

IV.C.6 HyMARC (Support): LBNL Effort

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Project Start Date: October 1, 2015
Project End Date: Project continuation and direction determined annually by DOE.

Overall Objectives

- Develop in situ infrared spectroscopy as a tool for characterizing emerging H₂ storage materials that may allow for a driving range greater than 300 miles.
- Materials sought with the potential for meeting the DOE targets of reversible uptake.
- Validate new concepts for H₂ storage mechanisms in adsorbents.
- Provide accurate computational modeling for H₂ adsorbed in porous materials.

Fiscal Year (FY) 2017 Objectives

- Research and development of metal-organic framework materials with high volumetric and gravimetric H₂ capacities (Barrier A, B, C).
- Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization (Barrier N, O).
- Assist the DOE Hydrogen Materials – Advanced Research Consortium (HyMARC) seedling projects.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (E) Charging/Discharging Rates

- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (P) Reproducibility of Performance

Technical Targets

This project is conducting validation studies of various framework materials, sorbents, hydrides, and model compounds. Concurrently, the team also is developing new characterization tools for the rapid enhancement of materials development. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE onboard 2020 automotive hydrogen storage targets.

- 1.5 kWh/kg system (4.5 wt% H₂)
- 1.0 kWh/L system (0.030 kg H₂/L)
- Cost of \$10/kWh (\$333/kg H₂ stored)
- Operating at ambient temperatures (-40°C to 60°C)
- Onboard efficiency of 90% and minimum hydrogen delivery pressure of 5 bar
- Total refuel time of 5 minutes

FY 2017 Accomplishments

- Received and set up infrared spectrometer with in situ gas dosing capabilities.
 - Designed and built optical sample cell with in situ gas loading capabilities for DRIFTS measurements.
 - Validated the performance of the instrument at a resolution of 4 cm⁻¹ by observing an infrared (IR)-active gas dosed into the sample cell and known reference materials.
 - Validated the high-pressure performance of the instrument at a resolution of 4 cm⁻¹ by observing hydrogen adsorption on Ni₂(*m*-dobdc) at 100 bar.
- Targeted the synthesis of a room-temperature hydrogen adsorbent with a high density of unsaturated metal sites.
 - Synthesized several frameworks featuring protected catechol groups with high crystallinity and high surface area.
 - Extensively investigated deprotection protocol for these materials, yielding frameworks with complete incorporation of catechol functionalities with high crystallinity and high surface area.

- Performed theory calculations to understand both the desolvation process of metals bound to catechols and the binding of H₂ in calcium oxalate.
 - Used computational methods to understand the mode of H₂ binding in calcium oxalate.
 - Calculated the binding energies of additional H₂ to the metal-catecholate system and the influence of bound solvent.



INTRODUCTION

Efficient onboard storage of molecular hydrogen remains a key challenge faced by the hydrogen economy. The development of new hydrogen storage materials is a promising route towards replacing conventional compression methods requiring both high pressures and low temperatures, thereby overcoming one of the key limitations of the hydrogen economy. New materials will need to be validated and compared; therefore the development of world-class measurement methods and standards is crucial in ensuring that new materials may be validated and compared.

This national laboratory collaboration brings together internationally recognized leaders in hydrogen storage materials characterization and development at National Renewable Energy Laboratory, Pacific Northwest National Laboratory, LBNL, and the National Institute of Standards and Technology, as the HyMARC support team (also known as the Hydrogen Storage Characterization and Optimization Research Effort [HySCORE]). This collaboration is predicated on a synergistic approach to further validate hydrogen storage concepts and develop the key core capabilities necessary for accurate evaluation of hydrogen storage materials capacity, kinetics, and sorption/desorption physio-chemical processes. The overall approach involves collaborative experimental and modeling efforts. We are validating concepts and utilizing core capabilities to rapidly define, model, synthesize, and characterize the appropriate materials necessary for achieving the 2020 Hydrogen Storage goals set forth by DOE. The approach is multifaceted to mitigate risk and ensure success as we bridge the gap between physisorption and chemisorption to provide the basis for a new generation of hydrogen storage materials technologies.

Specific to this project, LBNL is constructing a state-of-the-art variable temperature DRIFTS instrument with high-pressure in situ gas dosing as a new core capability. Installation and validation of the IR spectrometer, optical array, gas dosing, and high-pressure capabilities have been completed, demonstrating accurate measurements of materials at up to 100 bar of H₂ pressure at room temperature. Cryogenic variable-temperature capabilities are currently under installation. Concurrently, novel

adsorbent materials with strong binding sites are being developed computationally and synthetically, focusing on a strategy which will lead to enhanced storage properties at temperatures relevant to onboard applications.

APPROACH

IR spectroscopy is a powerful technique which can be used to gain site-specific adsorption information through the spectroscopic observation of vibrational modes associated with adsorbed hydrogen. As the vibrational modes of background gas-phase hydrogen molecule are not IR active, this technique is particularly suited for in situ gas dosing measurements examining sorbent-sorbate interactions. Different H₂-sorbent interactions give rise to discrete signals in the IR, allowing identification and quantification of specific adsorption sites and the extraction of thermodynamic parameters. The DRIFTS geometry is particularly suitable due to both enhancement of weak adsorbate signals and lenient sample morphology requirements, allowing this core capability to measure and compare a wide range of samples.

Physisorption of hydrogen into porous materials is a promising route towards achieving reversible storage with fast recharge times, however due to the weak interactions, capacity at ambient temperatures is low. Computational efforts have determined that metal-catecholate motifs are able to bind strongly to multiple H₂ molecules. As such, we are concurrently pursuing frameworks incorporating these motifs in order to synthesize advanced hydrogen storage materials.

RESULTS

Characterization Techniques

The DRIFTS setup consists of a Bruker Vertex 70 Fourier transform infrared spectrometer, an Oxford Instruments top-loading optical cryostat, and a custom designed optical array allowing DRIFTS measurements to be taken in the cryostat chamber. A high-pressure sample cell and dosing manifold was designed and constructed in-house, and the system was coupled to a Micromeritics ASAP2020 Plus instrument. Control of the atmosphere inside the sample cell was demonstrated by dosing of CO₂, an IR-active gas, into the cell at varying pressures, and the DRIFTS measurement mode was validated by ex situ measurement of a known material. These measurements confirmed the working state of the spectrometer and the gas dosing apparatus.

Gas dosing measurements were performed on Ni₂(*m*-dobdc) (*m*-dobdc⁴⁻ = 4,6-dioxido-1,3-benzenedicarboxylate), a material previously synthesized by our lab which demonstrates strong physisorption of H₂. Peaks corresponding to different H₂ binding sites in the material were observed in good agreement to previous measurements.

Difference spectra were collected up to a pressure of 100 bar at approximately 10 bar intervals, and an increase of the signal originating from adsorbed H_2 was observed as expected (Figure 1).

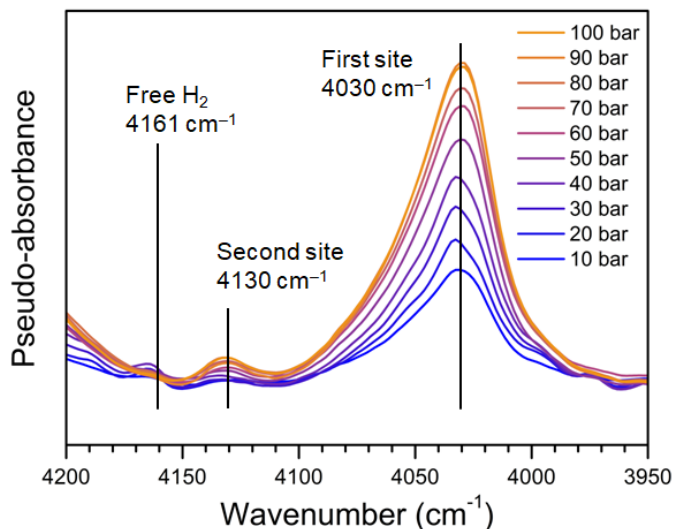


FIGURE 1. Room-temperature in situ DRIFTS spectra showing H_2 adsorbed in $Ni_2(m\text{-dobdc})$ at H_2 pressures of 10–100 bar. The peak position of H_2 bound to the first ($4,030\text{ cm}^{-1}$) and second ($4,130\text{ cm}^{-1}$) sites are in good agreement with literature.

Materials Discovery

Computations predict the binding of multiple hydrogen molecules to a metal-catecholate fragment with high binding energies. We have developed a synthetic route towards incorporating these fragments into a porous material in order to improve H_2 uptake under relevant conditions. A protection—framework assembly—deprotection strategy was successfully employed to functionalize two different framework morphologies with catechol groups which could not be incorporated into the framework via direct synthesis. We are able to synthesize highly crystalline frameworks with high surface areas and full incorporation of the catechol ligand by employing this strategy (Figure 2), and metalation trials are forthcoming.

Furthermore, extensive computational modeling has been performed on a range of materials. In a collaboration with the National Renewable Energy Laboratory, H_2 binding in calcium oxalate has been modeled and compared with experiment. H_2 was found to bind in a non-specific manner which was dominated by dispersion interactions (Figure 3). The effect of binding multiple H_2 molecules as well as the effect of residual solvent on the metal-catecholate system has been further studied (Figure 4). Usable capacities for a potential framework incorporating this system has been estimated, with a Ca-catecholate fragment contributing around 30 g/L H_2 to the capacity.

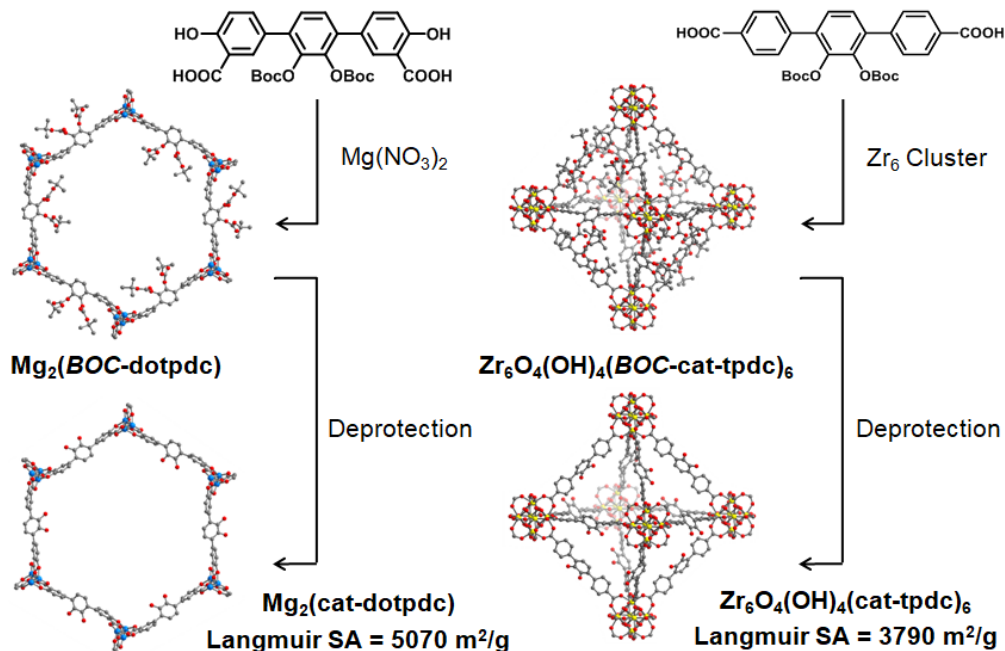


FIGURE 2. Catechol-functionalized frameworks with high crystallinity and surface area (SA) prepared from a protection—framework assembly—deprotection method. The organic linker is protected with a thermolabile group, solvothermal synthesis is performed to assemble the framework, and the resulting material is deprotected post-synthetically to yield free catechol groups in the framework. Structural models were generated using *Materials Studio* software. Atom colors: C, gray; O, red; Mg, blue; Zr, yellow. H atoms are omitted for clarity.

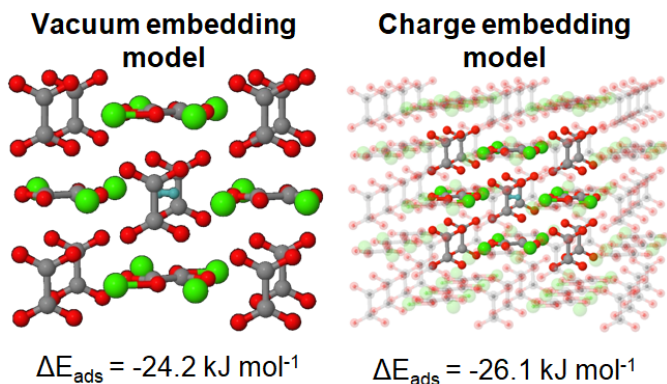


FIGURE 3. H₂ molecules adsorbed in calcium oxalate. H₂ does not interact with exposed metals, but instead is held in small pores by dispersion forces.

TABLE 1. Differential Adsorption Energies for Various Metal-Catecholate Systems (Figure 4) upon Adsorption of the *n*-th H₂ (kJ/mol)

n	Mg-catecholate	Ca-catecholate	Mg-thiocatecholate
1	-23.8	-15.9	-18.7
2	-22.2	-15.5	-12.8
3	-15.4	-15.1	-7.4
4		-14.7	-8.4

CONCLUSIONS AND UPCOMING ACTIVITIES

The successful installation and validation of the DRIFTS instrument with in situ high pressure gas loading capabilities has been demonstrated, and will be a core capability for the measurement and validation of a wide variety of internal and external samples. Following previous computational efforts, a catechol linker has been successfully incorporated into a metal-organic framework with high crystallinity and high surface area. Computational efforts have further investigated multiple H₂ binding in the metal-catecholate system, demonstrating high usable capacities resulting from our strategy of utilizing metals with multiple unsaturated sites. Future work will validate the low-temperature performance of the DRIFTS instrument, and develop synthetic routes towards metalation of the catechol frameworks.

FY 2017 PUBLICATIONS

1. Teo, J.M.; Coghlan, C.J.; Evans, J.D.; Tsivion, E.; Head-Gordon, M.; Sumbly, C.J.; Doonan, C.J. "Hetero-bimetallic Metal-Organic Polyhedra," *Chem. Commun.* **2016**, 52, 276.
2. DeSantis, D.; Mason, J.A.; James, B.D.; Houchins, C.; Long, J.R.; Veenstra, M. "Techno-economic Analysis of Metal-Organic Frameworks for Hydrogen and Natural Gas Storage," *Energy Fuels* **2017**, 31, 2024.

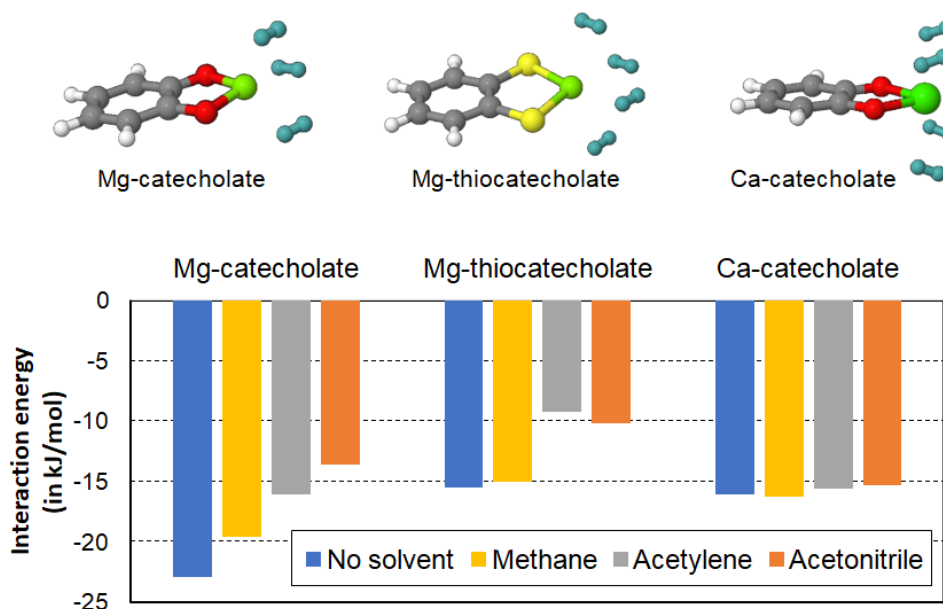


FIGURE 4. Top: H₂ molecules adsorbed on metalated catechols. Bottom: Differential adsorption energies of H₂ in metal-catecholate systems (blue) pre-adsorbed with methane (yellow), acetylene (grey) and acetonitrile (orange).

3. Tsivion E.; Veccham, S.P.; Head-Gordon, M. “High Temperature Hydrogen Storage of Multiple molecules: Theoretical Insights from Metalated Catechols,” *ChemPhysChem* **2017**, *18*, 184.

4. Tsivion, E.; Head-Gordon, M. “Methane Storage: Molecular Mechanisms Underlying Room-Temperature Adsorption in $Zn_4O(BDC)_3$ (MOF-5),” *Submitted*.

5. Kapelewski, M.T.; Runčevski, T.; Tarver, J.D.; Jiang, H.Z.H.; Ayala, A.; Gennett, T.; FitzGerald, S.A.; Brown, C.M.; Long, J.R. “Evaluating Metal–Organic Frameworks for High-Pressure H_2 Storage: Record High Volumetric Capacity in $Ni_2(m-dobdc)$,” *Submitted*.

FY 2017 PRESENTATIONS

1. Kapelewski, M.T.; Runčevski, T.; Jiang, H.Z.; Hurst, K.E.; Gennett, T.; FitzGerald, S.A.; Brown, C.M.; Long, J.R. “ H_2 Storage on Open Metal Coordination Sites — Best Performance in $Ni_2(m-dobdc)$ and Two H_2 Molecules on One Metal in $Mn_2(dsbdc)$,” 5th International Conference on Metal-Organic Frameworks, Long Beach, CA (September 15, 2016).

2. Kapelewski, M.T.; Head-Gordon, M. “Hydrogen Storage in Metal–Organic Frameworks,” DOE H_2 Tech Team Meeting, Southfield, MI (March 16, 2017).

3. Runčevski, T.; Long, J.R. “*In Situ* Diffraction and Spectroscopic Studies of Metal–Organic Frameworks under Variable Temperature and Gas Pressure,” 253rd ACS National Meeting & Exposition, San Francisco, CA (April 2, 2017).