

IV.C.5 Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

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Project End Date: September 30, 2011

- Gravimetric density: 1.8 kWh/kg
- Volumetric density: 1.3 kWh/L
- Cost: \$2/kWh net

FY 2011 Accomplishments

- Successfully designed and synthesized a series of B-containing POPs with high specific surface areas (SSA) and narrow pore size distributions (PSD). Hydrogen uptake and isosteric heat of adsorption measurements found enhanced adsorption enthalpy for the POPs with higher boron-to-carbon ratio.
- Successfully designed and synthesized a series of metalloporphyrin POPs (PPOR) containing transition metals such as nickel, cobalt and iron. Excess H₂ storage capacities of 0.035 kgH₂/(kg_{Adsorbent}+H_{2adsorbed}) and 0.0026 kgH₂/L_{Adsorbent} were achieved. Hydrogen adsorption enthalpy over PPOR was found to be dependent on the type of metal exchanged into macrocyclic ring with Ni having the highest value.
- Successfully designed and synthesized two POPs incorporated with high level transition metals through hydroxyquinoline ligation. Both Co and Ni were used for the synthesis and the adsorption enthalpy of 9.9 kJ/mol was achieved.
- Conducted measurement for hydrogen adsorption/desorption kinetics over a representative POP at both ambient and liquid nitrogen temperatures. The result indicated the surface equilibrium can generally be reached within 10 to 20 seconds.

Fiscal Year (FY) 2011 Objectives

- To design, synthesize, and evaluate POPs as hydrogen storage adsorbents for transportation applications.
- To support POP development with in-depth understanding of hydrogen-adsorbent interactions through modeling/simulation and advanced characterization.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cells Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability

Technical Targets

The focus of this project is to prepare new POPs as hydrogen adsorbents with improved storage capacity and heat of adsorption through rational design, guided by computational modeling and advanced characterization. It supports DOE's initiative in developing adsorption-based storage technology with high uptake capacity, reversibility, and stability. The successful outcome of the project will produce a new storage material that meets DOE 2015 targets:



Introduction

On-board hydrogen storage represents a critical technology for implementing H₂-powered fuel cell vehicles. To achieve a practical driving range, the storage system must meet the gravimetric and volumetric densities set by DOE. Our team addresses these challenges by exploring a new class of hydrogen adsorbent, POPs. Compared with other adsorbents, POPs have excellent thermal stability and tolerance to contaminants such as moisture. POPs also have low skeleton density and high intrinsic porosity generated by covalent bonds, capable of maintaining SSA during high pressure pelletizing for better volumetric density. Furthermore, they can be produced at a commercial scale with the existing industrial infrastructure. Significant progress has been made with the focus on improving hydrogen uptake capacity and the heat of adsorption by enhancing SSA, porosity, and surface-adsorbate interactions through rational design at the molecular level [1-5].

Approach

A key technology challenge for the physisorption based hydrogen storage media, in addition to capacity and cost, is the heat of adsorption which should be in the range of 15 to 20 kJ/mol for practical applications. Our design principles of improving POP's storage capacity at ambient temperature include: (a) high SSA to provide sufficient interface with H_2 ; (b) narrow pore diameter to enhance van der Waals interactions through confined space; and (c) "metallic" characters, either through π -conjugation or metal doping, to promote electronic orbital interactions with H_2 . Since the inception of this project, we have prepared over 100 different POPs targeting to these properties, including aromatic, hetero-aromatic and transition metal (TM)-doped systems, and investigated the surface structural and chemical impacts to the adsorption enthalpy. In FY 2011, we remain focused on H_2 isosteric heat of adsorption improvement. Several new POPs were systematically designed and synthesized. One series is polycarborane POPs. We developed a synthetic strategy to successfully incorporate high level of boron in form of carborane in POPs with high SSA narrow PSD. We found clearly the adsorption enthalpy improvement through inclusion of boron. Another example is a series of TM-doped PPORs prepared via several parallel crosslinking chemistries. We successfully added three TM ions (Co^{+2} , Fe^{+3} , Ni^{+2}) into PPORs through chelation with porphyrin's N_4 macrocycle. We identified different impacts

to the heat of adsorption depending on the type of TM. To increase the level of TM in POP therefore higher adsorption enthalpy, we also developed a new synthetic approach in preparing stable, porous framework through ligation between Co^{+2} or Ni^{+2} with hydroxyquinoline. We found indeed the enhanced hydrogen adsorption enthalpy over the new POP systems.

Results

From our cumulative experiences of over hundred synthesized POPs under three property categories, we conclude that the adsorbent pore size, within synthetically achievable sub-nanometer range, has relatively low influence to the hydrogen adsorption enthalpy [2]. Surface modification by introducing selected non-C main group elements or metals, on the other hand, does improve the interaction between hydrogen and POPs. Polycarborane POP represents an example of main-group elemental substitution. Boron-doped carbon cluster is known to promote non-dissociative hydrogen binding with adsorption energy of 19 kJ/mol was predicated [6]. Experimentally, improved adsorption energy was found in B-doped carbon produced by pyrolysis although the surface area was somewhat limited [7]. In our laboratory, we designed three different carborane-containing POPs, BPOP-1, 2 and 3 using trimerization and Friedel Crafts alkylation reactions. An example of the reaction scheme for BPOP-2 is shown in Figure 1. These

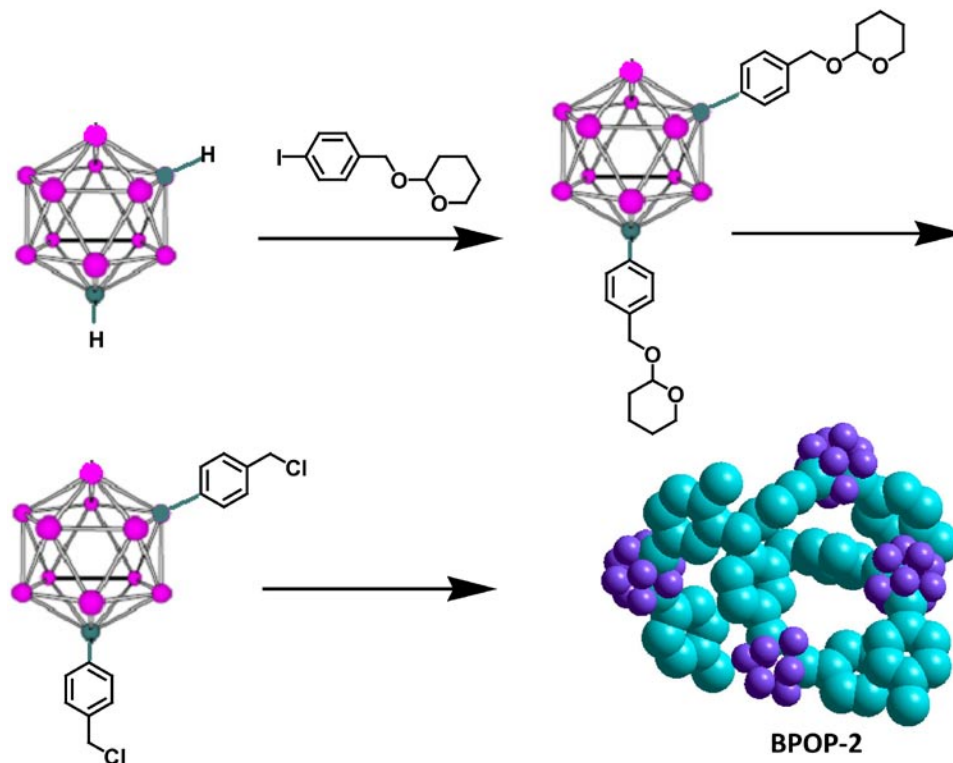


FIGURE 1. Synthetic Scheme for Preparing BPOP-2

cross-linking reactions yielded B-containing POPs with relatively high SSA from 400 to 1,100 m²/g, narrow PSD, and perhaps most importantly, high B/C ratio in the composition. Table 1 lists the surface properties, hydrogen storage uptake and isosteric heat of adsorption obtained from N₂-Brunauer-Emmett-Teller (BET) and Sievert isotherm measurements. It demonstrates a positive correlation between B/C ratio and the adsorption enthalpy.

A second series we investigated is PPOR with different TMs exchanged into the macrocyclic ring. In such system, the TM ions are ligated by four nitrogens in a square-planar

configuration, leaving the metals exposed to the interaction with hydrogen at both sides. We successfully prepared a variety of PPORs using several synthetic schemes, as are shown by the examples in Figure 2, and incorporated ionic Fe, Co and Ni into the POPs. We also measured surface property, excess hydrogen storage capacity and isosteric heat of adsorption. We found that while the impact to enthalpy by metal is limited with values in the range of 8 to 9 kJ/mol, their inclusion clearly enhances POPs interaction with hydrogen. The difference in adsorption enthalpy is relatively minor with respect to TM type used in this

TABLE 1. Surface Properties, Hydrogen Adsorption Capacities and Enthalpies of Different BPOPs

	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 @ 77 K (kgH ₂ /kgAds+H ₂)	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	1,164	0.57	0.30	0.76	0.021	1/1.6	9.0
BPOP-3	1,037	1,497	1.12	0.33	0.77	0.028	1/3.0	8.2

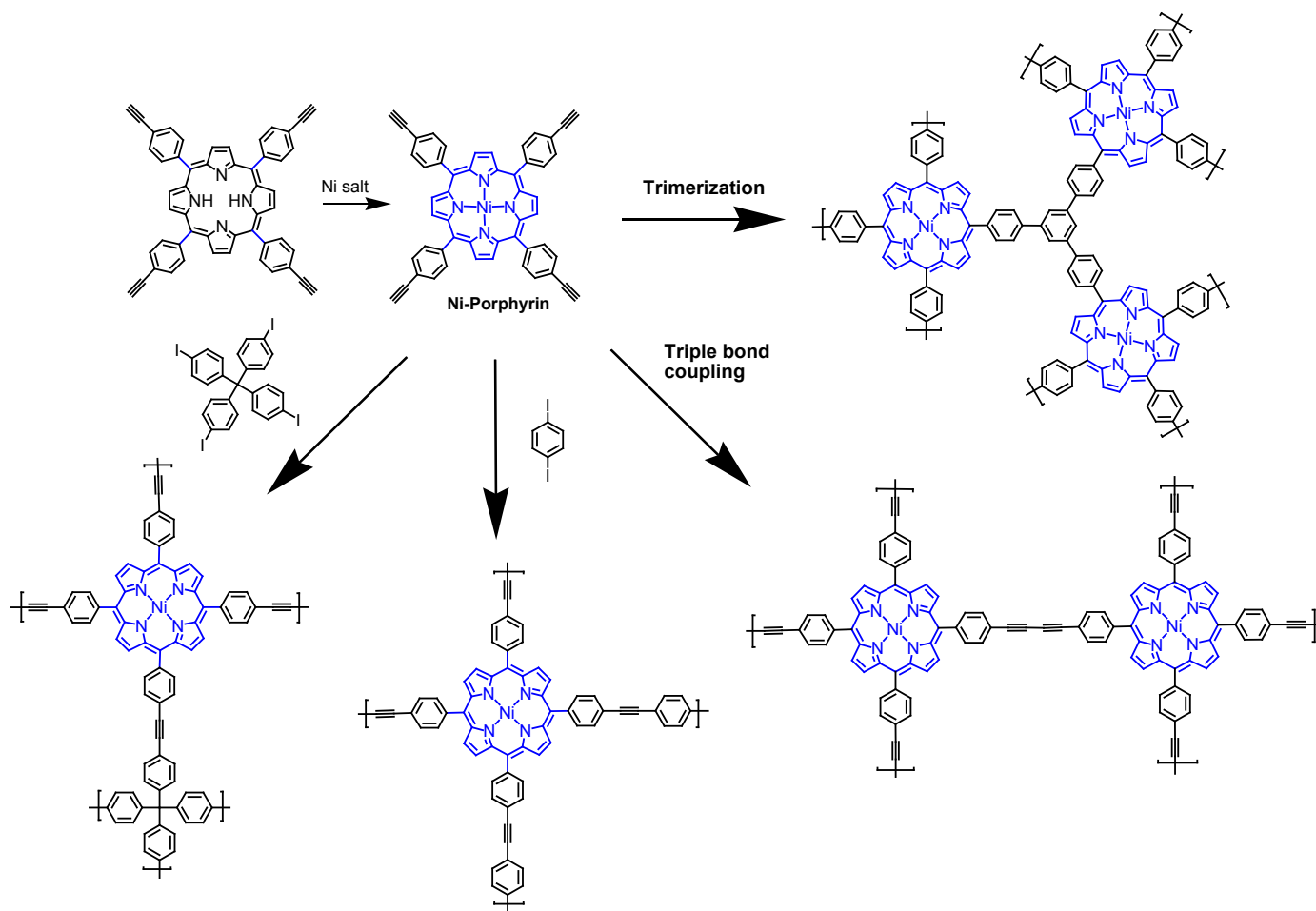


FIGURE 2. Four Parallel Synthetic Schemes for Preparing Different Ni-PPORs

study. The storage capacity is still mainly dominated by the SSA of the PPORs. To verify if the heat of adsorption behaves differently under different TM coordination, we also conducted a parallel study of two TM-containing POPs, prepared through chelation of Ni⁺² or Co⁺² with hydroxyquinoline. Both POPs have high metal contents (~14% by weight) and similar SSAs (~600 m²/g). The key difference is that one is connected through square-planer (nickel) and the other through tetrahedral (cobalt) coordination. Our BET analysis showed that POP formed through the tetrahedral linkage has an average pore diameter of 0.8Å larger than that formed through the square-planer connection. Interestingly, the Co-based POP showed nearly 10 kJ/mol adsorption enthalpy, almost 2 kJ/mol higher than of Ni-based POP.

Conclusions and Future Directions

In summary, we produced a broad range of POP-based adsorbents with high SSA, narrow PSD, and excellent chemical stability. These POPs, particularly those with metal exchange capability or B-incorporated backbone, could serve as excellent platforms for further development of materials with better adsorption enthalpy for ambient temperature applications:

- New metal elements, from both transition and main groups, could be exchanged into POPs through chemical or physical means, to achieve sufficient adsorption enthalpy suitable for near-ambient temperature application as predicated by theory.
- New surface modification techniques, departing from the conventional synthetic approaches, could have the potential to produce high binding energy sites.
- New POP designs with tailored surface property and chemical composition could serve as the precursors for further chemical/physical processing to improve H₂ binding energy.

FY 2011 Publications/Presentations

1. “Porous Organic Polymers Containing Carborane for Hydrogen Storage”, Shengwen Yuan, Desiree White, Alex Mason, and Di-Jia Liu, Accepted by *Int. J. of Energy Research*.
2. “Exploring applications of nanomaterials for fuel cell & hydrogen storage”, Di-Jia Liu, Shengwen Yuan, Gabriel Goenaga, Junbing Yang, Desiree White and Alex Mason, *Preprint Paper Am. Chem. Soc., Div. Fuel Chem.* 55 (1), xxxx (2010).
3. “Exploring applications of nanomaterials for fuel cell & hydrogen storage”, Di-Jia Liu (invited) Presentation at American Chemical Society National Meeting, Anaheim, CA, March 26–31, 2011.
4. “Improving Hydrogen Adsorption Enthalpy through Coordinatively Unsaturated Cobalt in Porous Polymer”, S. Yuan, D. White, A. Mason, B. Repogle, L. Yu, and D-J Liu, to be submitted.

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