

IV.C.1f Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

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Objectives

- To design, synthesize, and evaluate porous organic polymers (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:

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

Accomplishments

- Successfully designed and synthesized a polyporphyrin-based POP with high Brunauer-Emmett-Teller (BET) specific surface area (SSA) and narrow pore size distribution. Gravimetric capacities of 5.0% at 77 K and 0.6% at ambient temperature were achieved. Iron was successfully exchanged into the new POP which improved hydrogen heat of adsorption.
- A series of aromatic POPs with similar BET SSA but variable pore sizes were prepared through facile ethynyl trimerization reaction. An H₂ isosteric heat of adsorption up to ~10 kJ/mol was achieved.
- New synthetic schemes were developed to integrate various non-C elements (B, N, etc.) into POPs while maintaining high surface areas and narrow pore diameters. Preliminary experiments demonstrated improvement in H₂ heat of adsorption.



Introduction

The capacity of on-board hydrogen storage is critical to H₂-powered fuel cell vehicles. For practical applications, the storage system must meet the gravimetric and volumetric densities as well as the cost target set by DOE. We plan to address 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 in the polymeric adsorbent research [1-3]. Our approach focuses 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.

Approach

Our design principles aim at improving the following POP attributes: (a) high SSA to provide sufficient interface with H₂, (b) narrow pore diameter to enhance van der Waals interactions in the confined space, and (c) “metallic” characters, either through π -conjugation or metal doping, to promote electronic orbital interactions with hydrogen. During Fiscal Year (FY) 2010, we focused our effort on improving H₂ isosteric heat of adsorption over POPs by controlling adsorbents’ surface chemical and physical properties. Several series of POPs were systematically designed and synthesized. One example is a polyporphyrin POP with relatively high SSA and narrow pore size distribution. The N4 macrocycle within the POP serves as a coordination site where transition metal (TM) ions can be exchanged in the center of the square-planar ring to bind with H₂. Another example is a series of aromatic POPs prepared by facile trimerization reaction with nearly identical SSA but variable pore sizes. Such system can be used to investigate the dependence of adsorption enthalpy on the pore dimension. The surface property, hydrogen uptake capacity, and isosteric heat of adsorption were measured through N₂-BET and Sievert isotherm methods. In addition, *ab initio* and density functional theory calculations were conducted to compare with the experimental results for a better understanding of the hydrogen-POP interaction.

Results

Isosteric heat of adsorption, ΔH_{ads} , is an important property for hydrogen adsorbents. To anchor H₂ at ambient temperature without consuming excessive energy for extraction, the preferred ΔH_{ads} is from 15 to 20 kJ/mol. Unsaturated metal ligated in a high surface area organic support could promote the interaction with molecular hydrogen through *d-s* orbital interaction. For example, theory suggested an enhanced H₂ adsorption energy over porphyrin when a selective group of TMs are exchanged into N4-macrocyclic ring [4]. We designed and prepared a polyporphyrin POP, poly-tetrakis(3,5-dithiophen-2-ylphenyl)-porphyrin (PTTPP) in FY 2010 and studied the improvement in ΔH_{ads} by comparing H₂ adsorption over the metal doped and undoped versions. Figure 1 shows a three-dimensional structure of iron-exchanged polyporphyrin Fe(PTTPP), where Fe is coordinated by four nitrogens in the porphyrin

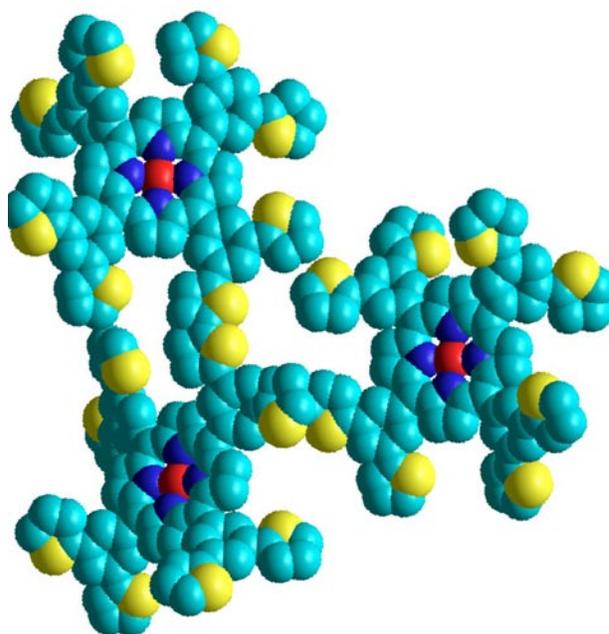


FIGURE 1. Three-dimensional structure of a segment of Fe(PTTPP) shows iron (red) is coordinated by four nitrogen atom (blue) in porphyrin ring.

ring. The surface properties of PTTPP and Fe(PTTPP) were investigated by N₂ adsorption isotherm and their hydrogen uptake capacities were measured by a Sievert isotherm apparatus. The results are listed in Table 1. We also investigated the H₂ adsorption isotherms at 77 K, 87K, 197 K, 273 K and 297 K. From which we extracted ΔH_{ads} at different hydrogen loadings, as are shown in Figure 2. The isosteric heat of adsorptions was indeed increased when Fe was exchanged into the porphyrin center. However, the enhancement is limited and still falls below the targeted value. We plan to use PTTPP system as a new platform for studying the impact of different metals on ΔH_{ads} , taking advantage of versatility of metal exchange through ligation chemistry with the porphyrin.

It has been postulated that the adsorbent pore size influences ΔH_{ads} and the preferred dimension should be slightly higher than the adsorbate’s van der Waals diameter in the range of 0.6 nm to 0.9 nm [5]. In FY 2010, we designed and prepared a series of aromatic POPs through trimerization reaction using monomers

TABLE 1. Surface Properties and Hydrogen Adsorption Capacities of PTTPP and Fe(PTTPP)

	BET SSA (m ² /g)	Langmuir SSA (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)	Pore Diameter (nm)	Excess H ₂ Ads. @ 65 bar & 77 K
PTTPP	1,522	2,030	0.85	0.67	0.85	5.0%
Fe(PTTPP)	1,248	1,665	0.68	0.54	0.82	4.6%

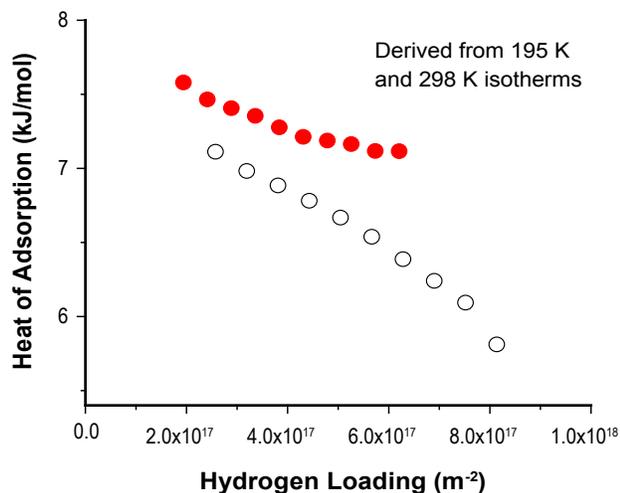


FIGURE 2. Heats of adsorption as a function of hydrogen loading for PTTPP (hollow circle) and Fe(PTTPP) (solid circle).

substituted with ethynyl groups at different position, shown as M1 to M4 in Figure 3a. The trimerization reaction led to the formation of four POPs (POP-1 to POP-4) with nearly identical SSAs but variable pore diameters ranging from 8 to 9 Å, as shown in Figure 3b. Hydrogen adsorption was subsequently performed at four temperatures from liquid nitrogen to ambient. Isosteric heats of adsorption, together with the uptake capacities, were obtained. Figure 4 shows ΔH_{ads} as the functions of hydrogen loading for all four POPs. Interestingly, no direct correlation between pore diameter and the heats of adsorptions was observed. Instead, we found a correlation between ΔH_{ads} and N_p where N_p represents the average number of phenyl

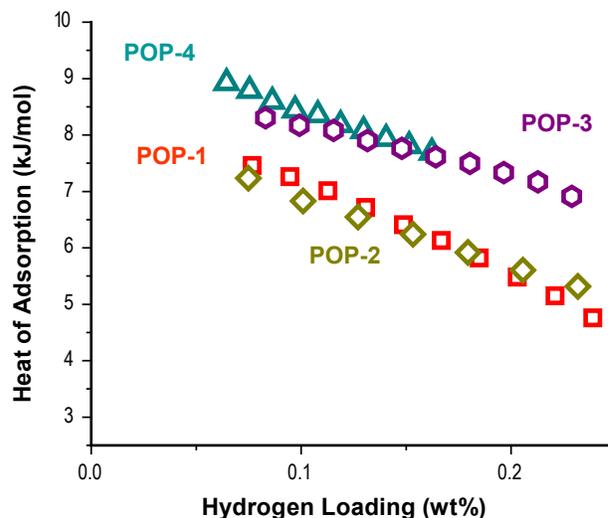


FIGURE 4. Heats of adsorption as a function of hydrogen loading for POP-1 (square), POP-2 (diamond), POP-3 (hexagon) and POP-4 (triangle).

groups connected to a benzene after trimerization. The N_p values for POP-2 (2.3) and POP-1 (2.5) are considerably lower than those for POP-3 (3) and POP-4 (3.5), leading to lower ΔH_{ads} values. We also performed a quantum mechanical calculation on the interaction between hydrogen and monomers in both open and confined configurations and found the results were consistent with our experimental observation.

Conclusions and Future Directions

In summary, we investigated several functionalized POP systems during FY 2010 in an effort to increase

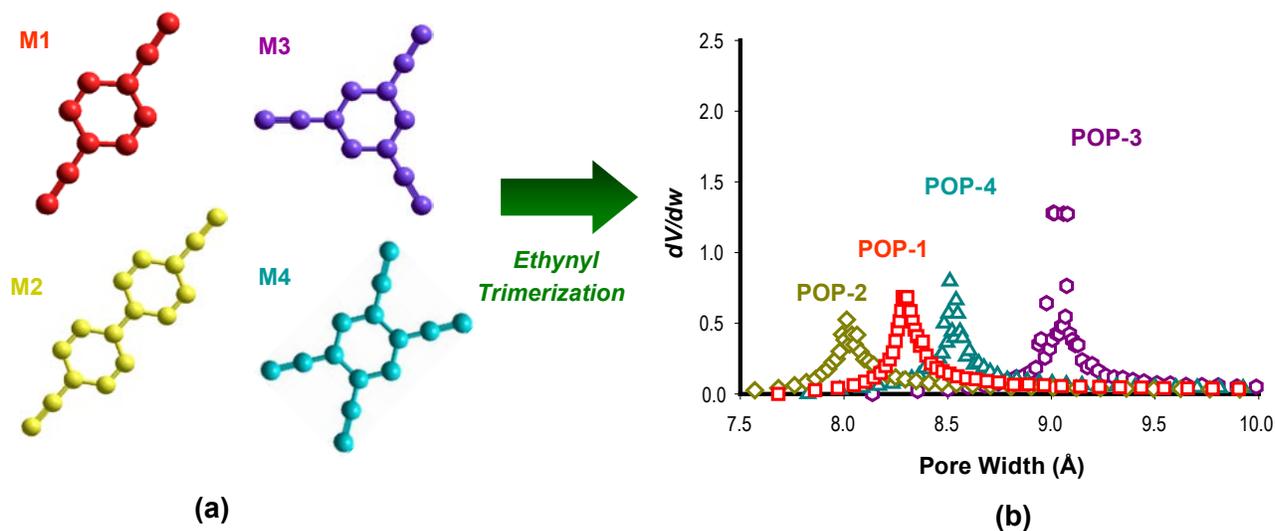


FIGURE 3. (a) Molecular structures of four monomers used for synthesis of POP-1, POP-2, POP-3 and POP-4; (b) differential pore volume distributions as a function of pore width for four POPs.

hydrogen adsorption enthalpy. The two examples we included in this report demonstrate that enhancement of ΔH_{ads} can be achieved through doping TM or altering chemical environment although further improvement is necessary to reach the preferred value. Our future study will focus on the following areas:

- Continue to incorporate metal and non-C elements to POPs for better hydrogen uptake and heat of adsorption.
- Explore non-conventional activation and doping methods for major improvement in storage capacity and temperature.
- Identify new pathway for next generation POP-adsorbent through rational design and advanced characterization.

Special Recognitions & Awards/Patents Issued

1. The POP-based adsorbent development was cited as one of the highlights of technical accomplishment by FreedomCAR and Fuel Partnership.
2. Member of Hydrogen Sorption Center of Excellence received 2010 DOE Hydrogen Program Team Award.
3. Poster Prize at 1st International Conference on Materials for Energy, Karlsruhe, Germany, July 4–8, 2010.

FY 2010 Publications/Presentations

1. “Microporous Polyphenylenes with Tunable Pore Size for Hydrogen Storage” S. Yuan, B. Dorney, D. White, S. Kirklin, P. Zapol, L. Yu and D.-J. Liu, *Chem. Commun.* **2010**, 46, 4547 – 4549.
2. “Nanoporous Polyporphyrin as Adsorbent for Hydrogen Storage” J. Xia, S. Yuan, Z. Wang, S. Kirklin, B. Dorney, D.-J. Liu and L. Yu, *Macromolecules*. **2010**, 43, 3325–3330.
3. “Porous Organic Polymers (POPs) for Hydrogen Storage” S. Yuan, B. Dorney, S. Kirklin, D. White, J. Xia, Z. Wang, L. Yu & D.-J. Liu, Poster presentation at 1st International Conference on Materials for Energy, Karlsruhe, Germany, July 4 – 8, 2010.
4. “Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)” D.-J. Liu, S. Yuan, D. White, A. Mason, P. Zapol, J. Xia, Z. Wang & L. Yu, Presentation ST-50, DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C. , June 7–11, 2010.
5. “Porous Organic Polymers (POPs) and their Hydrogen Uptake Properties”, S. Yuan, J. Xia, S. Kirklin, B. Dorney, D. White, L. Yu, & D-J Liu, Oral Presentation at American Chemical Society National Meeting, San Francisco, CA , March 21-25, 2010.
6. “Advanced Materials & Characterizations for Energy Storage & Fuel Cell Applications”, D.-J. Liu, Invited Presentation at Department of Chemistry, Northern Illinois University, Sept 28, 2009.
7. “Next Generation Materials and Characterization Techniques for Energy Efficiency and Renewal Energy Applications” D.-J. Liu, Invited Presentation at Department of Chemistry, University of Illinois, Nov 5, 2009.
8. “Advanced Materials for Energy Storage and Conversion” D.-J. Liu, Invited Presentation at Department of Chemistry, Hunter College, NY, Jan 27, 2010.

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