IV.C.6 New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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Objectives

- Develop new materials to meet DOE gravimetric and volumetric targets for hydrogen storage:
  - Develop and optimize strategies for introducing cations into metal-organic frameworks (MOFs).
  - Synthesize new polymeric-organic frameworks (POFs) that contain cations.
  - Use computational modeling to understand existing materials and design new materials for hydrogen storage.

Technical Barriers

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

(A) System Weight and Volume

(E) Charging/Discharging Rates

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is developing and testing new materials for hydrogen storage. These new materials can be applied in the future in the design of hydrogen storage systems that meet the following DOE 2010 hydrogen storage targets:

- System Gravimetric Capacity: 1.5 kWh/kg = 0.045 kg H_2/kg system
- System Volumetric Capacity: 0.9 kWh/L = 0.028 kg H_2/L system

Approach

Our approach has three strongly inter-related thrusts:

- Development and optimization of cation-doping strategies for MOFs.
- Synthesis of new, POFs that also contain cation sites.
- Computational elucidation and design as guidance and verification for experimental work.

MOFs provide an incredibly flexible platform for nanoporous materials design. They have completely uniform channels and pores of tunable diameters, and they are enormously tunable in chemical composition. In addition, MOFs have the lowest densities of any known crystalline materials. For hydrogen storage, the biggest problem is the low binding energy of hydrogen. Our main approach for overcoming this is to introduce lithium and other cations into MOFs. We are developing several methods for doing this based on 1) framework reduction, 2) synthesis of MOFs with pendant hydroxyl groups and ion-exchange of the hydroxyl H^+ with Li^+ or other cations, and 3) synthesis of MOFs having anionic frameworks balanced by cations.

As a complement to the MOFs, we are investigating new families of all-organic materials designed with rigid, bulky groups to prevent efficient packing of polymer chains and thus to produce microporosity and high internal surface areas. This new family of POFs can, in principle, have higher hydrogen loading capacities because their density on average is expected to be lower than MOFs. The proposed systems will have built-in functional groups which are intended to tune the enthalpy of interaction with adsorbed hydrogen. Functional groups such as $–NH_2$, -NH-, -OH can be

easily designed into the POFs allowing for Li^+, Ca^{2+}, or Mg^{2+} addition and enhanced H_2 sorption.

Molecular modeling is already playing an important role in the development of MOFs. We are using a combination of quantum chemical calculations and classical grand canonical Monte Carlo simulations. Quantum chemical calculations at the MP2 level are used to elucidate how hydrogen interacts with the lithiated functional groups in MOFs and POFs, providing estimates of heats of adsorption. We will also explore other cations such as Mg^{2+} as a guide for experiments. The Monte Carlo simulations then allow prediction of adsorption isotherms, using the quantum chemical energies as inputs. Modeling can be used to screen hypothetical MOFs before they are synthesized and to provide insights that are difficult to obtain by direct experiment.

Accomplishments

The project was initiated in February 2009.

- The MOF UMCM-1-NH_2 having pendant amine groups was synthesized according to literature procedures and characterized. Subsequently, an amine hydrogen was ion-exchanged with lithium. Hydrogen adsorption measurements were carried out at 77 K and 87 K on the materials before and after lithium exchange. Hydrogen uptake at 1 atm increases from 1.07 wt% in UMCM-1-NH_2 to 1.42 wt% in UMCM-1-NHLi as shown in Figure 1.
- The isosteric heats of adsorption (q_{st}) for hydrogen were determined from the 87 K and 77 K isotherms in UMCM-1-NH_2 and UMCM-1-NHLi. The maximum q_{st} for UMCM-1-NH_2 was determined to be 5.6 kJ/mol. After lithiation the material shows a q_{st} of 6.2 kJ/mol, a significant increase. See Figure 2.
- During the last three months, microporous POFs with specific surface areas up to 900 m^2g^{-1} have been developed by our group. Their synthesis is based on Schiff's base chemistry by forming imine linkages (C=N) from amines and aldehydes.
- Both linear and cross-linked POFs have been developed, many using inexpensive and commercially available starting materials. Synthesis conditions were optimized to obtain higher surface area and micropore volume.
- Synthesized POFs have been characterized by N_2 porosimetry to determine specific surface area, micropore volume, and total pore volume. All materials are microporous, and surface areas vary from 200 to 900 m^2/g as shown in Table 1.
- The linear chain POFs with the highest surface areas and micropore volumes (POF-1, POF-2 and POF-5) were examined for hydrogen storage by volumetric adsorption of H_2 at 77 K and ambient pressure. The H_2 adsorption isotherms are presented in Figure 3. The uptake of H_2 for the samples POF-1 and -2 achieves approximately 1 wt%, and POF-5, which has the highest micropore and total pore volume, exhibits uptake around 1.5 wt%.
- We predicted adsorption isotherms for hydrogen in a diverse set of 43 MOFs using grand canonical Monte Carlo simulations. Isotherms were predicted up to 120 bar at 77 K and 298 K.
- Using the simulated isotherms, we tested simple correlations (based on surface area and pore

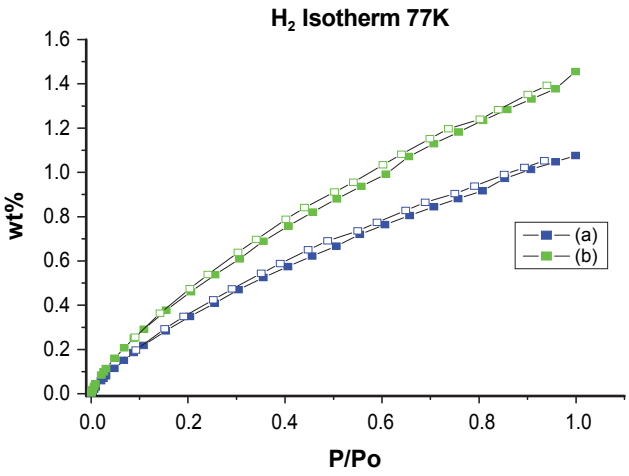

FIGURE 1. Hydrogen isotherms at 77 K of (a) UMCM-1-NH_2 as synthesized and (b) UMCM-1-NHLi (1.4:1 Li:amine loading). Closed symbols are adsorption, open symbols desorption.

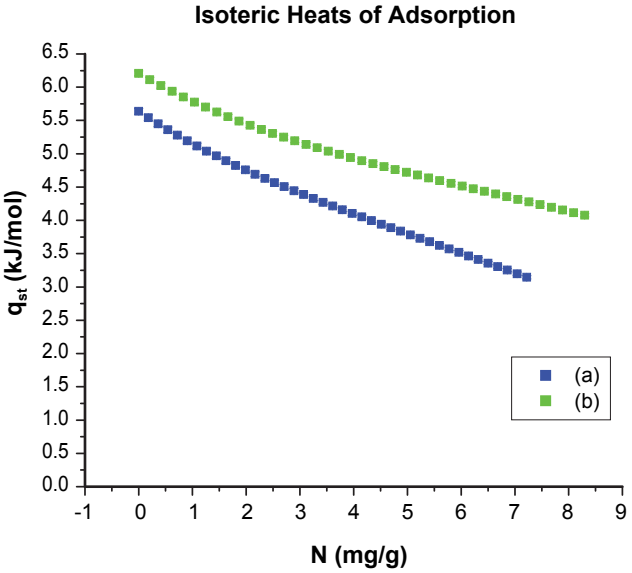

FIGURE 2. Hydrogen Isosteric Heats of Adsorption (q_{st}) for (a) UMCM-1-NH_2 as Synthesized and (b) UMCM-1-NHLi

TABLE 1. Porous Features of POFs

Sample Name	Specific Surface Area (m^2g^{-1})	Micropore Volume (cm^3g^{-1})	Total Pore Volume (cm^3g^{-1})
POF-1	820	0.33	0.40
POF-2	760	0.30	0.41
POF-3	625	0.23	0.43
POF-4	545	0.19	0.35
POF-5	878	0.35	0.54
POF-6	207	0.01	0.3
POF-7	919	0.31	1.13
POF-8	866	0.29	1.01
POF-9	585	0.19	0.42
POF-10	465	0.15	0.43

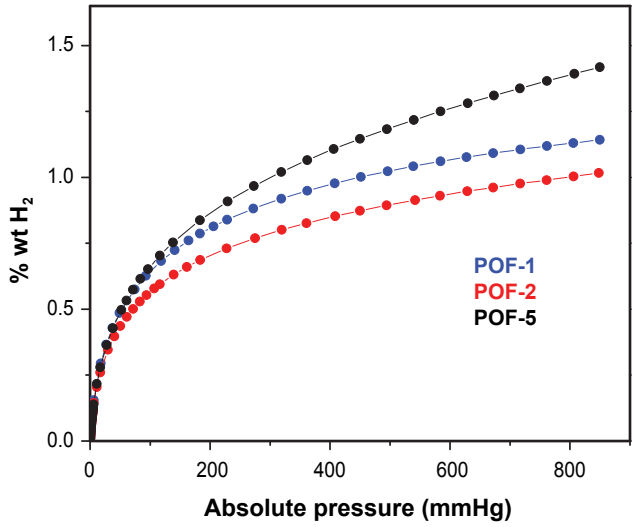

FIGURE 3. H_2 Adsorption Isotherms for POF-1, POF-2 and POF-5 at 77 K

volume) that could be used to very rapidly estimate hydrogen uptake in MOFs. The results indicate that hydrogen uptake at 77 K can be reliably estimated simply from the free volume for MOFs that do not contain cations.

- All of the simple correlations tested for rapidly estimating hydrogen uptake in MOFs failed at 298 K because the density of adsorbed hydrogen is low. This result underscores the main thrust of this project: significant increases in the binding energy of hydrogen will be required to increase room temperature hydrogen storage in MOFs and POFs.

Future Directions

- Additional cation-containing MOFs will be synthesized. By varying the attachment chemistry, the nature of the cation, and the solvent removal procedure, we anticipate achieving adsorption enthalpies of 10 kJ/mol.
- Hydrogen uptake in our MOFs will be measured at 298 K and up to 100 bar.
- The cross-linked POFs in hand will be analyzed for hydrogen uptake in the very near future.
- POFs will be functionalized with –OH (hydroxyl) groups, and the materials will be lithiated to increase the hydrogen uptake. We anticipate very robust materials for hydrogen storage.
- Additional POFs will be synthesized using a variety of chemistries.
- Hydrogen uptake in our POFs will be measured at 298 K and up to 100 bar.
- Quantum chemical modeling will be performed for the MOFs and POFs synthesized within this project.
- A procedure will be developed for seamlessly incorporating energies calculated quantum mechanically into classical Monte Carlo simulations. This will allow prediction of adsorption isotherms in existing and hypothetical materials. By screening a large number of materials computationally, we anticipate developing insights into how combinations of cation sites, pore sizes, and other properties should be optimized for maximum hydrogen storage near room temperature.

References

1. H. Frost, T. Düren, R.Q. Snurr, *J. Phys. Chem. B* **2006**, *110*, 9565.