Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

Di-Jia Liu[1], Shengwen Yuan[1], Desiree White[1], Alex Mason[1], Briana Reprogle[1], Zhuo Wang[2] & Luping Yu[2]

[1]Argonne National Laboratory

[2]The University of Chicago

DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting
Washington, D.C. , May 9-13, 2011

Project ID ST050

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start: July 2007
- Project end: October 2011
- % complete: 75%

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 FY2010
  - $ 500 K
- Funding for FY2011
  - $ 400 K

Partners

- Interactions/collaborations
  - Argonne National Laboratory (Lead)
  - U of Chicago (Subcontractor)
  - HSCoE Members
    - NREL
    - UNC
  - Non HSCoE Members
    - U of Hawaii (Sample exchange)
    - GM (Sample exchange)

Objective - Relevance

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

Potential Advantages of POP H_2 Adsorbent & Their Impact on Technology Barriers

- **System Weight and Volume** – POPs are light weight and can be converted to high volumetric density by engineering process such as compression, pelletizing, etc.
- **System Cost** – POPs can be scaled-up for industrial production with the existing infrastructure at competitive cost.
- **Efficiency** – POP-H_2 interaction is based on physi-adsorption/desorption principle with minimum parasitic energy consumption.
- **Durability/Operability** – POPs are stable under the temperature and humidity conditions required for hydrogen storage application.

Approach - Milestones

Month/ Year	Milestones	Status Update
11/10	Complete the design, synthesis, and characterization of B-doped POPs	**80% Completed**. Surface properties, H_2 storage capacities and ΔH_{ads} were Investigated for three new three B-doped POPs. Finding is accepted for publication.
02/11	Complete the synthesis of an ultra-high surface area aromatic POPs	**Completed**. Duplicated a literature report on porous aromatic framework as benchmark comparison for POP capacity and heat of adsorption investigation.
05/11	Complete adsorption kinetics and charging time investigation for selected POPs	**Completed**. Adsorption/desorption kinetics of two representative POPs were studied.
08/11	Complete H_2 storage capacity and heat of adsorption optimization through design/synthesis of new metal-doped POPs	**60% completed**. Seven new transition metal doped POPs were prepared. Measurement of surface property, H_2 adsorption uptake and isosteric heat of adsorption 50% finished.

The focus of FY2011 is to improve and understand the key factor for isosteric heat of adsorption targeting for ambient temperature storage application

Approach – Development Strategy

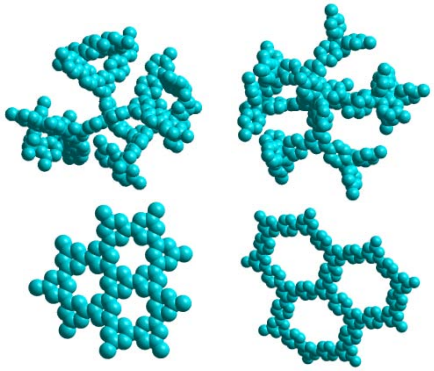
New Polymer Exploration (UofC/ANL)	Characterization & Optimization (ANL)	Modeling & Simulation (ANL)
▪ New POP synthesis through rational design at molecular level ▪ Structure characterization ▪ Post synthesis modification	▪ H_2 storage capacity & heat of adsorption measurement ▪ Surface property characterization ▪ Engineering process development	▪ H_2-POP interaction study via *ab initio*, DFTB & MD methods ▪ Advanced characterization

- Prepare 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 POP-H_2 interaction by incorporating heteroaromatic functional groups
- Develop fundamental understanding through modeling and advanced characterization

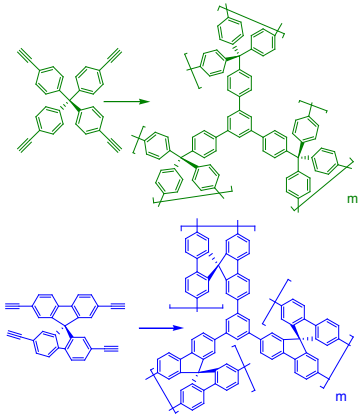
- **Over 100 POPs in three categories, aromatic, heteroaromatic and metal doped systems with high surface areas and narrow pore size distribution were designed and prepared**
- **Hydrogen uptake capacities of 0.055 (kg_{H2}/kg_{ads}) and 0.022 (kg_{H2}/L_{ads}), and the isosteric heat of adsorption of ~10 kJ/mol were achieved**
- **The correlations between surface property, H_2 storage capacity and adsorption enthalpy were found through combined experiment/simulation effort for better understanding on H_2-POP interaction**

Technical Approach – Summary on Hydrogen Storage via Aromatic POPs

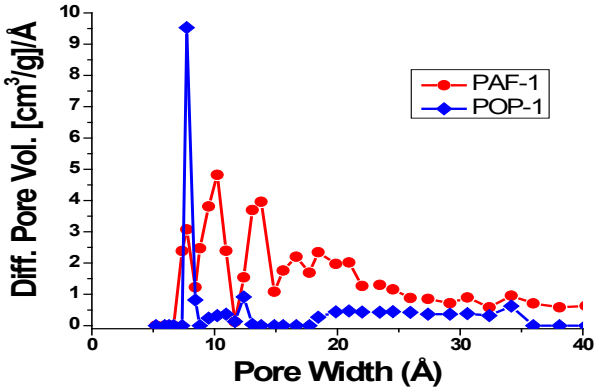
3-D structures of aromatic POPs...



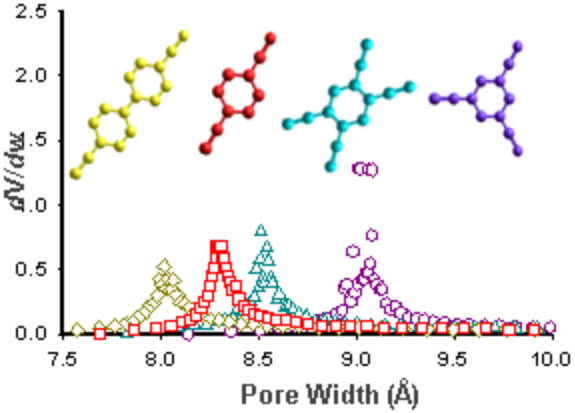
...formed by crosslinking with contorted core...



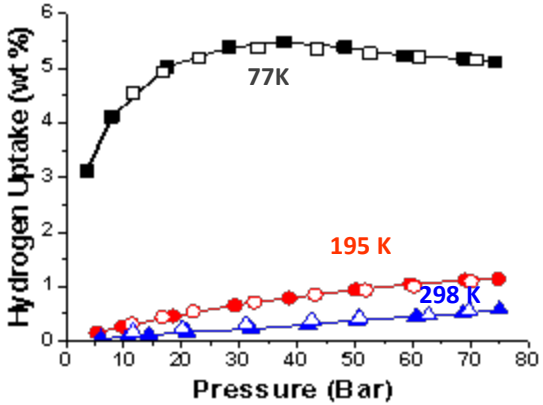
... and very high surface area/narrow pore size...



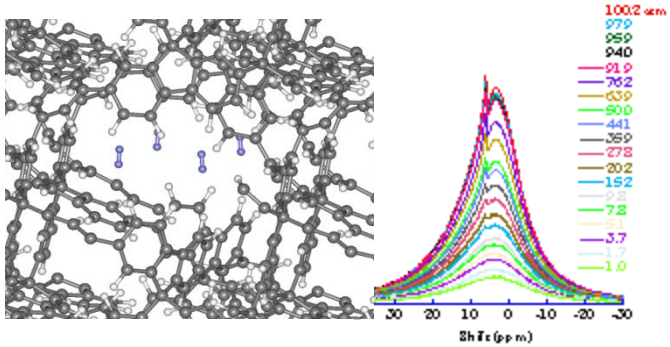
...with adjustable pore dimension...



... capable for high H_2 uptake ...



... elucidated by modeling/characterization

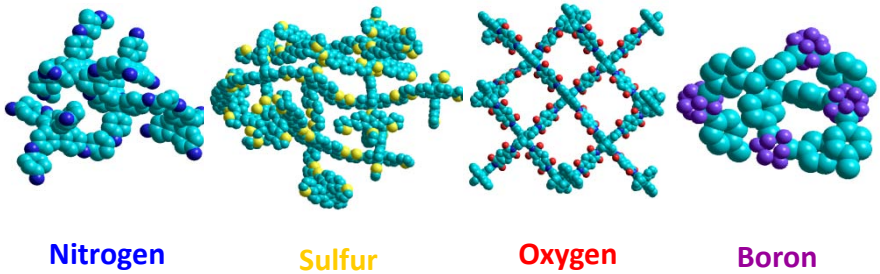


DFT calculation on H_2 distribution & NMR study on H2 in POP

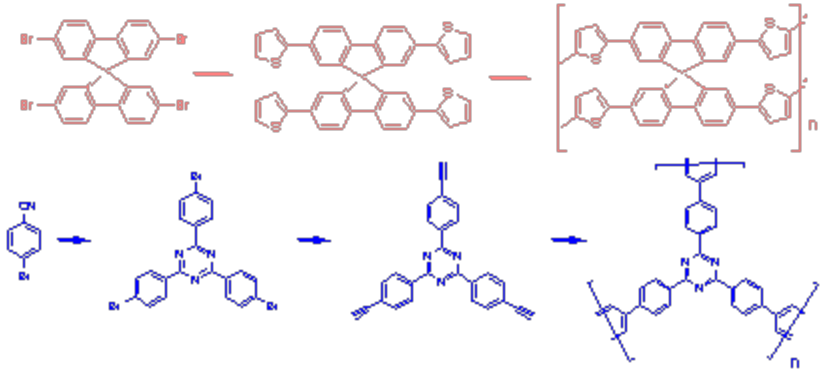
- Over 50 aromatic POPs were prepared, high BET surface (> 3200 m^2/g) and tunable pore sizes (7Å to 10Å) achieved
- H_2 uptakes up to 5.5% at 77K and 0.5% at RT were achieved, heat of adsorptions are usually limited at ~6 kJ/mol
- High SSA leads to higher gravimetric hydrogen uptake at 77 K, but not necessarily higher volumetric uptake

Technical Approach – Summary on Hydrogen Storage via Heteroaromatic POPs

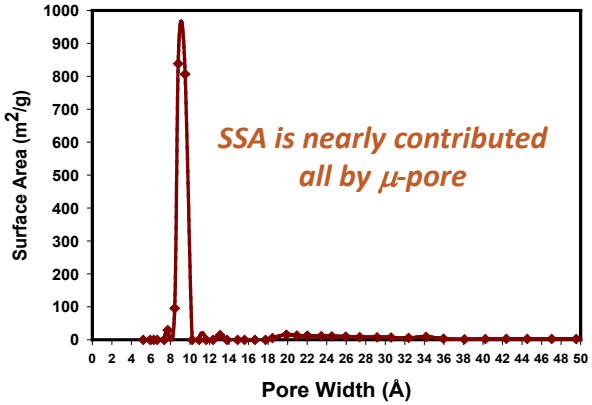
POPs containing non-C elements ...



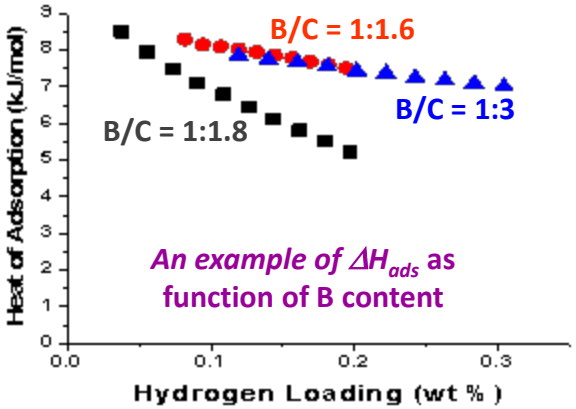
... were synthesized using various monomers and crosslinking schemes...



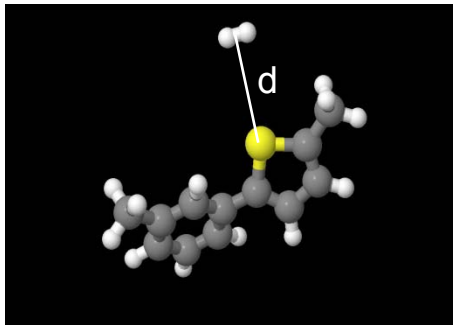
...with high SSA and narrow pore distribution...



...and element-sensitive H_2 adsorption enthalpy...



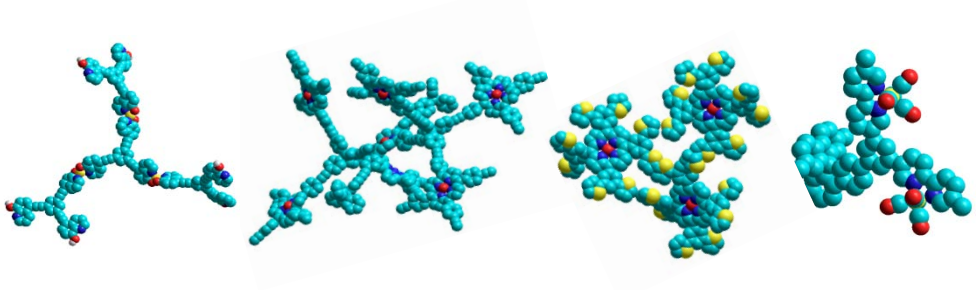
...verified by computational modeling



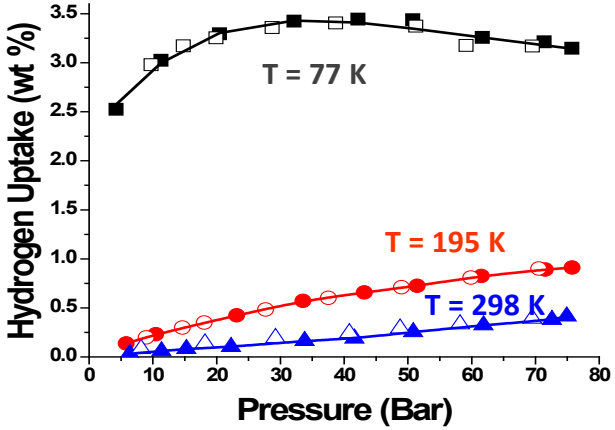
- Over 30 heteroaromatic POPs were prepared containing B, N, S, etc., high BET surface (> 1000 m^2/g) and narrow pore sizes (~8Å) achieved
- H_2 uptakes ~ 3% at 77K and the heat of adsorptions > 9 kJ/mol were achieved
- Improvement of ΔH_{ads} is element-dependent, for example, S and N → $\Delta H_{ads}\downarrow$, B → $\Delta H_{ads}\uparrow$

Technical Approach – Summary on Hydrogen Storage via Metal Doped POPs

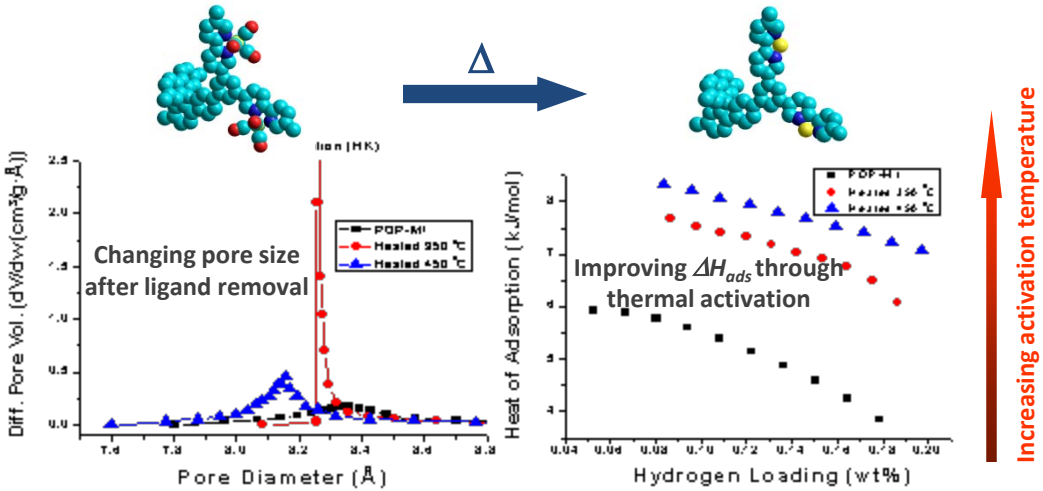
POPs with different TM-ligand coordinations were prepared ...



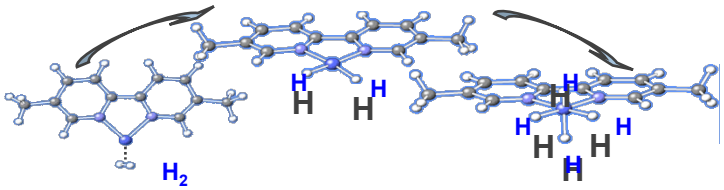
... for direct hydrogen storage evaluation ...



...or through thermal activation to generate coordinatively unsaturated site...



...to increase uptake capacity and heat of adsorption.

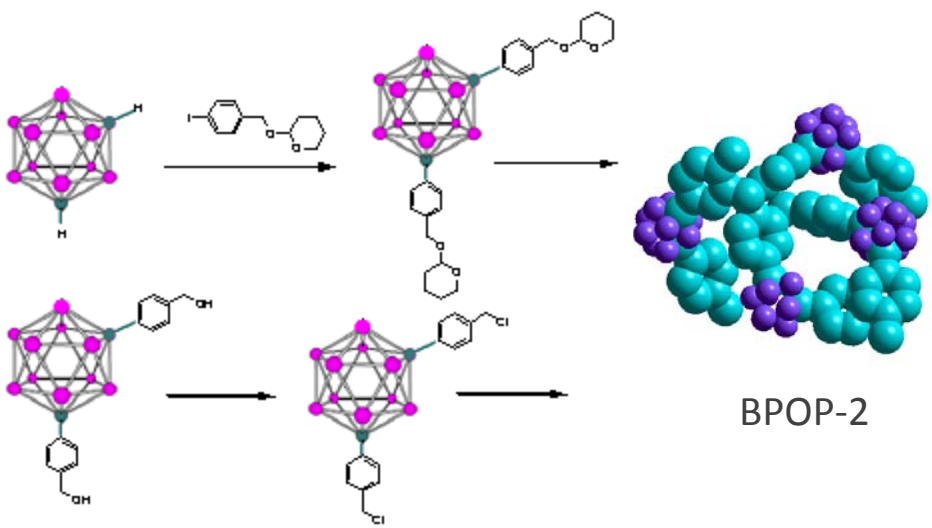

H
H
H

FY2011 Technical Accomplishment 1 – Design & Synthesis of High Surface Area Carborane-containing POPs

Rationale

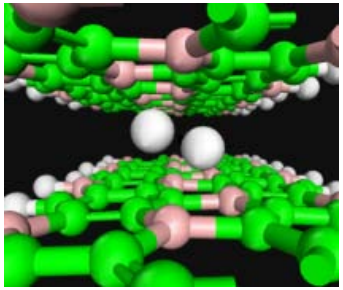
- Computational modeling studies from HSCoE suggest non-dissociative binding energy of 19.2 kJ/mol between H_2 and boron doped carbon cluster (Kim, et. al. *Phys. Rev. Lett*. 2006)
- Isotherm and spectroscopic studies from HSCoE found enhanced ΔH_{ads} over B-doped graphitic carbon (T. Chung, *et. al. JACS* 2008, A. Kleinhammes, et. al. *JPCC* 2010)
- High surface area B-doped polymer can serve as precursor of high SSA adsorbent via further activation

Synthetic Scheme - An Example



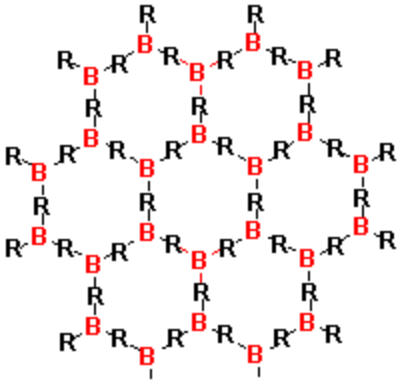
BPOP-2

HSCoE Studies on H_2 in BC_3 system



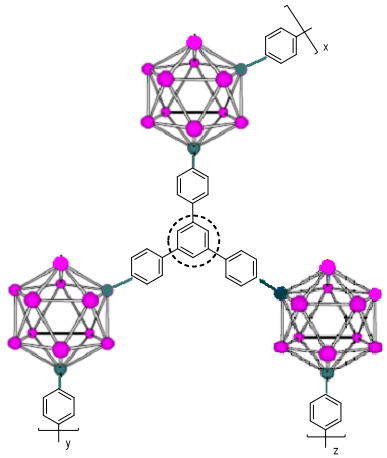
Simulation by Cooper/Cheng
Airproducts, HSCoE

ΔH_{ads} = 12~13 kJ/mol
observed by Chung's group

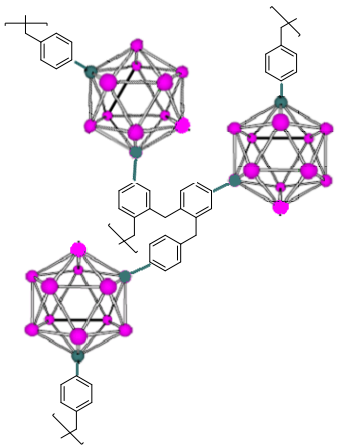


Desired B-C framework
Chung – Penn State, HSCoE

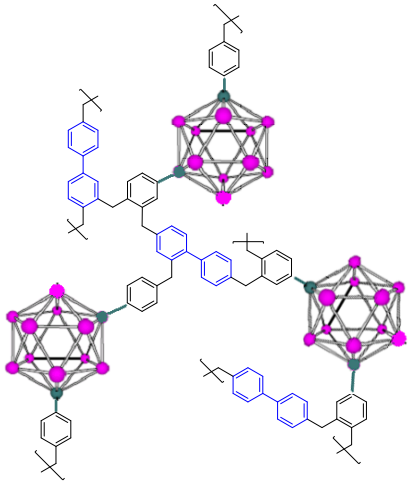
FY2011 Technical Accomplishment 1 – Surface Properties & H_2 Storage Capacity of Carborane-containing POPs



BPOP-1, BET SSA = 422 m^2/g

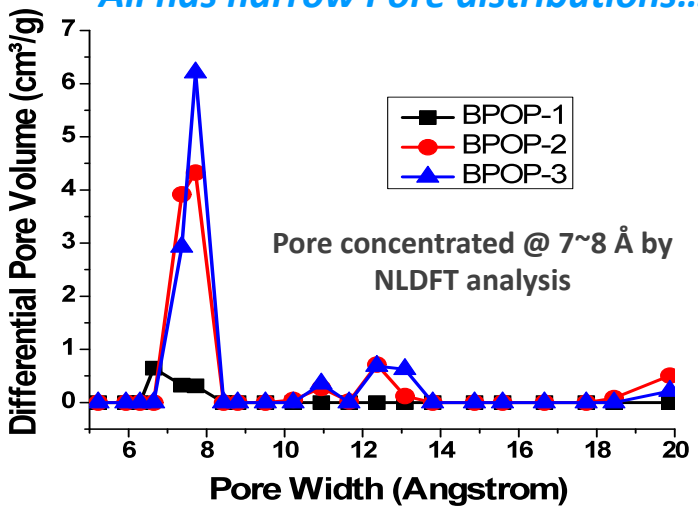


BPOP-2, BET SSA = 864 m^2/g

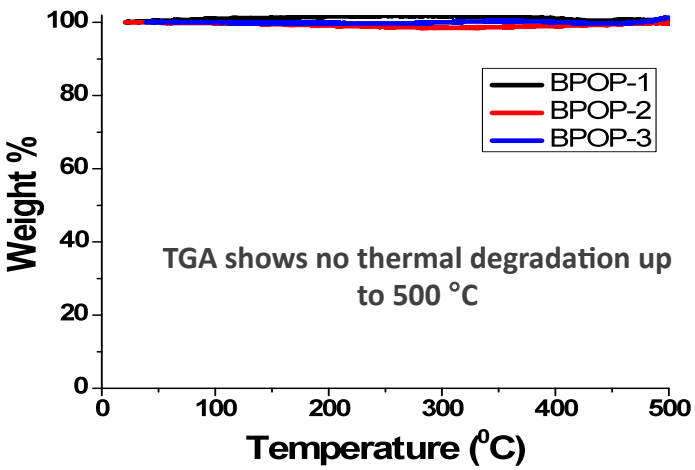


BPOP-3, BET SSA = 1037 m^2/g

All has narrow Pore distributions…

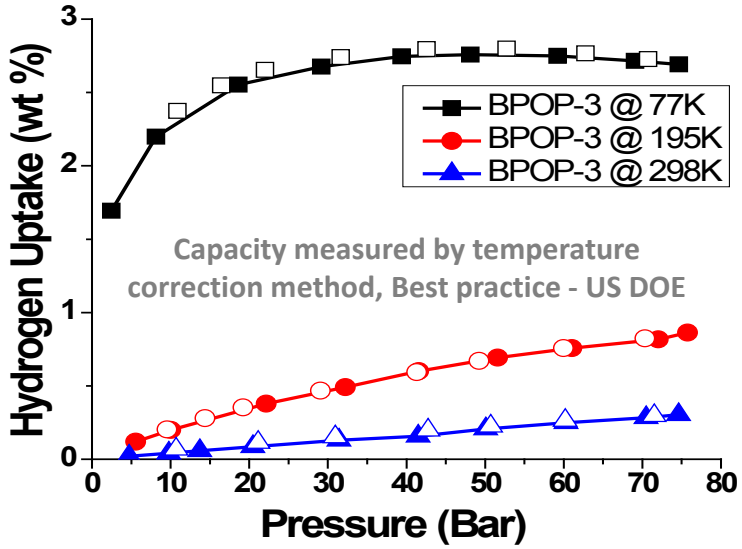


…And robust thermal stability

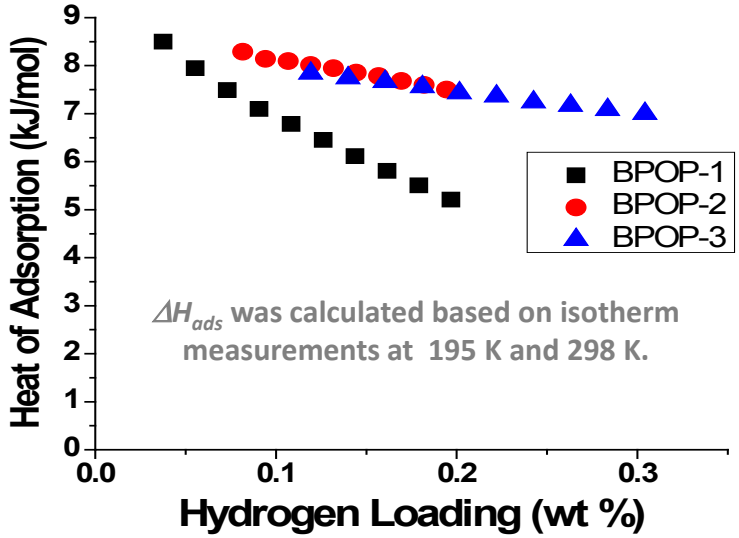


FY2011 Technical Accomplishment 1 – Improving ΔH_{ads} through B-doped POPs

H_2 adsorption isotherms at different T



ΔH_{ads} as function of hydrogen uptakes



	BET SSA (m^2/g)	Langr. SSA (m^2/g)	Tot Pore Vol (cm^3/g)	μ-pore Volume (cm^3/g)	Pore Diameter (nm)	H_2 Gr. Uptake @ 77K (kg_{H2}/kg_{Ads+H2})	B/C ratio	ΔH_{ads} (kJ/mol)
BPOP-1	422	592	0.14	0.04	0.68	0.014	1/1.8	10.2
BPOP-2	864	1164	0.57	0.30	0.76	0.021	1/1.6	9.0
BPOP-3	1037	1497	1.12	0.33	0.77	0.028	1/3.0	8.2

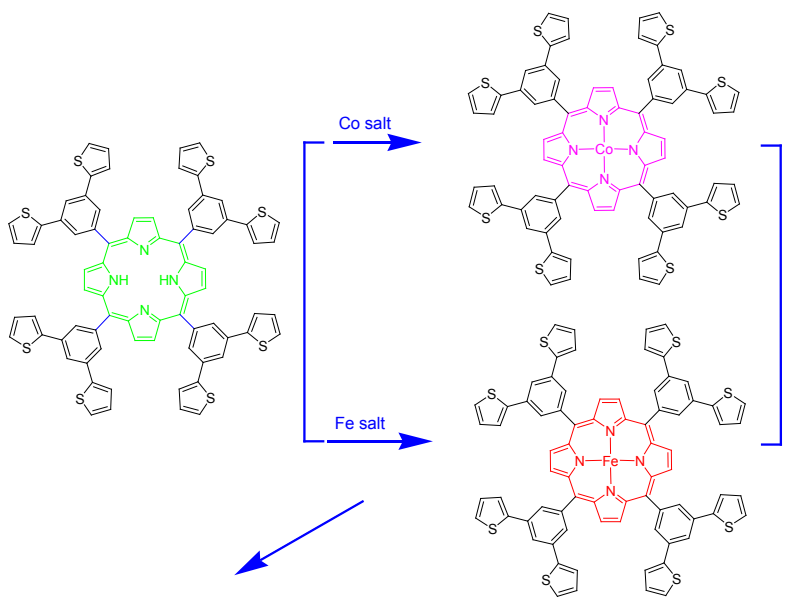
- ΔH_{ads} improves with higher B content in POPs, but it decays quickly with increase of hydrogen loading
- Carborane POPs will be evaluated as precursors of adsorbents with improved ΔH_{ads} through further activation

FY 2011 Technical Accomplishment 2 – Design & Synthesis of TM/Polyporphyrin POPs

Rationale

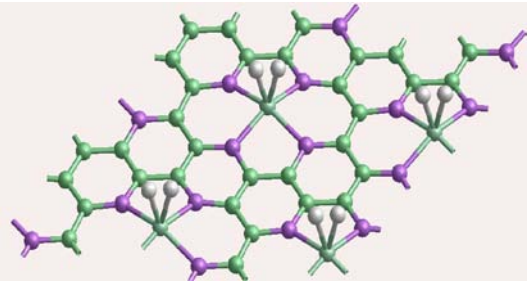
- Unsaturated transition metal/hydrogen interaction could form H_2··TM bond, leading to improved heat of adsorption (ΔH_{ads}) without dissociation (Kubas interaction)
- Computational modelings suggest enhanced ΔH_{ads} can be achieved by decorating TM in graphene plane (M. Yoon et. al. ORNL) or macrocyclic plane (Kim & Zhang NREL/RPI)
- ANL/UC team successfully prepared and characterized several TM doped POPs with high surface area and narrow pore size distribution

Synthetic Scheme: Fe-Co/Por



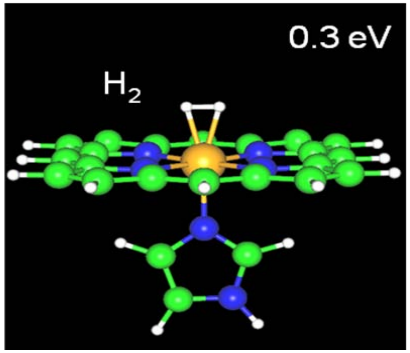
Fe-Co/Por, BET SSA = 1571 m^2/g

HSCoE theoretical studies on H_2 over TM doped surfaces



√7 x √7 TM-Decorated Graphene Model
M. Yoon, et.al., HSCoE - ORNL

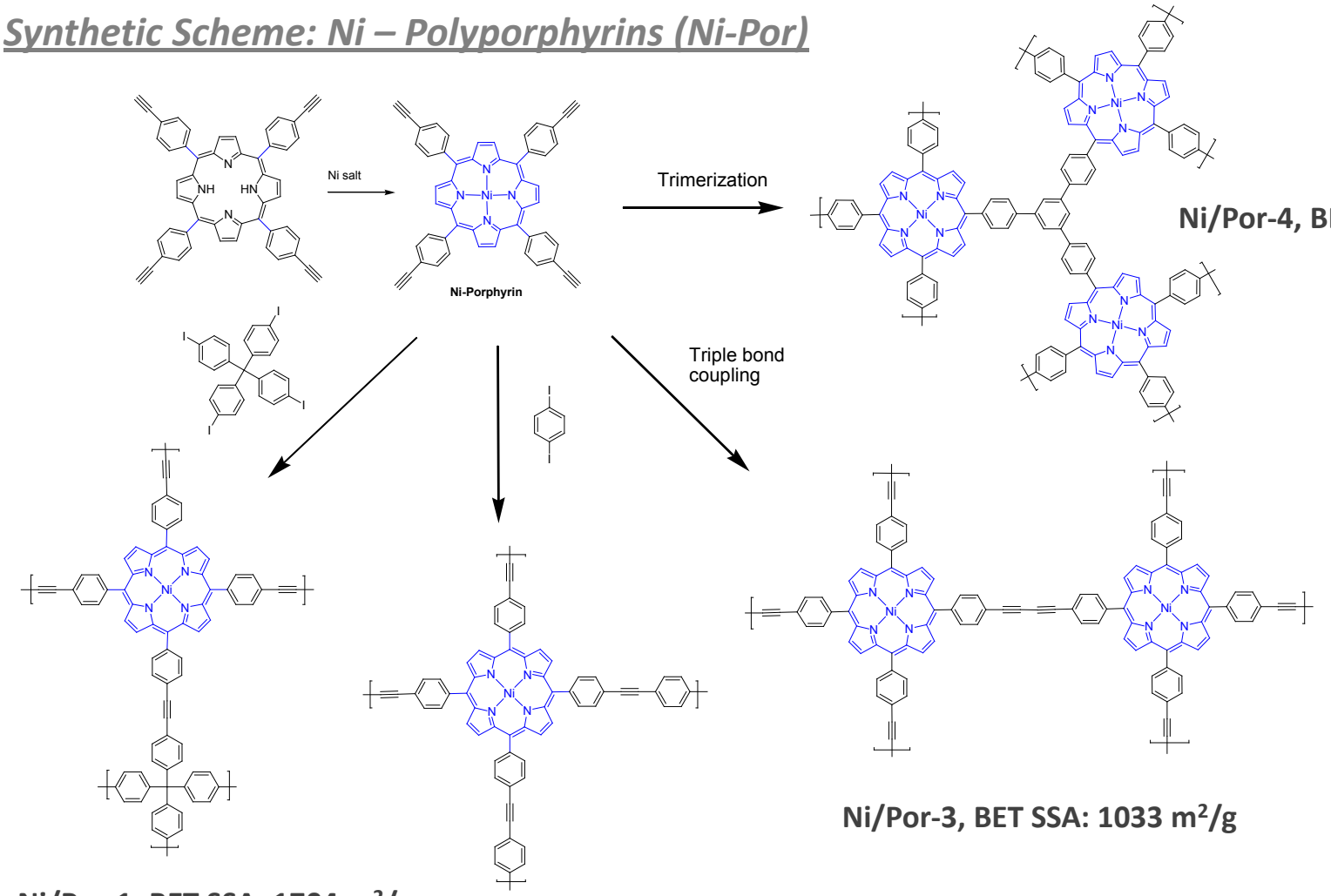
Suitable ranges of ΔH_{ads} for storage are suggested through non-dissociative binding of H_2/square-planar TM coordination site



H_2/HEME Model
Kim & Zhang, HSCoE - NREL/RPI

FY 2011 Technical Accomplishment 2 – Design & Synthesis of TM/Polyporphyrin POPs

Synthetic Scheme: Ni – Polyporphyrins (Ni-Por)



Ni/Por-4, BET SSA: 624 m²/g

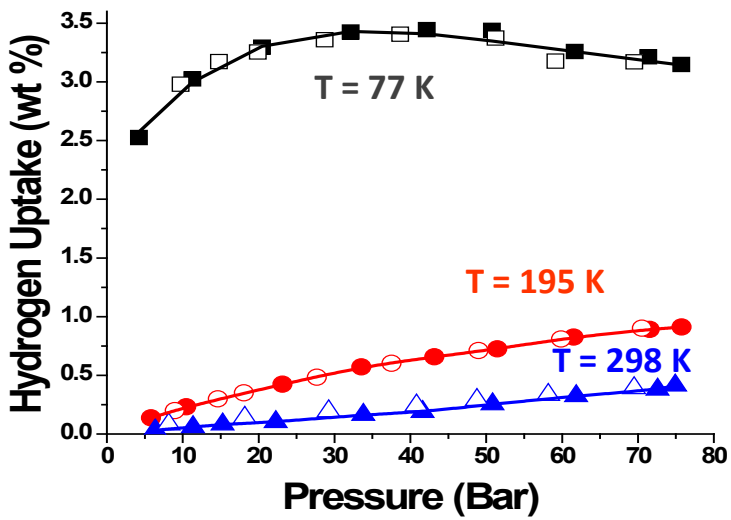
Ni/Por-3, BET SSA: 1033 m²/g

Ni/Por-1, BET SSA: 1704 m²/g

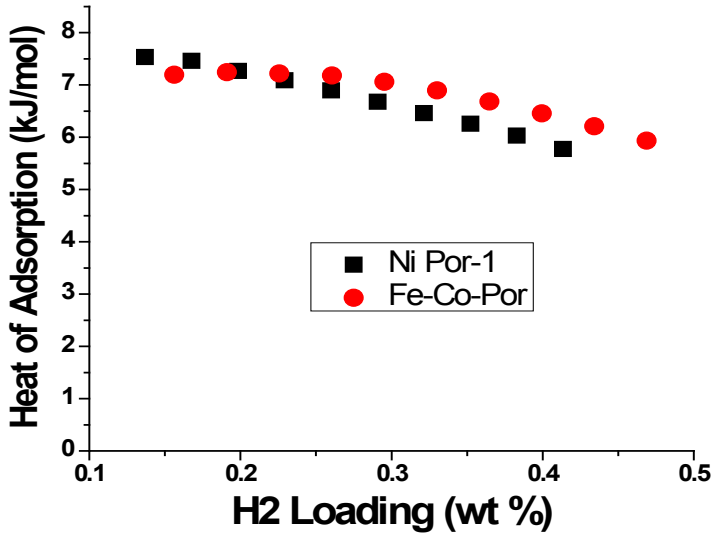
Ni/Por-2, BET SSA: 572 m²/g

FY 2011 Technical Accomplishment 2 – Improving H_2 Storage Capacity & Heat of Adsorption over TM/Polyporphyrin POPs

H_2 adsorption isotherms for Ni/Por-1 at different T



Comparison of ΔH_{ads} as function of H_2 uptakes



	BET SSA (m^2/g)	*Langr. SSA (m^2/g)*	*Tot Pore Vol (cm^3/g)*	*μ-pore Volume (cm^3/g)*	*Pore Diameter (nm)*	*H_2 Gr. Uptake @ 77K (kg_{H2}/kg_{Ads+H2})*	*ΔH_{ads} (kJ/mol)*
Ni/Por-1	1704	2291	0.91	0.66	0.80	0.034	8.0
Fe-Co/Por	1571	2098	0.97	0.63	0.80	0.033	7.4

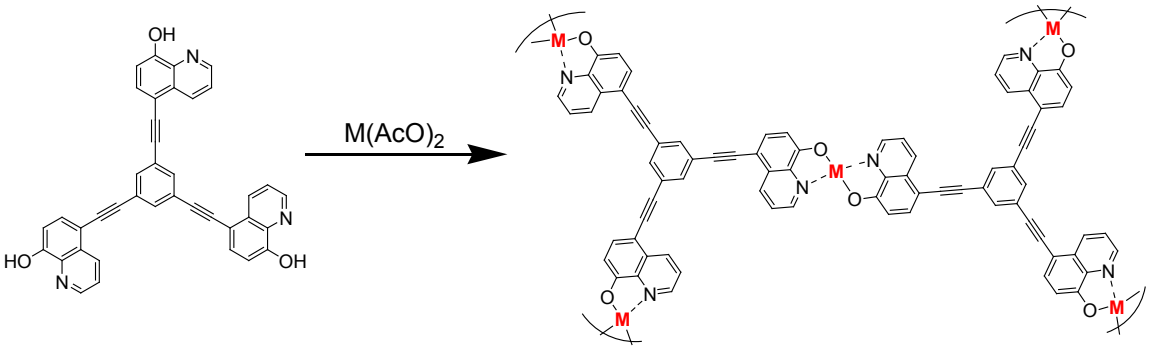
- Transition metal (Ni, Co, and Fe) addition improves ΔH_{ads} , mechanism needs to be studied
- Other promising metals (Ti, V, Mg, etc.) need to be explored with different doping method

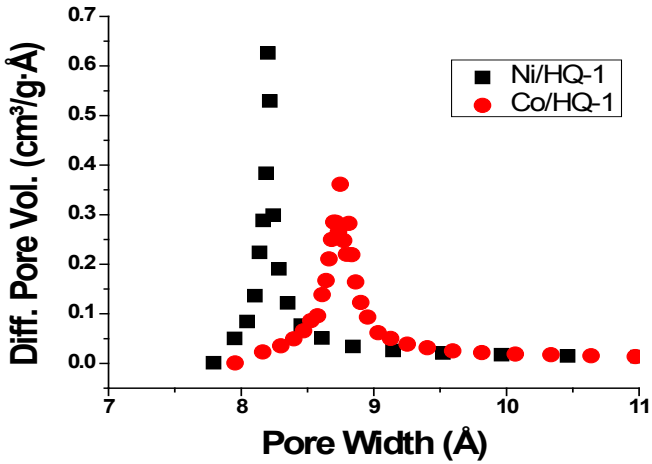
FY 2011 Technical Accomplishment 3 – Design & Synthesis of TM/POPs Coordinated through Hydroxyquinoline

Rationale

- POPs crosslinked through TM-hydroxyquinoline bonds are very stable towards humidity and other contaminants
- Coordination geometry between TMs and ligand (square-planar vs. tetrahedral) may shed light on hydrogen-metal interaction

Synthetic Scheme: Metal Coordinated Hydroxyquinoline





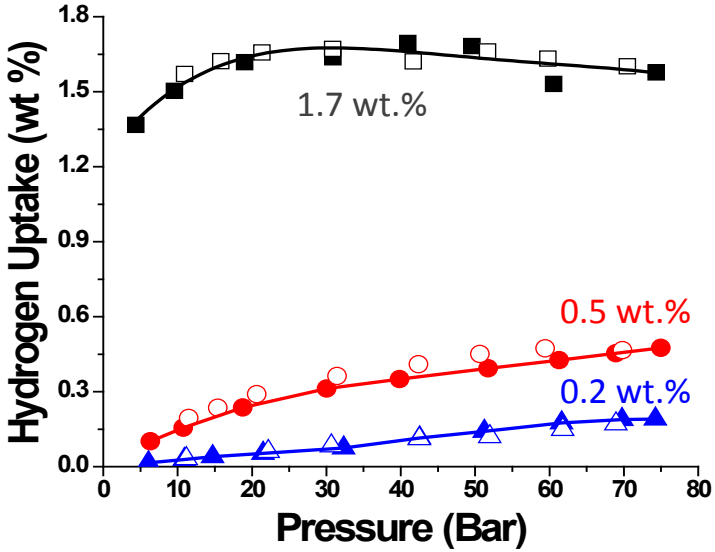
Co/HQ-1, BET SSA: 580 m^2/g; Ni/HQ-1, BET SSA: 596 m^2/g

Other TM/HQ POPs was also prepared with high SSAs

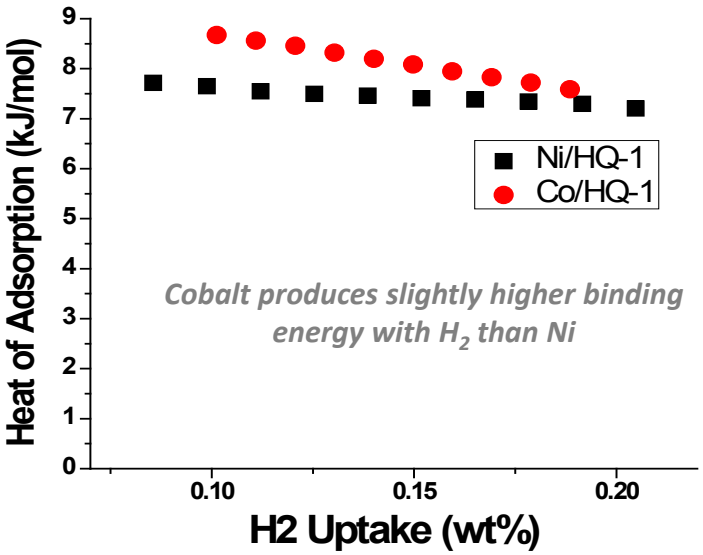
The tetrahedral (Co) metal-ligand coordination led to POP with a slightly larger pore size than that with square-planar (Ni) ligation

FY 2011 Technical Accomplishment 3 – Surface Properties, H_2 Storage Capacity & ΔH_{ads} of TM/HQ-1s

H_2 adsorption isotherms of Co/HQ-1 at different T



Comparison of ΔH_{ads} as function of H_2 uptakes

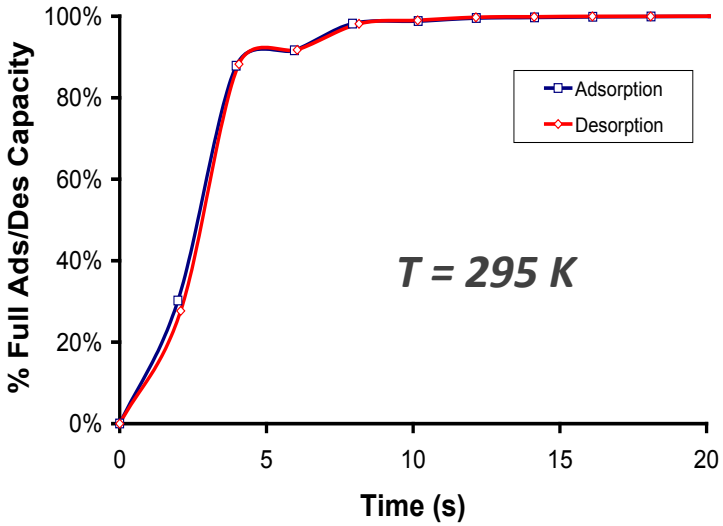


	BET SSA (m^2/g)	*Langr. SSA (m^2/g)*	*Tot. Pore Vol. (cm^3/g)*	*μ-pore Volume (cm^3/g)*	*Pore Diameter (nm)*	*H_2 Gr. Uptake @ 77K (kg_{H2}/kg_{Ads+H2})*	*ΔH_{ads} (kJ/mol)*
Ni/HQ-1	596	807	0.59	0.22	0.82	0.017	8.0
Co/HQ-1	580	786	0.58	0.22	0.87	0.017	9.9

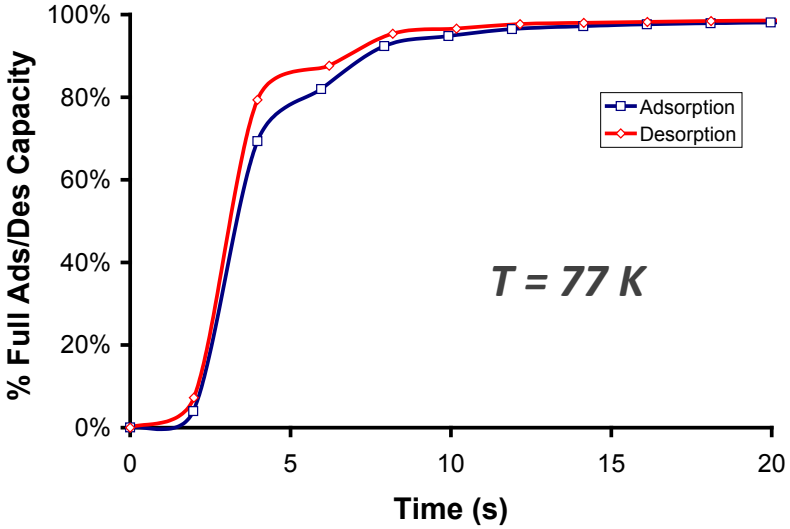
Co-hydroxyquinoline POP produced a higher isosteric heat of adsorption (9.9 kJ/mol) than its nickel counterpart, suggesting a possible metal dependent H2-TM/POP interaction.

FY 2011 Technical Accomplishment 4 - Adsorption/Desorption Kinetics Study

Adsorption/desorption time dependence at ambient temperature



Adsorption/desorption time dependence at liquid nitrogen temperature



- **The temporal profiles between adsorption and desorption are nearly identical**
- **The system reaches equilibrium in a faster pace at ambient temperature than 77 K, all within 20 seconds**

Summary Table

H_2 storage capacities for selected POPs by Argonne – UofC Team in FY2011

Sample	BET SSA (m^2/g)	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 (RT, 70 bars) (kg H_2/L adsorbent)	μ-Pore /Total Pore (cm^3g^{-1}/ cm^3g^{-1})	Skeleton Vol. [b] (cm^3g^{-1})	ΔH_{ads} ($kJmol^{-1}$)
PAF-1 (A)	3143	0.055	0.020	0.0053	0.0018	1.08/2.08	0.82	6.5
PTA-3 (H)	870	0.029	0.021	0.0024	0.0017	0.40/0.66	0.80	6.6
BPOP-1 (H)	422	0.013	0.014	0.0016	0.0017	0.04/0.14	0.81	10.2
BPOP-2 (H)	864	0.021	0.014	0.0018	0.0012	0.30/0.57	0.94	9.0
BPOP-3 (H)	1037	0.027	0.016	0.0030	0.0015	0.33/1.12	0.87	8.2
Ni/Por-1 (M)	1704	0.035	0.021	0.0038	0.0022	0.66/0.91	0.85	8.0
Fe-Co/Por (M)	1571	0.034	0.022	0.0041	0.0026	0.63/0.97	0.65	7.4
Ni/HQ-1 (M)	596	0.017	0.015	0.0019	0.0017	0.22/0.59	0.56	8.0
Co/HQ-1 (M)	580	0.017	0.016	0.0019	0.0017	0.22/0.58	0.53	9.9

A – Aromatic POP; H – Heteroaromatic POP; M – Metal doped POP

a. Volumetric capacity is calculated based on the measured skeleton density plus total pore volume density.
b. Skeleton volume is measured using helium as calibration gas
c. Rate of ΔH_{ads} (kJ/mol) change as function of gravimetric uptake C_g (%) at ambient temperature near the zero coverage point.

- System with the highest gravimetric capacity does not necessarily have the highest volumetric capacity
- Transition metal and boron doping can improve adsorption enthalpy

Collaboration

Partnership within and outside of Hydrogen Sorption Center of Excellence

- Teaming between 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
- Collaboration with NREL (HSCoE member) on measurement validation
- Information exchange with ORNL (HSCoE member) and RPI on computational modeling and simulation

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 study
- Up-to-date information on new developments in sorption based materials

Future Work

- Complete the investigation on TM exchanged polyporphyrin POPs
- Complete the investigation on improving heat of adsorption for B-doped POP via activation
- Evaluate potential application of other emerging technologies to sorption based hydrogen storage and recommend further research direction to DOE
- Prepare final project report

FUTURE DIRECTION

- POP is becoming a great platform as hydrogen adsorbent due to its high surface area and narrow pore (vs. carbon) and excellent chemical stability (vs. MOF)
- Unmodified aromatic POPs will unlikely reach desired H_2 adsorption enthalpy for room temperature application even with increased surface area or adjustable porosity
- To achieve near-ambient temperature application, the surface of POP needs to be modified by incorporating metal or other elements promoting H_2 binding
- New surface modification techniques, departing from the conventional synthetic approaches, have the potential to produce high binding energy sites predicted by theory
- POPs with tailored surface property and chemical composition can also serve as precursor of fabricating new adsorbent after additional chemical/physical processing