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Hydrogen Storage through Nanostructured Polymeric Materials

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U.S. DEPARTMENT OF ENERGY

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ST_27_Liu**

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Overview

Timeline

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

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

Barriers

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

Partners

- Interactions/collaborations
 - Argonne National Laboratory (Lead)
 - U of Chicago (Subcontractor)
 - HSCoE Members
 - *U of N. Carolina (¹H 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 uptakes 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 H₂ storage capacity over last AMR report!

Approach

New Polymer Exploration (UofC/ANL)

- New polymer synthesis through rational design at molecular level
- Molecular structure characterization

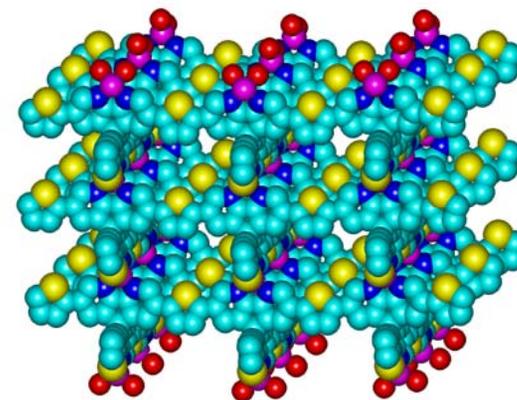
Measurement & Optimization (ANL)

- H₂ storage capacity measurement
- Surface structure characterization
- Synthesis method improvement

Modeling & Characterization (ANL/HSCoE)

- H₂-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-H₂ interaction by incorporating functional groups with hetero (non-C) elements
- Develop fundamental understanding through modeling and advanced characterization

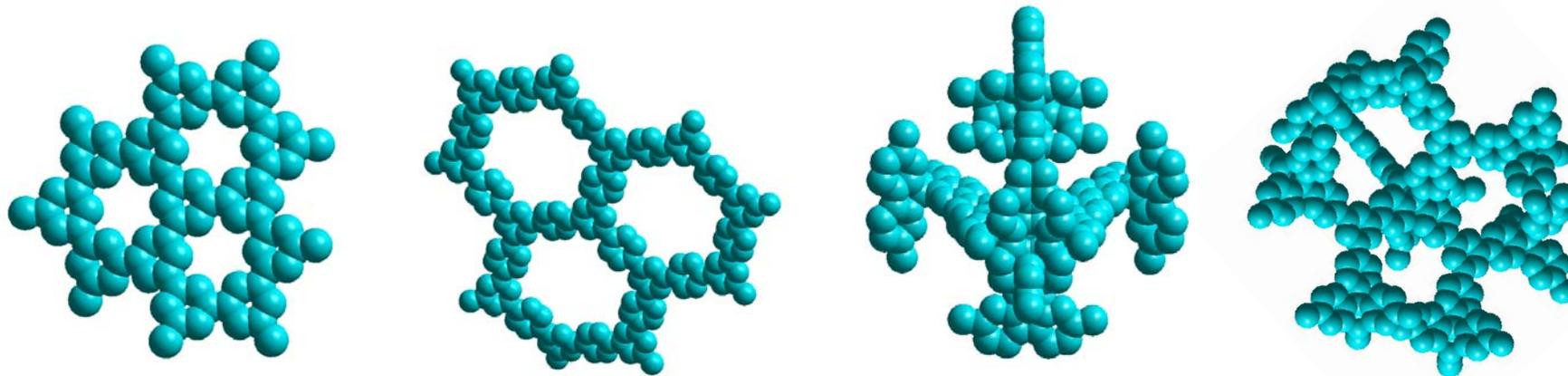


An example of ANL/UofC polymer with conductive backbone incorporated with different elements

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 & H₂ adsorption capacity/energy is underway.

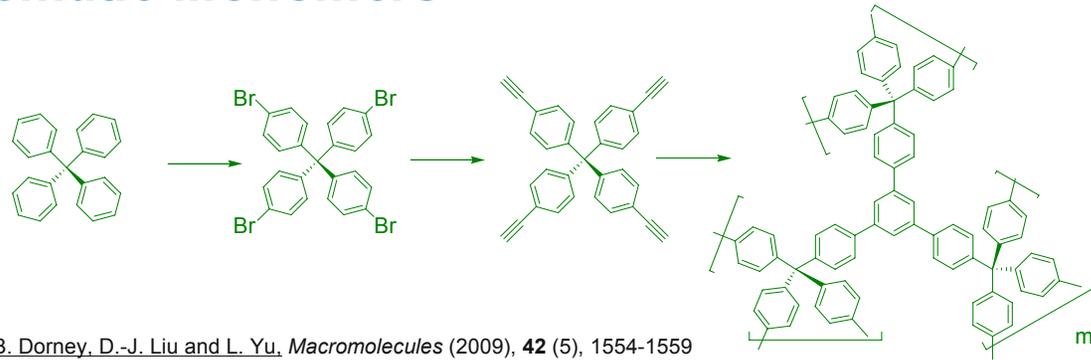
3-D structures of selected aromatic polymers prepared at Argonne and U of Chicago



High surface area (1000 M²/g ~ 1800 M²/g) & narrow pore size (6Å to 10Å) were achieved!

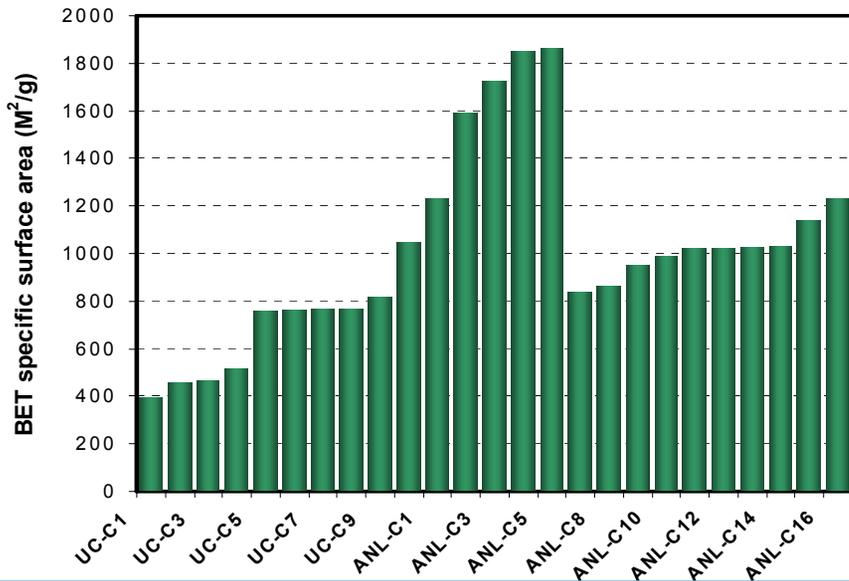
Progress Update – Design, Synthesis & Surface Properties of Porous Polymers from Aromatic Monomers

An example of generating microporosity through contorted monomers

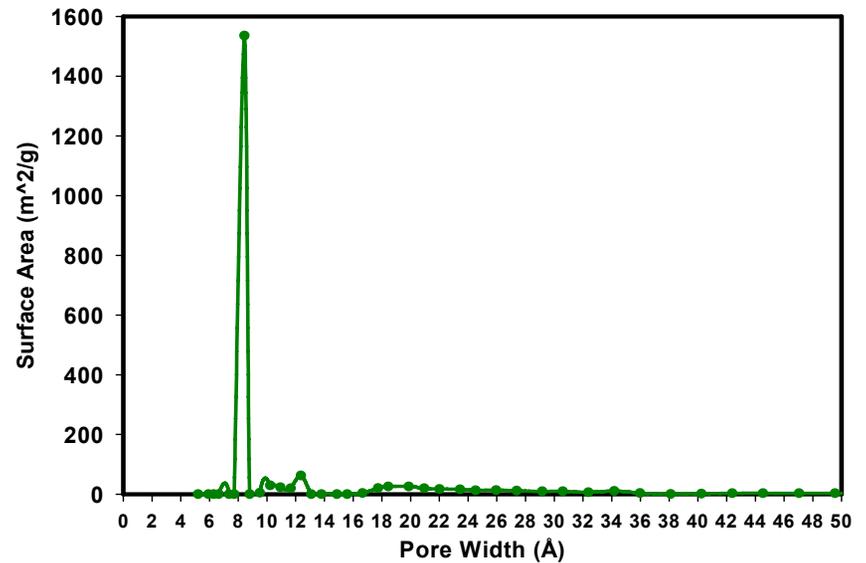


S. Yuan, S. Kirklín, B. Dorney, D.-J. Liu and L. Yu, *Macromolecules* (2009), 42 (5), 1554-1559

BET surface areas of selected polymers



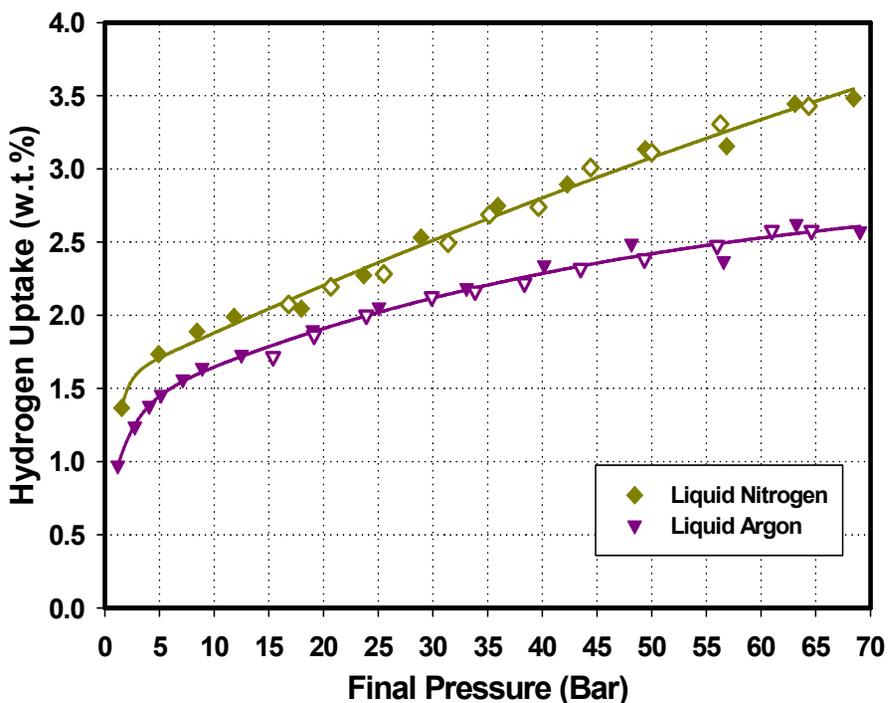
An example of SSA distribution ~ pore size



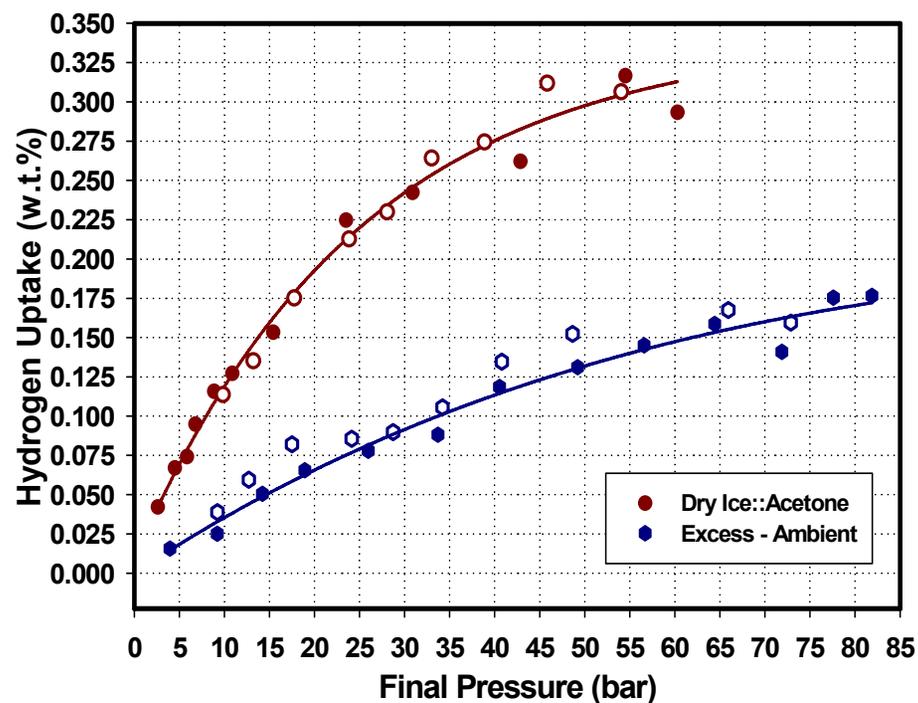
Majority of polymers showed narrow pore size distribution following our design principle. Systematically controlling pore dimension for better H₂ trapping is underway.

Progress Update – H₂ Storage Capacity Measurements

Excess H₂ adsorption measurements at 77K and 87K*



Excess H₂ adsorption measurements at 197K, and 297K*

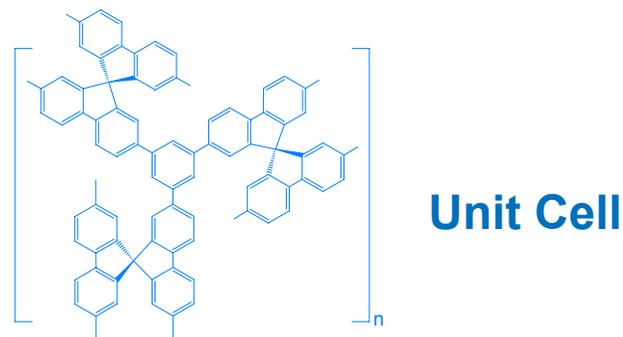
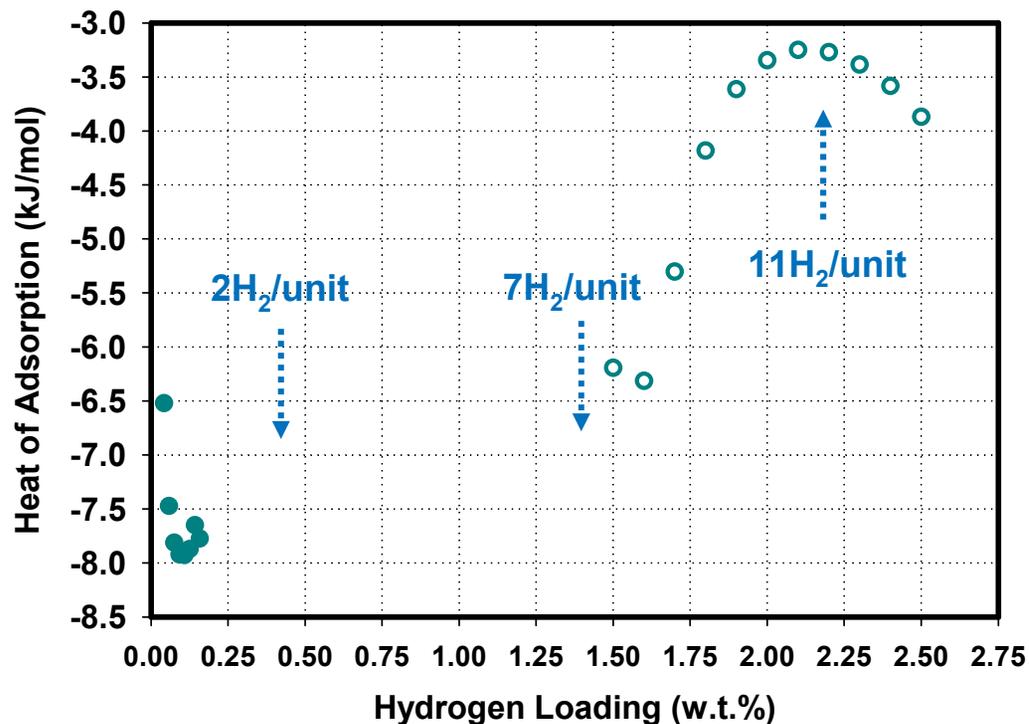


*Solid symbol – adsorption: Hollow symbol – desorption

- 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



ΔH_{ads} from theory

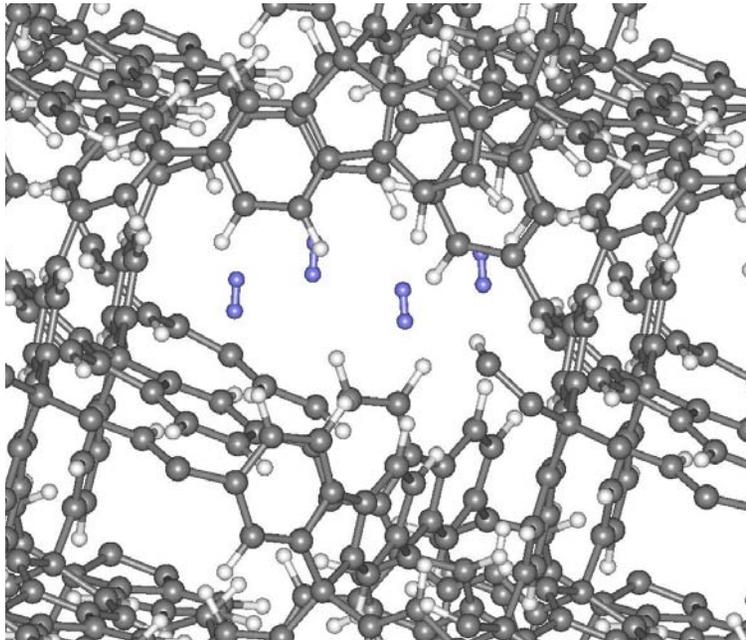
# H ₂ /unit cell	Gr. uptake (%)	ΔH_{ads} (kJ/mol)
2	0.4	6.77
11	2.2	6.53
21	4.2	5.29

DFT calculations (PW91)

- Experimentally determined ΔH_{ads} demonstrated dependence on H₂ coverage.
- DFT calculation correctly predicted the same trend.

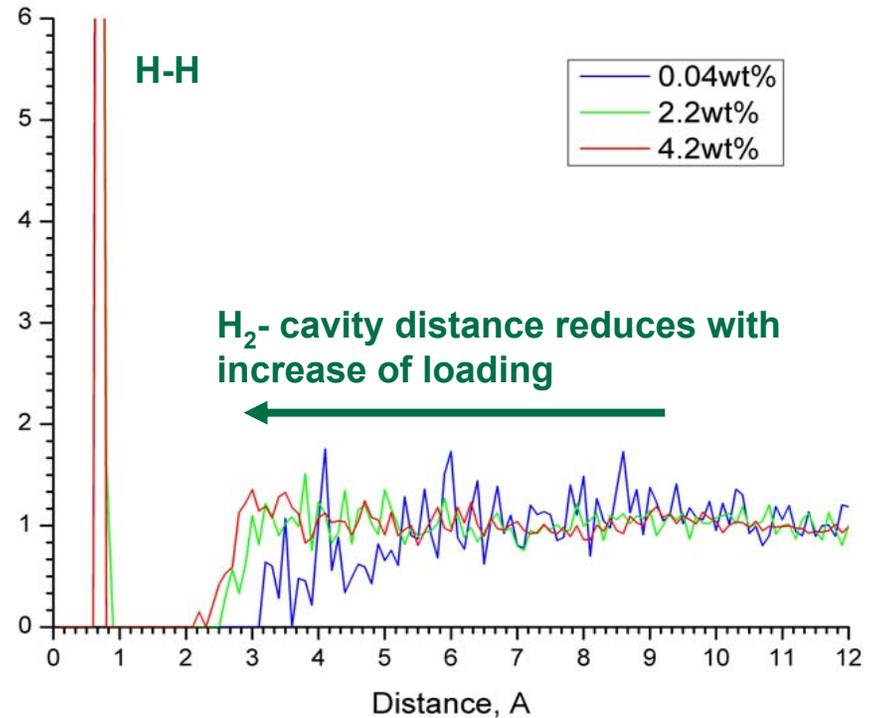
Progress Update – Theoretical Investigation of H₂-Polymer Interaction

Polymer structure optimization and interaction with H₂



H₂ loading = 0.4 wt%

Partial radial distribution function (RDF) of H₂ in adsorbent

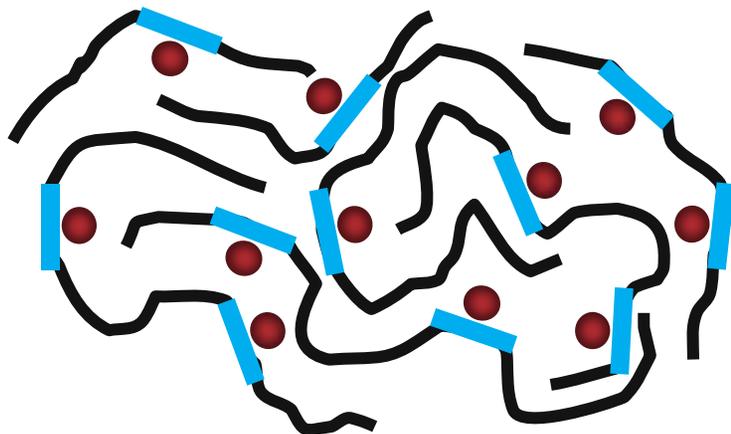


- Optimized 3-D structure through DFT duplicated the experimental pore size.
- RDF calculation revealed the interatomic distance changes between H₂ & adsorbent.
- Further study will include the prediction of H₂ packing limit.

Progress Update – Porous Polymers Containing Transition Metals

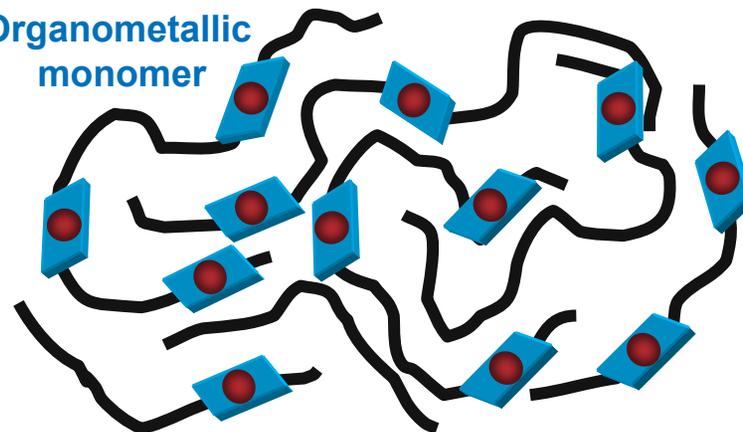
- To promote the orbital interaction between H_2 and adsorbent, transition metals were atomically dispersed into nanoporous space within the polymers.
- Fifteen samples were designed and prepared containing transition metals ($M = Co, Ni, Fe, Cu, \text{etc.}$).
- Metals were incorporated either through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

Anchoring site



Adding metal through post-doping

Organometallic monomer

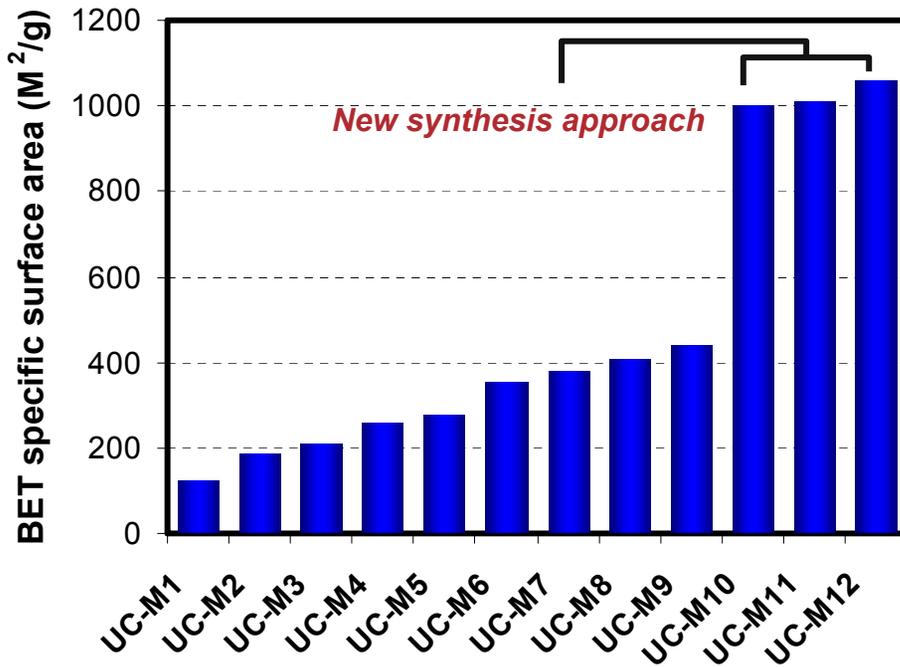


Adding metal through synthesis

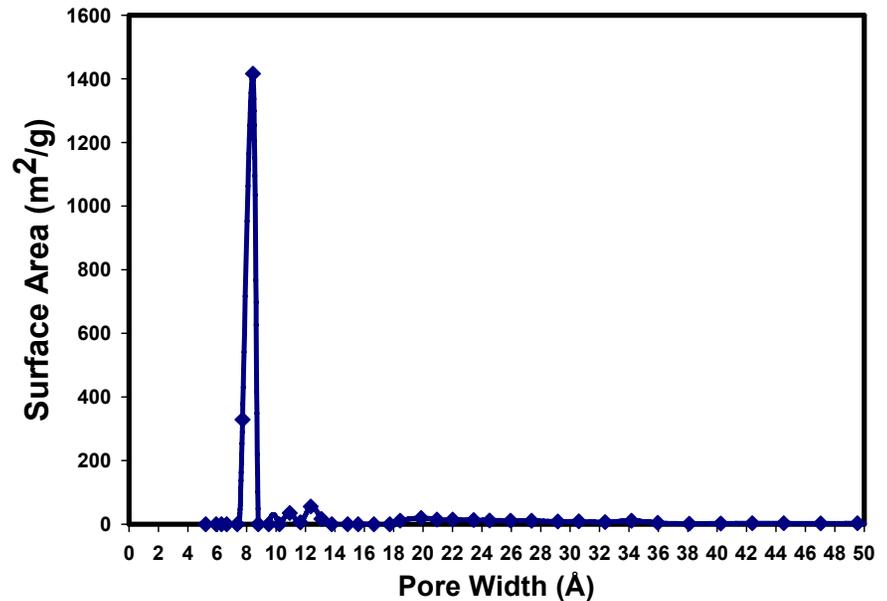
Progress Update – Porous Polymers Containing Transition Metals

- 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



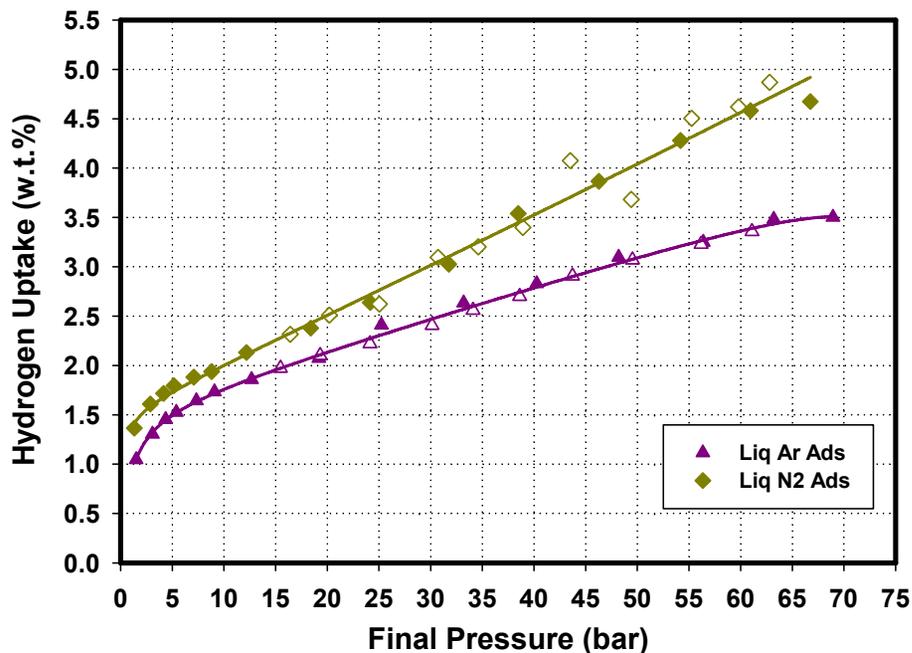
An example of SSA distribution ~ pore size



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

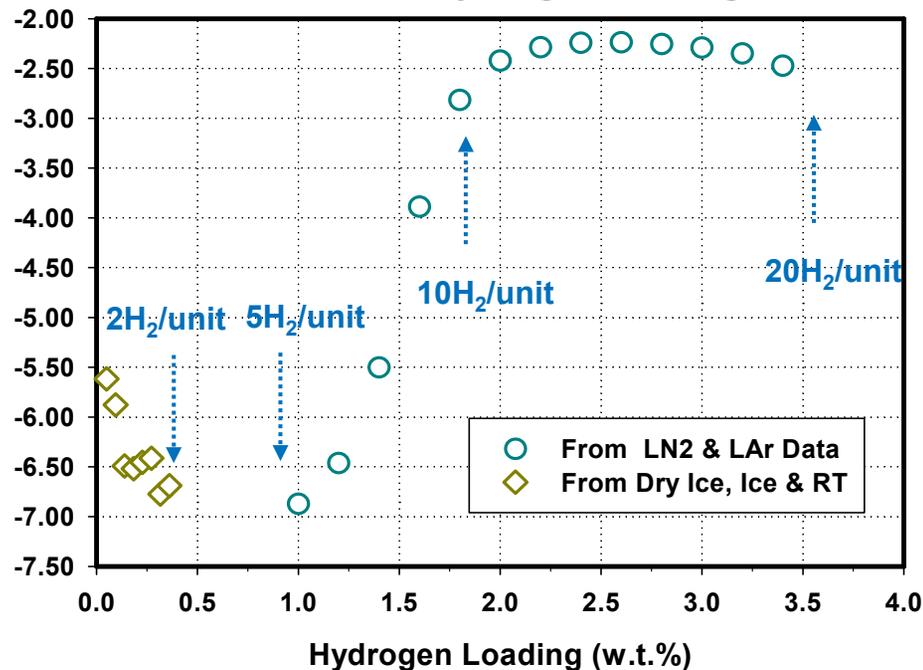
Progress Update – H₂ Uptake Isotherm & Isothermic Heat of Adsorption Measurements for Metal-containing polymer

Excess H₂ adsorption measurements at 77K and 87K*



*Solid symbol – adsorption; Hollow symbol – desorption

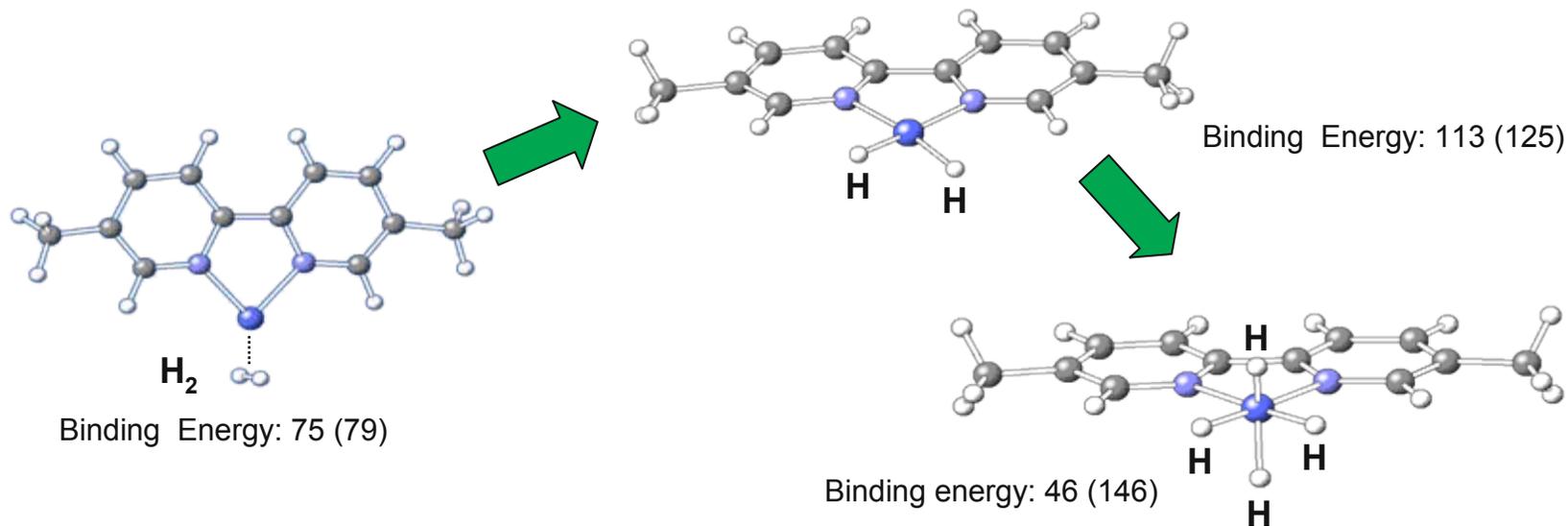
Isosteric heat of adsorption as the function of hydrogen loading



Decreasing heat of adsorption with the increase of storage capacity suggests additional H₂ 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



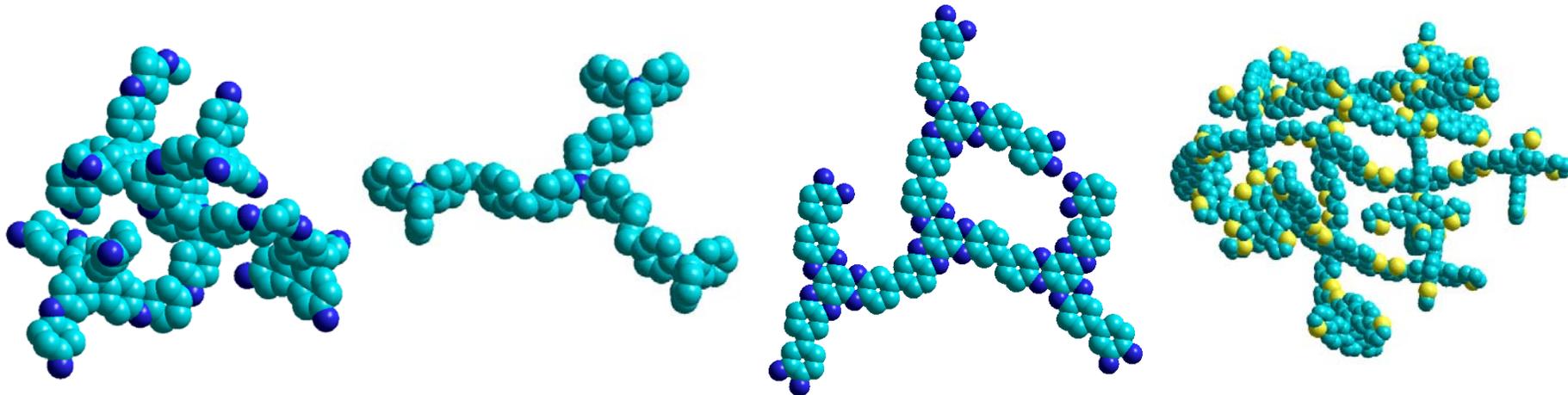
* Binding energy relative to H_2 in kJ/mol; Theory level: B3LYP/6-31G*//B3LYP/6-31G* (PW91/g4mp2large//B3LYP/6-31G*); g4mp2large is a triple-zeta basis set

** 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

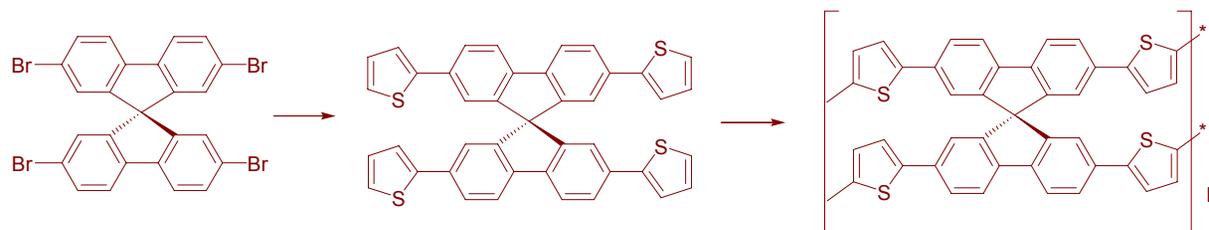
- To generate “dipole” - “induce dipole” and electronic interactions, non-C element substitution is used to create C-X bonds (X = N, S, B, P, O, ...) within the nano-space of polymers.
- Over 20 such porous polymers with different 3-D structures were designed and prepared.

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

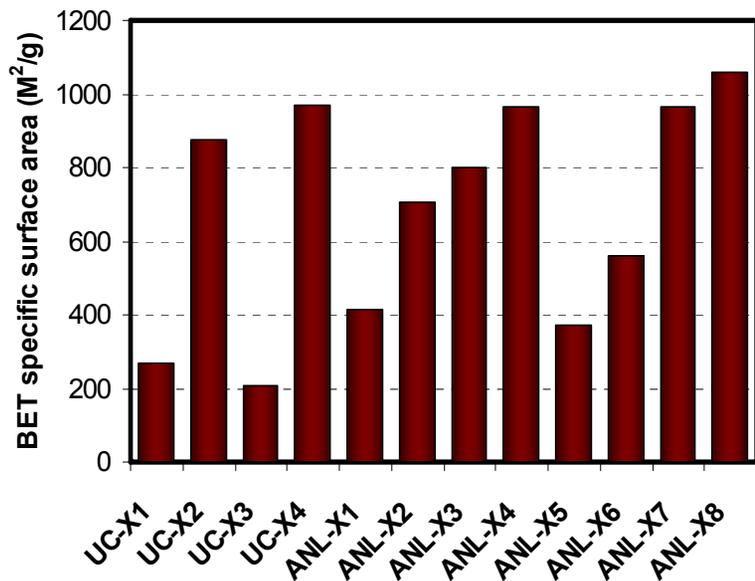


Progress Update – Porous Polymers Prepared from Monomers with Non-C Element

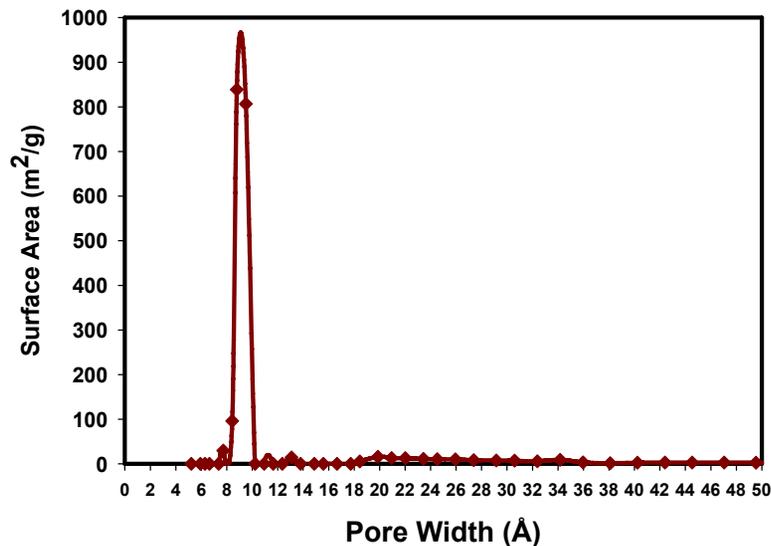
An example of introducing S in porous framework



BET surface areas of selected polymers



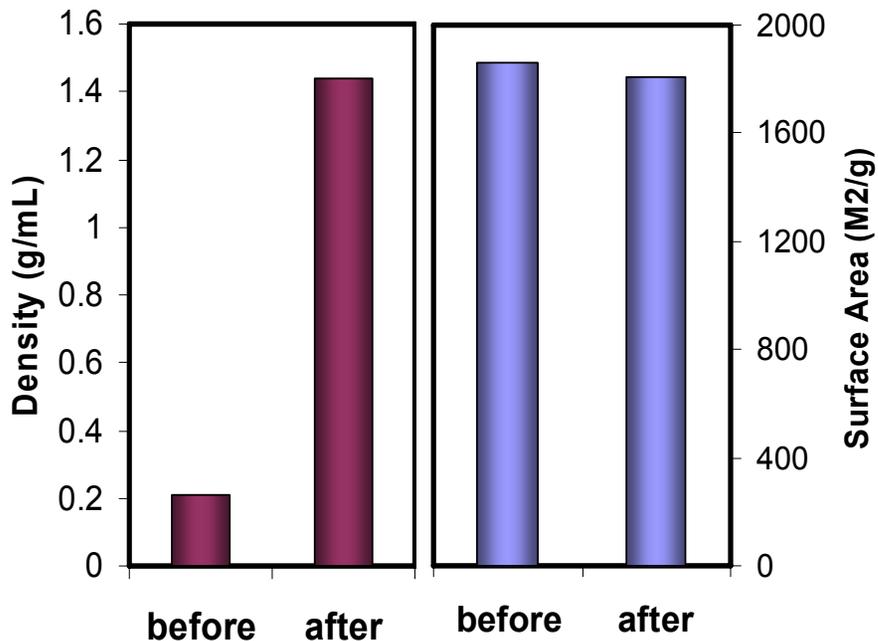
An example of SSA distribution ~ pore size



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

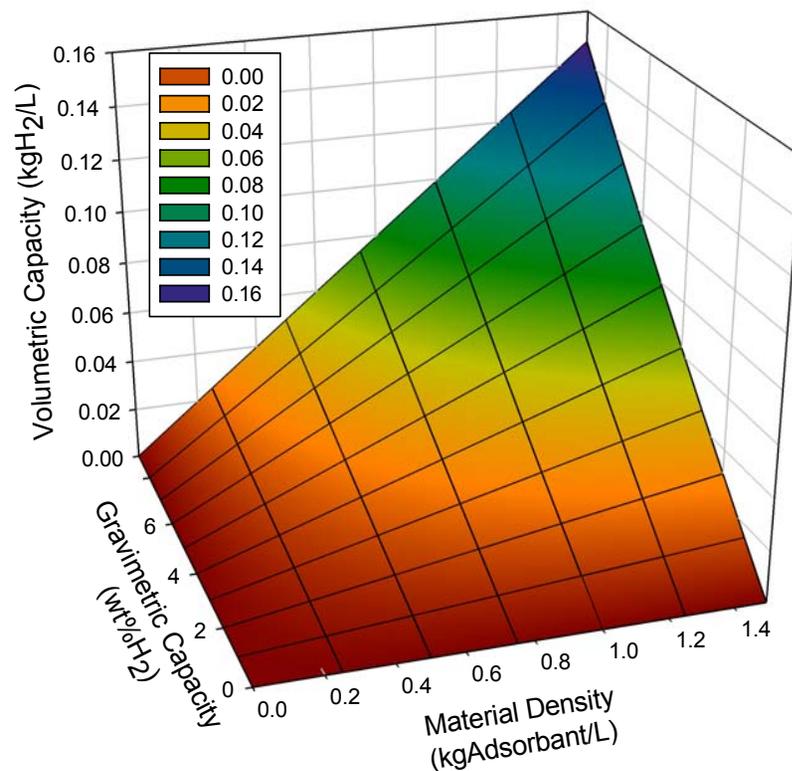
Density ~ SSA changes under compression - a case study, $P = 50,000 \text{ lb/in}^2$



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 ^1H 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

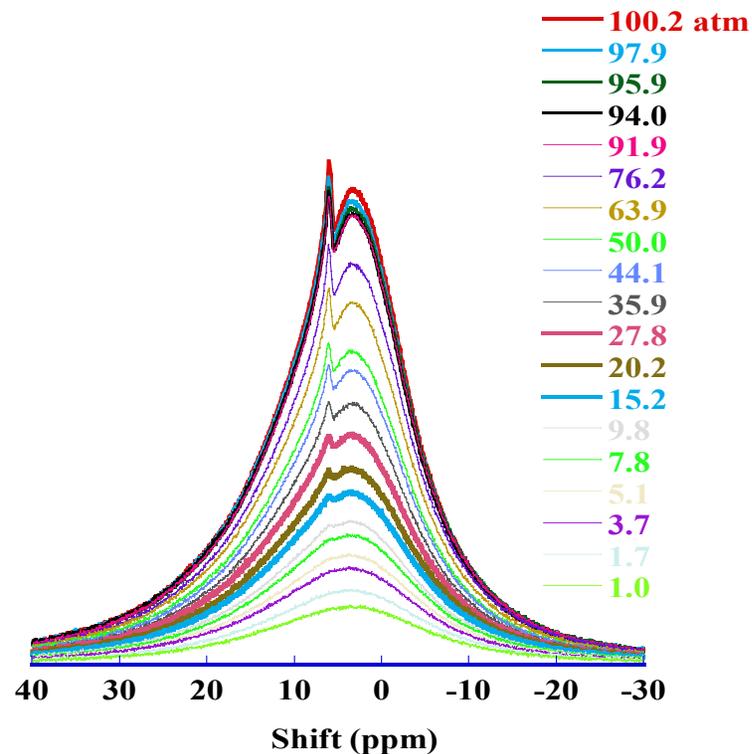
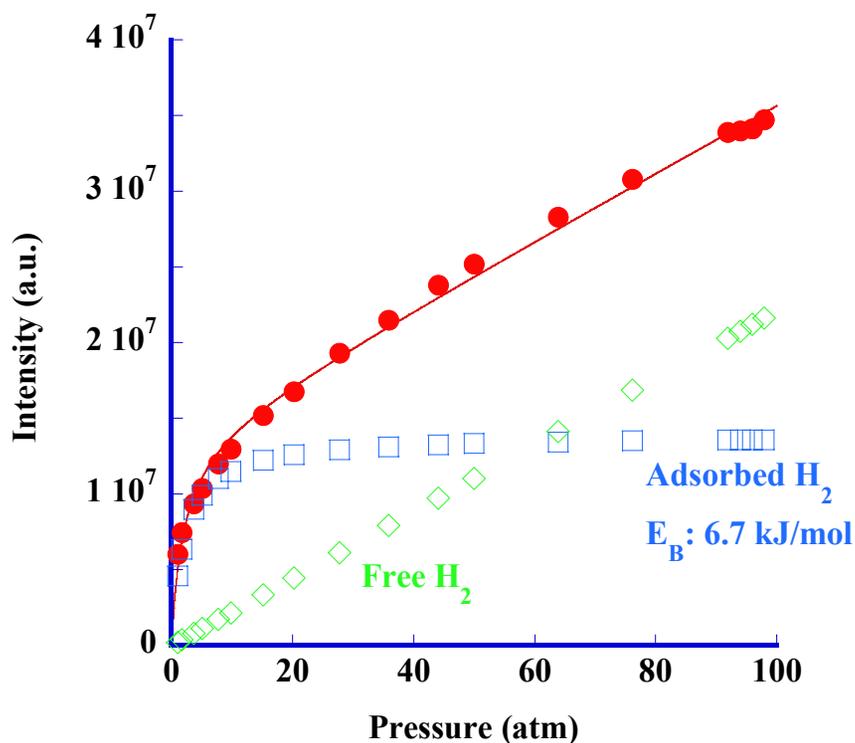
Technology Transfer through HSCoE

- 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 ^1H 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 H₂-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 H₂-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 H₂ 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 to 1800 m²/g) and narrow pore sizes (6Å to 10Å) achieved.
- H₂ 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 H₂-polymer interaction via theory & advanced characterization

Summary Table

H₂ storage capacities for selected ANL – U of Chicago polymers

Sample	Gr. Uptake (77K, 40 bars) (kg H ₂ /kg adsorbent+H ₂ _{ads})	Vol. Uptake ^a (77K, 40 bars) (kg H ₂ /L adsorbent)	Gr. Uptake (RT, 70 bars) (kg H ₂ /kg adsorbent+H ₂ _{ads})	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

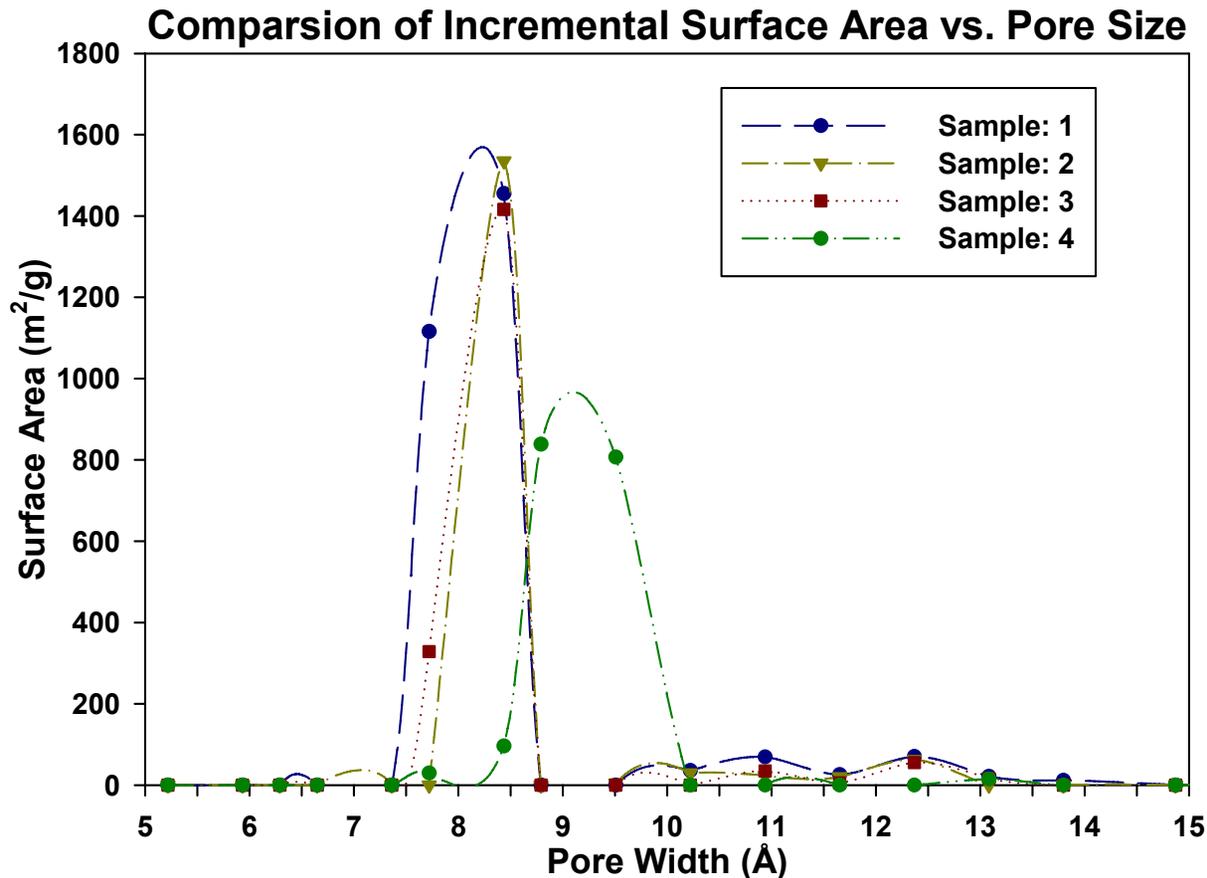
- a. Volumetric capacity is calculated based on the actual density of loose polymer powders, which ranges from 0.15 to 0.5. These capacities can be increased by x2 to x5 through compression.
- b. **C** = polymers contains only aromatics, **X** = polymers with non-C element substitutions, **M** = polymers incorporated with transition metals

Additional Slides



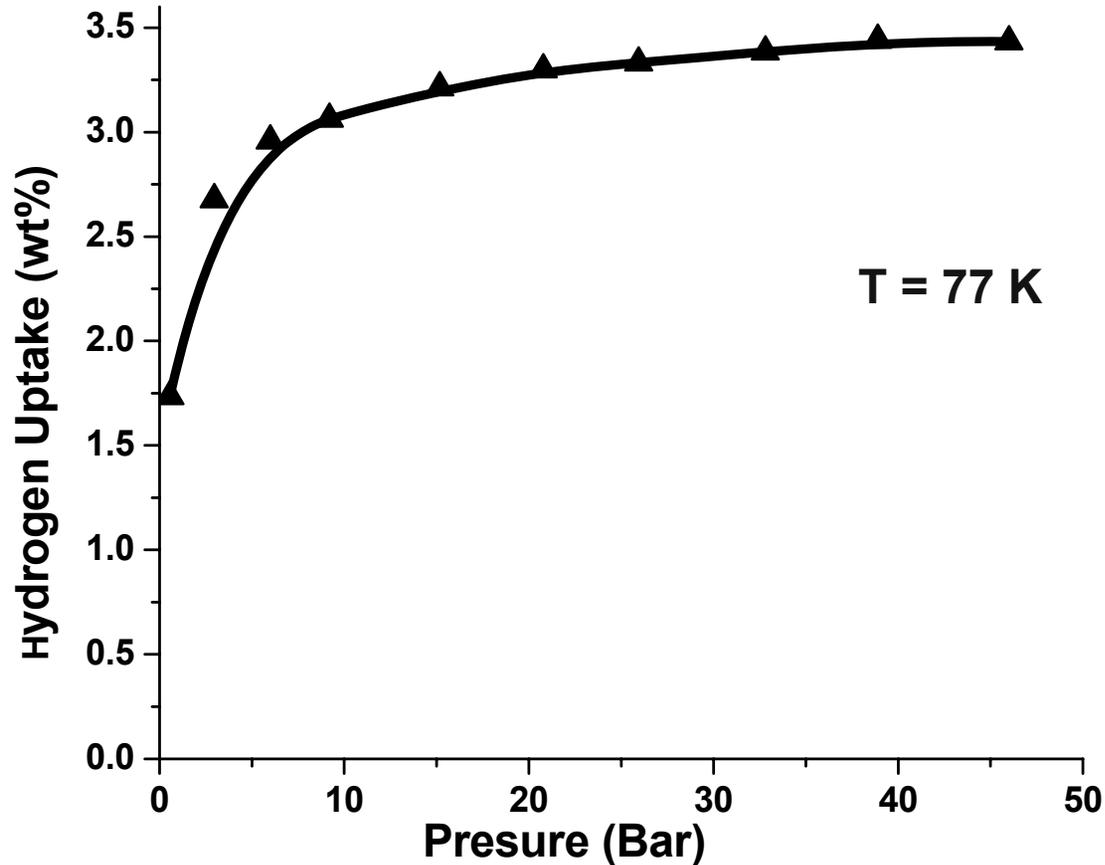
Supplemental Info – An example of our effort in controlling pore size through new synthetic approach

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