-adsorbent interaction, provide guidance to the polymer design
- Investigate the kinetics and transient properties of hydrogen adsorption over polymers

FY10

- Explore new non-C element substituted polymers for higher adsorption energies and storage capacity
- Continue to collaborate with HSCoE in structural & mechanistic studies (e.g. NMR, neutron, etc.)
- Explore new polymer activation methods to enhance surface property and storage capacity

Summary

Relevance: Developing the nanostructured porous polymers as H_2 storage media to meet DOE performance targets for transportation applications

Approach: Rational design and synthesis at the molecular level supported by computational modeling and advanced characterization

Accomplishments:

- Over 50 polymers from three different categories were prepared since last AMR with high surface areas (up to1800 m^2/g) and narrow pore sizes (6Å to 10Å) achieved.
- H_2 uptakes up to 5.1% at 77K and 0.5% at RT were achieved, representing significant improvement over last AMR report.
- Combined ΔH_{ads} measurement & computational modeling improved understanding on adsorption mechanism.

Collaboration: Argonne (prime) and U of Chicago (sub) partnering with HSCoE, information dissemination & experimental collaboration

Future Work:

- Continue new polymer exploration and optimization
- Explore the “hidden capacity” through activation approach
- Improve the understanding of H_2-polymer interaction via theory & advanced characterization

Summary Table

H_2 storage capacities for selected ANL – U of Chicago polymers

Sample	Gr. Uptake (77K, 40 bars) (kg H_2/kg adsorbent+H_{2ads})	Vol. Uptake [a] (77K, 40 bars) (kg H_2/L adsorbent)	Gr. Uptake (RT, 70 bars) (kg H_2/kg adsorbent+H_{2ads})	Vol. Uptake [a] (RT, 70 bars) (kg H_2/L adsorbent)	BET SSA (M^2/g)	Type of polymer [b]
ANL-C1	4.0%	0.010	0.21%	0.0005	1233	C
ANL-C2	4.4%	0.009	0.35%	0.0007	1593	C
ANL-C5	5.1%	0.011	0.52%	0.0012	1863	C
UC-C10	2.8%	0.010	0.18%	0.0006	1043	C
UC-X4	3.2%	0.0085	0.45%	0.0012	971	X
UC-M12	3.6%	0.0051	0.40%	0.0006	1060	M

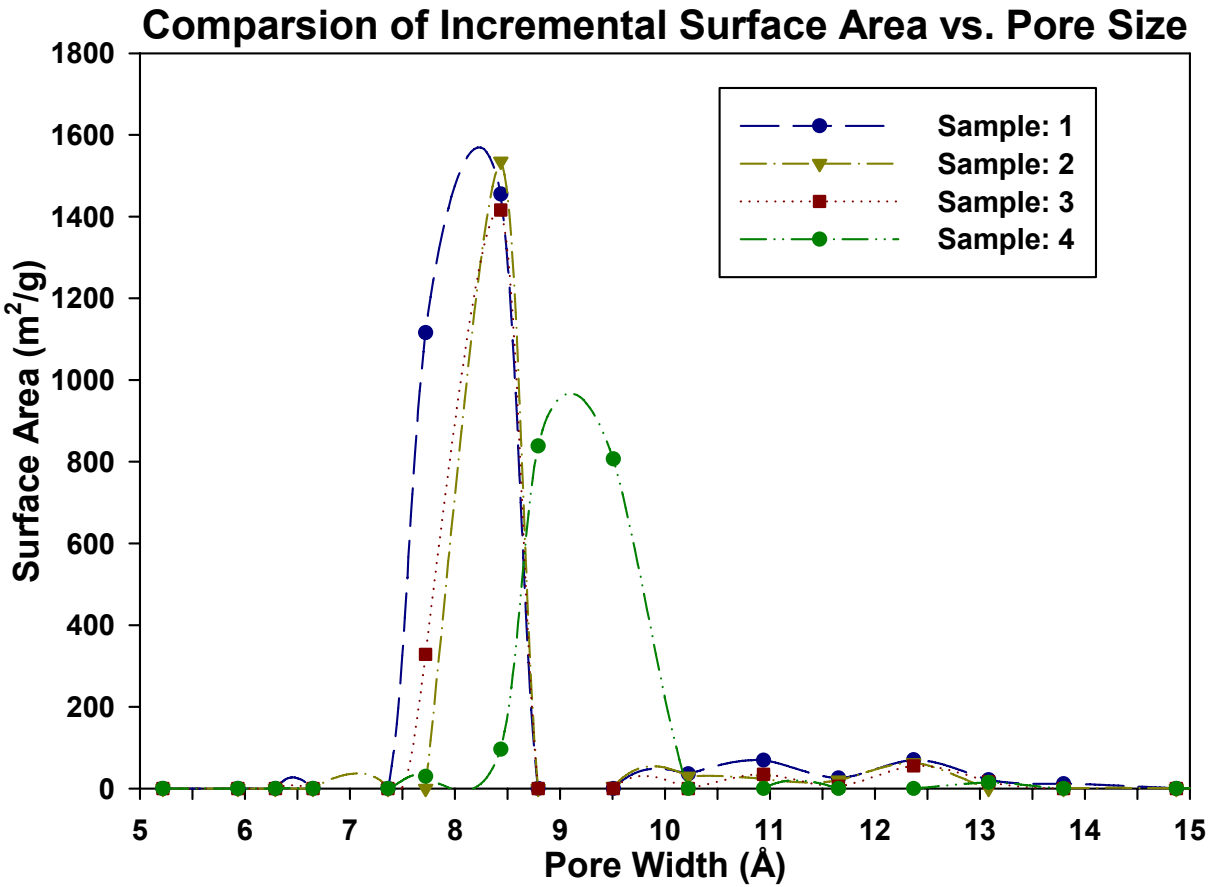
a. Volumetric capacity is calculated based on the actual density of loose polymer powders, which ranges from 0.15 to 0.5. These capacities can be increased by x2 to x5 through compression.

b. C = polymers contains only aromatics, X = polymers with non-C element substitutions, M = polymers incorporated with transition metals

Additional Slides

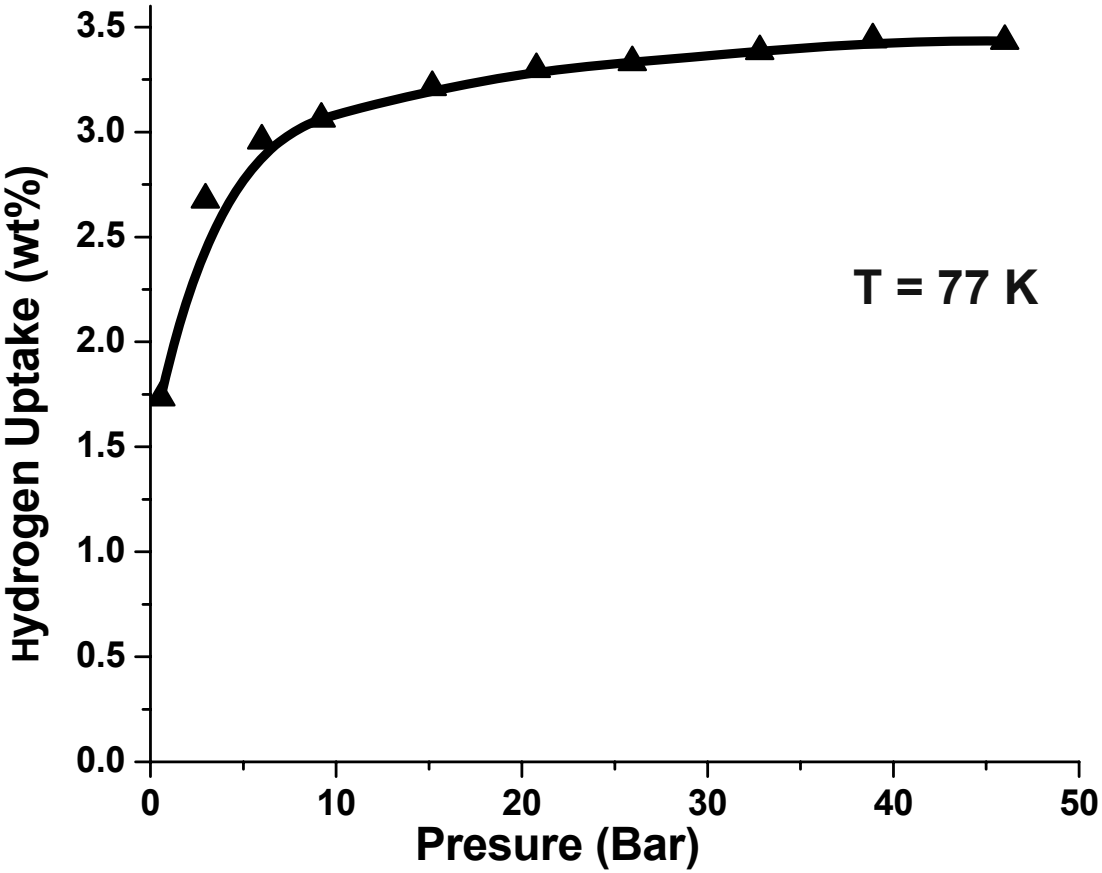
Supplemental Info – An example of our effort in controlling pore size through new synthetic approach

Experimental pore sizes (NLDFT) calculated from N2-BET measurement



Pore diameters can be varied by using different synthetic precursors and techniques

Supplemental Info – Benchmark study on H_2 storage capacity of a Cu-MOF



H_2 uptake of Cu-BTC measured with our Sievert apparatus showed the same capacity and P-dependent saturation as the published results