

IV.C.8 Hydrogen Storage in Metal-Organic Frameworks

Jeffrey Long (Primary Contact),
Martin Head-Gordon

Lawrence Berkeley National Laboratory
1 Cyclotron Road
Berkeley, CA 95720
Phone: (510) 642-0860
Email: jrlong@berkeley.edu

DOE Managers

HQ: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov
GO: Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@go.doe.gov

Subcontractors:

- National Institute of Standards and Technology, Gaithersburg, MD (Craig Brown)
- General Motors Corporation, Warren, MI (Anne Dailly)

Project Start Date: April 1, 2012
Project End Date: March 31, 2015

- Quantify site-specific interactions of hydrogen with newly synthesized materials using inelastic neutron scattering
- Finish calculations of the binding of H₂ with the M-BTT linker and compare with experimental values for primary and secondary binding sites
- Assess performance of different computational methods for the M-BTT-H₂ binding problem
- Commence calculations of H₂ binding to carboxylate-substituted aromatic linkers decorated with light metal ions.
- Validate the excess adsorption measurement and data acquisition system through measurements on benchmark materials such as activated carbons and MOF-177

Technical Barriers

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

(A) System Weight and Volume

Technical Targets

Specific efforts are focused on the research and development of onboard systems that allow for a driving range greater than 300 miles. Materials are sought with the potential for meeting the 2017 DOE targets of reversible uptake and, subsequently, the “ultimate full fleet” targets (see Table 1).



Fiscal Year (FY) 2012 Objectives

- Demonstration of the ability to prepare five mixed functionality ligands
- Development of *in silico* pore surface screening
- Preparation of metal-organic frameworks with high metal:ligand ratios
- Demonstrate ability to locate and uncover detailed descriptions of high-enthalpy H₂ binding sites in high-valent metal-organic frameworks
- Extract vital structural snapshots of the D₂-M²⁺ in systems exhibiting coordinatively unsaturated metal centers using neutron diffraction

TABLE 1. Progress towards Meeting Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles

Storage Parameter	Units	2017 Target	Ultimate Target	2012 Status [†]
System Gravimetric Capacity: Usable, specific-energy from H ₂ (net useful energy/max system mass) [*]	kWh/kg (kg H ₂ /kg system)	1.8 (0.055)	2.5 (0.075)	(0.016 kg H ₂ /kg adsorbent)
System Volumetric Capacity: Usable, energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	1.3 (0.040)	2.3 (0.070)	(0.011 kg H ₂ /L adsorbent)

^{*} Generally the full mass (including hydrogen) is used; for systems that gain weight, the highest mass during discharge is used. All capacities are net useable capacity able to be delivered to the power plant. Capacities must be met at end of service life.

[†] Since the project deals with the development of storage materials, the performance status is given in terms of storage capacity for storage materials, not the whole storage system.

Approach

Metal-organic frameworks are promising solid sorbents for storage of H₂ at room temperature. They can be tailored to incorporate a large number of selected metal ions, thereby tuning the H₂ binding energy. The overall aim of the project is to synthesize new metal-organic frameworks capable of achieving the -20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures.

This research involves investigators with a range of capabilities—including synthesis and characterization of new materials, electronic structure calculations, neutron diffraction and scattering studies, and high-pressure gas sorption measurements. The team performs work in four areas: Task 1) Synthesis of Metal-Organic Frameworks (Long-LBNL), Task 2) Characterization of Framework-H₂ Interactions (Brown-NIST), Task 3) First-Principles

Calculations of Hydrogen Binding Enthalpies (Head-Gordon-LBNL), Task 4) High-Pressure H₂ Adsorption Measurements (Dailly-GM).

FY 2012 Accomplishments

- Five new ligands with carboxylate and pyridine functionalities have been prepared (Figure 1).
- Opposing surface area distribution program has been written and submitted for publication [1].
- A number of new metal-organic frameworks containing accessible metal centers (Ni²⁺, Fe²⁺, Co²⁺, Ti³⁺) have been prepared. The Ni²⁺ framework (Figure 2) displays an H₂ binding enthalpy approaching the year two target of -12 kJ/mol (Figure 3).

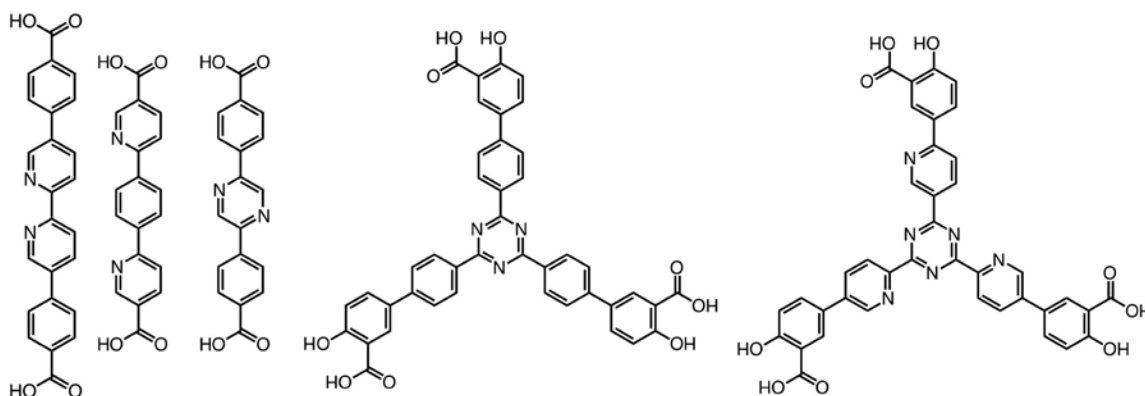


FIGURE 1. New di- and tritopic ligands containing both carboxylate and pyridine functional groups

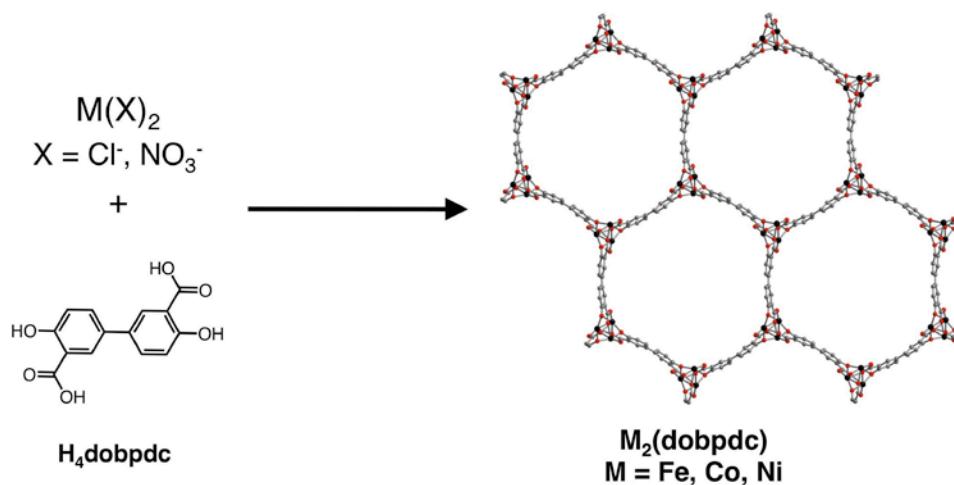


FIGURE 2. Recently synthesized metal-organic frameworks are expanded analogues of MOF-74 and feature high surface areas and a high density of open metal sites

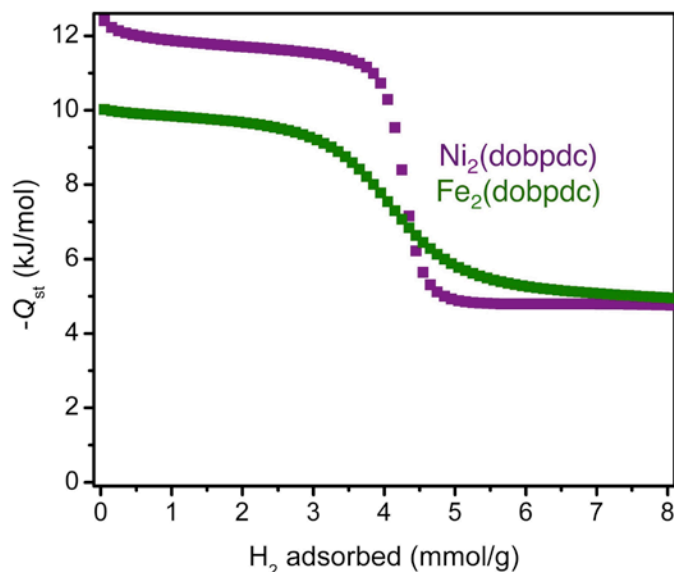


FIGURE 3. Isosteric heat of H_2 adsorption in $Fe_2(dobpdc)$ and $Ni_2(dobpdc)$. The heat of adsorption in the Ni^{2+} material approaches the year 2 target of -12 kJ/mol.

Future Directions

- Metal-organic frameworks containing the mixed functionality ligands reported herein will be synthesized and post-synthetically loaded with metal cations.
- Further analysis of the recently synthesized Ni^{2+} , Co^{2+} , Ti^{3+} frameworks by powder neutron diffraction, infrared spectroscopy, and high pressure H_2 adsorption experiments will be performed to obtain insight into which combination of surface area, pore volume, and open metal cations sites will lead to optimal room temperature H_2 storage properties.

- We will utilize a number of techniques, including neutron diffraction and inelastic neutron scattering to explore site-specific interactions of hydrogen with newly synthesized materials and the energetics of those binding events.
- We will reveal atomically detailed information about these adsorbates, extracting vital structural snapshots of the D_2-M^{2+} in systems exhibiting coordinatively unsaturated metal centers. The site-specific adsorption sites in these systems will be identified from sequential loadings corresponding to a progression from strong to weak adsorption sites, mirroring the site-specific enthalpy of adsorption.
- Continue calculations of H_2 binding to carboxylate-substituted aromatic linkers decorated with light-metal ions.
- Commence integrated quantum mechanics/molecular mechanics modeling of metal-organic framework systems to go beyond isolated linkers.
- Perform excess adsorption measurements on newly synthesized metal-organic framework samples.

FY 2012 Publications/Presentations

1. "Opposing Surface Area Distribution (OSAD) as a Characterization Tool for Microporous Metal-Organic Frameworks" Sumida, K.; Rogow, D.L.; Herm, Z.R.; Long, J.R. *Langmuir* submitted.

References

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