

## IV.C.1d Neutron Characterization in Support of the Hydrogen Sorption Center of Excellence

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direction determined annually by DOE

### Objectives

- Quantify the amount, location, bonding states and dynamics of hydrogen in hydrogen sorption materials.
- Direct partner synthesis efforts based on the understanding gained through the use of scattering techniques.
- Demonstrate the fundamental characteristics of useful hydrogen storage materials.

### Technical Barriers

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

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

NIST provides important materials metrologies for Hydrogen Sorption Center of Excellence (HSCoE) partners using neutron-scattering measurements to understand and characterize hydrogen-substrate interactions of interest to the Center.

### Enhanced Hydrogen Storage using Supported Metal Centers

This project is conducting fundamental studies of how hydrogen binds in metal organic frameworks (MOFs) with exposed metal sites. Insights gained from these studies will be used by Center partners and applied toward the design and synthesis of hydrogen storage materials that meet the following DOE hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

### Accomplishments

- Characterized the hydrogen environment upon adsorption in graphite intercalation materials despite lack of periodic crystal structure. Characterized the hydrogen diffusion mechanism and geometry.
- Determined multiple binding sites for H<sub>2</sub> in one of an isostructural series of benzene tris-tetrazole (BTT) compounds. Partial understanding of the local adsorption potential is obtained from the current inelastic neutron scattering data.
- For the first time we have observed a significant perturbation of the hydrogen rotational levels in a high surface area B-doped carbon.
- Further understood the surface chemistry and hydrogen adsorption capacities in zeolite-templated carbons loaded with Pt nanoparticles. Failed to observe any spillover in these materials.



### Introduction

To obtain the DOE levels of hydrogen storage in a timely manner, it is imperative that trial-and-error testing of materials be avoided. Thus, the focus must be upon the rational design of new systems. From a thorough understanding of the physics and chemistry that governs the hydrogen-substrate interactions, we will be able to make a more concerted effort to push the frontiers of new materials. The key to improving materials is a detailed understanding of the atomic scale locations of the hydrogen and determining how it gets there and how it gets out. Neutron scattering is perhaps the premier technique for studying hydrogen and the NIST Center

for Neutron Research is currently the leading facility in the U.S. for studying these materials.

## Approach

NIST provides important materials characterization for Center partners using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of hydrogen in carbon-based materials such as polymers, MOFs, and carbonaceous materials such as carbon nanohorns. NIST works directly with Center partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine and resolve the fundamental issues that need to be addressed.

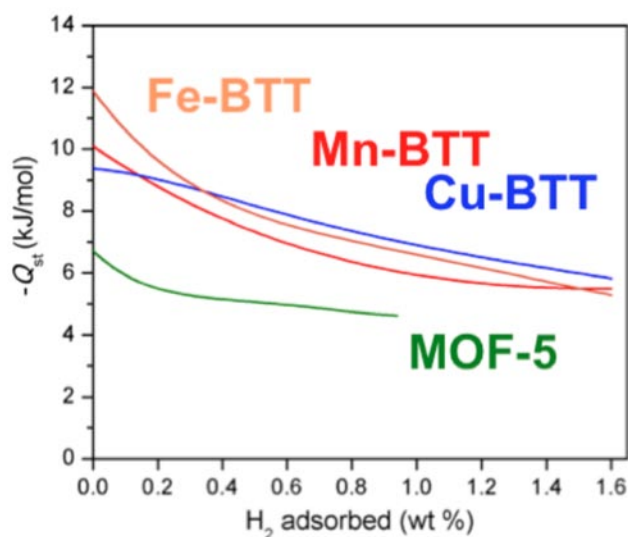
## Results

### MOFs

MOFs have recently come under intense investigation for gas storage and separation applications, owing to their high internal surface areas, convenient modular synthesis, and chemical tenability. Previously, we have reported a number of MOFs in which removal of a solvent molecule from the coordination sphere of the framework metal cations yields strong adsorption sites for  $H_2$ . One possibility for improving the isosteric heat of adsorption within this structure type would be through constructing the structure with  $M^{2+}$  cations having a smaller radius. The greater charge density of the exposed metal cations on the framework surface should then be more effective at inducing a dipole in  $H_2$ , leading to stronger binding.

The synthesis of a new framework structure with open  $Fe^{2+}$  coordination sites, Fe-BTT [1], has confirmed that the large isosteric heat of adsorption for  $H_2$  in Fe-BTT is associated with the presence of open  $Fe^{2+}$  coordination sites associated with the  $[Fe_4Cl]^{7+}$  clusters of the framework. The initial isosteric heats are larger than those in isostructural  $Mn^{2+}$  and  $Cu^{2+}$  derivatives (Figure 1) and much greater than the prototypical MOF-5. Combined with neutron diffraction data and inelastic neutron scattering spectroscopy we have shown that these exposed  $Fe^{2+}$  sites provide a strong interaction with  $H_2$ , drawing it close to the surface. There is a correlation between the higher initial enthalpies in this series and how close the  $D_2$  molecules can approach the metal ion. The relative distance increase from 2.17(5) Å, 2.27 Å and 2.47 Å, for  $Fe^{2+}$ ,  $Mn^{2+}$  and  $Cu^{2+}$  ions, respectively. Increasing the adsorbed amount of  $D_2$ , reveals a progression of site fillings away from the cation with 10 sites identified at saturation (Figure 2).

The  $H_2$  loading characteristics of Fe-BTT have been further probed by inelastic neutron scattering. In the lowest loading data (< 0.5 wt%), there is an absence of



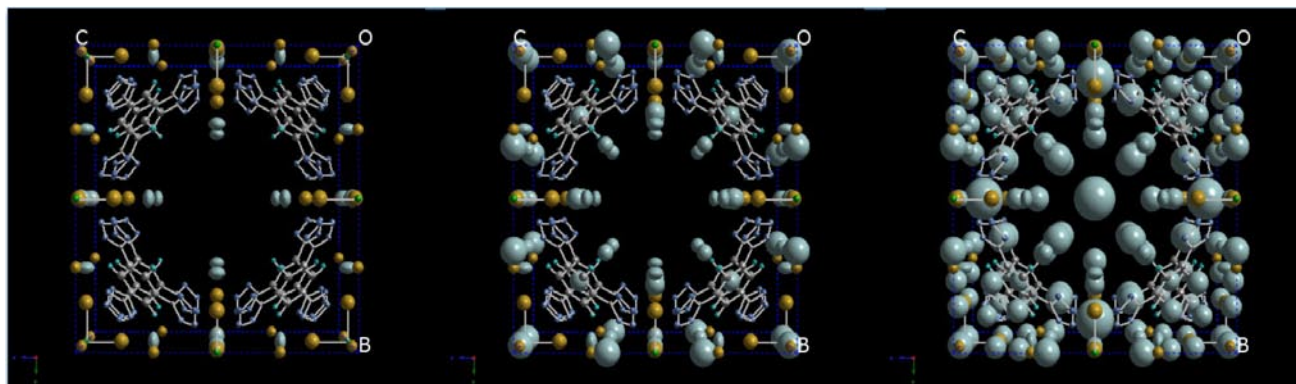
**FIGURE 1.** Isosteric heat of adsorption as a function of hydrogen uptake in Fe-BTT (orange), Mn-BTT (red), Cu-BTT (blue), and MOF-5 ( $Zn_4O(1,4\text{-benzenedicarboxylate})_3$ ) (green).

a rotational line at 14.7 meV that would correspond to the first rotational transition of free hydrogen. This is indicative of a strong rotational hindering potential of the binding sites occupied at these levels, consistent with the large initial isosteric heat of  $H_2$  adsorption. At this low loading the strongest adsorption sites are populated, giving rise to two transitions observed at  $\approx 13.2$  and  $\approx 19.7$  meV. These peaks gain intensity upon increasing the loading to 0.5 wt% of  $H_2$ , and can be assigned as rotational lines that correspond to a rotational barrier of approximately 15 meV. Upon increasing the loading, weaker sites become occupied and features closer to the expected 'free hydrogen' energy are seen.

The low pressure (1 bar) adsorption of 2.3 wt% at 77 K, and 1.6 wt% at 87 K, is completely reversible, and the steep initial portion of each isotherm is also indicative of the presence of strongly-polarizing binding sites with a high affinity for  $H_2$ . The strongly polarizing  $Fe^{2+}$  affords an enhanced storage capacity at 298 K 1.1 wt% and 8.4 g/L; the total uptake in Fe-BTT at 95 bar constitutes a 16% increase in volumetric density compared to that of pure  $H_2$  gas at the same pressure. This work was performed in collaboration with J.R. Long (University of California, Berkeley) and A. Dailly (General Motors).

### Neutron Imaging of Adsorption

The development of new tools that may be of potential beneficial to enabling the engineering of storage tanks is presented. Briquettes of compressed activated carbon (Pfeifer, Missouri), were cut into cylindrical slugs and placed in a thick walled aluminum cell with a gas loading apparatus attached via a capillary.



**FIGURE 2.** Neutron diffraction allows the identification of 10  $D_2$  adsorption sites in Fe-BTT.

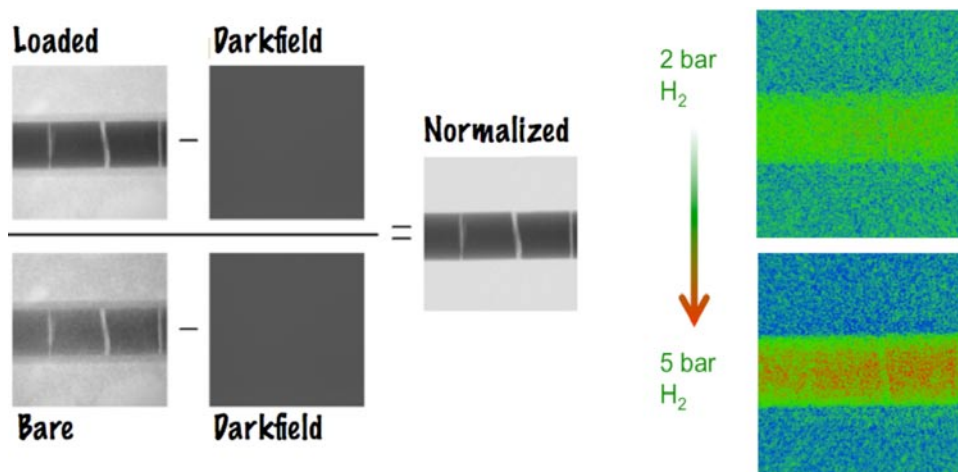
Illuminating the cell, and recording the image on a neutron sensitive charge-coupled device camera, gives an image as shown in Figure 3; darker pixels indicate more neutrons have been scattered away from the camera at that pixel. Subtracting the ‘noise’ through the darkfield image, and normalizing a hydrogen-loaded image to that of the bare material highlights only the adsorbed hydrogen. Images can be captured using this technique at specific loadings and with relative good statistics in under a second (instrumentation limit is much faster); we averaged 5 seconds to generate the images in Figure 3. As expected, this room temperature adsorption showed little time dependence at room temperature within the measurement timescale. A false color image of the hydrogen adsorbed in the system on increasing pressure from 2 bar to 5 bar is shown in the right panel of Figure 3. The shape of the briquettes are easily observable at 5 bar. While this data has not been taken to the point where we can be quantitative about the amount of hydrogen adsorbed, it would be a relatively simple exercise to complete that and compare

to traditional adsorption isotherms. Of some note is that this technique could distinguish the amount of gas in the free space away from the briquettes and that in the briquette itself.

### Conclusions and Future Directions

We have continued our primary task of performing various neutron characterization measurements in support of other HSCoE members focusing on optimizing our knowledge of hydrogen interactions for current and future materials development. Specifically we achieved the following results this year:

- Characterized the hydrogen environment upon adsorption in graphite intercalation materials despite lack of periodic crystal structure. Characterized the hydrogen diffusion mechanism and geometry.
- Determined multiple binding sites for  $H_2$  in one of an isostructural series of BTT compounds. Partial



**FIGURE 3.** Neutron transmission images of activated carbon cylindrical briquettes under a hydrogen atmosphere are normalized (left) to highlight only the adsorbed hydrogen at successive loadings with a false color scale (blue→green→red with increasing  $H_2$ ) (right).

understanding of the local adsorption potential is obtained from the current inelastic neutron scattering data.

- For the first time we have observed a significant perturbation of the hydrogen rotational levels in a high surface area B-doped carbon.
- Further understood the surface chemistry and hydrogen adsorption capacities in zeolite-templated carbons loaded with Pt nanoparticles. Failed to observe any spillover in these materials.
- Performed preliminary test-bed work on a macroscopic imaging of hydrogen adsorption in a high surface area carbon.

This work can be extended in the future. In particular there are issues pertaining to: limits for the enthalpy of adsorption of hydrogen in MOFs; understanding electrostatic/morphological control of hydrogen diffusion rates; chemistry of the nanoparticle and substrates used to obtain significant amounts of hydrogen spillover; clearly distinguishing physisorbed hydrogen from spillover hydrogen; obtaining quantitative interpretation of imaging adsorption in storage beds; and extending imaging facilities to include cryogenic sample environment.

### Special Recognitions & Awards/Patents Issued

1. Craig Brown, Department of Commerce Silver Medal.
2. Craig Brown, 2010 Neutron Scattering Society of America Science Prize.
3. Craig Brown, Presidential Early Career Award for Scientists and Engineers (PECASE).
4. Dan Neumann, Fellow of the APS.
5. Dan Neumann, Fellow of the Neutron Scattering Society of America.
6. Jae-Huyk Her, Young Scientist Travel award July 2009, American Crystallographic association, Toronto, ON, Canada.

### FY 2010 Publications/Presentations

1. *Hydrogen Storage Properties and Neutron Diffraction Studies of Mg<sub>2</sub>(2,5-dioxido-1,4-benzenedicarboxylate)*, K. Sumida, C.M. Brown, Z.R. Herm, S. Chavan, S. Bordiga, and J.R. Long (Submitted 2010).
2. *Micro-channel Development and Hydrogen Adsorption Properties in Templated Microporous Carbons Containing Platinum Nanoparticles*, Y. Yang, C.M. Brown, C. Zhao, A.L. Chaffee, B. Nick, D. Zhao, P.A. Webley, J. Schalch, J.M. Simmons, Y. Liu, J.-H. Her, C.E. Buckley and D.A. Sheppard (Submitted Apr. 2010).
3. *Hydrogen Storage and Carbon Dioxide Capture in an Iron-Based Sodalite-Type Metal-Organic Framework (Fe-BTT) Discovered via High-Throughput Methods*, K. Sumida,

S. Horike, S.S. Kaye, Z.R. Herm, W.L. Queen, C.M. Brown, F. Grandjean, G.J. Long, A. Dailly, and J. R. Long, *Chem. Sci.* **1** (2010) 184.

4. *Understanding physisorbed hydrogen systems using neutrons*, C.M. Brown, K. Sumida, J.R. Long American Chemical Society National Meeting, Washington, D.C., ACS Division of Fuel Chemistry, Preprints, vol. 54(2), (2009).
5. *Crystal structure of Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and the role of cation size on the structural behavior of the alkali-metal dodecahydro-closo-dodecacaborates*, J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, American Chemical Society National Meeting, Washington, D.C., ACS Division of Fuel Chemistry, Preprints, vol. 54(2), (2009).
6. *The role of cation size on the structural behavior of the alkali-metal dodecahydro-closo-dodecacaborates*, J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, *J. Phys. Chem. C*, 2009, 113, 11187.
7. *The nature of adsorbed hydrogen in HKUST-1: a Combined Inelastic Neutron Scattering and First-Principles Study*, C.M. Brown, Y. Liu, T. Yildirim, V.K. Peterson, and C.J. Keper, *Nanotechnology* 2009, 20 4025.

### Presentations

1. Craig Brown, *Understanding how hydrogen interacts with materials using neutrons*, American Conference on Neutron Scattering, June 2010, Ottawa Canada.
2. Craig Brown, *Neutron Scattering in Support of the Hydrogen Sorption Center of Excellence*, DOE Hydrogen and Vehicle Technology Programs Annual Merit Review, June 2010, Washington D.C.
3. Craig Brown, *Structure and Dynamics of Hydrogen in Physisorption Systems*, International Energy Agency – Task 22, Apr 2010, Death Valley, CA.
4. Craig Brown, *Where's my Hydrogen Car? Concepts and reality for gas storage in materials*, Seminar, Physics Dept. Howard University, Sept 2009, Washington, D.C.
5. Craig Brown, *Where's my Hydrogen Car? Concepts and reality for gas storage in materials*, CAMP Seminar, Physics Dept. Penn State, Sept 2009, State College, PA.
6. Craig Brown, *Understanding Physisorbed Hydrogen Systems Using Neutrons*, ACS National Meeting, Aug 2009, Washington, D.C.
7. Craig Brown, *From metal hydrides to physisorbed H<sub>2</sub>-systems: what we are learning with neutrons*, Metal Hydrogen-Metal Systems Gordon Conference, July 2009, Lucca, Italy.
8. Jae-Hyuk Her, *Crystal structures of M<sub>n</sub>B<sub>12</sub>H<sub>12</sub> (n=1,2) compounds – possible intermediate species in the decomposition of Mn(BH<sub>4</sub>)<sub>2</sub>*, July 2009, ACA Toronto, Canada.
9. Jae-Hyuk Her, *Crystal structure of Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and the role of cation size on the structural behavior of the alkali-metal dodecahydro-closo-dodecacaborates*, ACS National Meeting, Aug 2009, Washington, D.C.

## References

1. Hydrogen Storage and Carbon Dioxide Capture in an Iron-Based Sodalite-Type Metal-Organic Framework (Fe-BTT) Discovered via High-Throughput Methods, *K. Sumida, S. Horike, S.S. Kaye, Z.R. Herm, W.L. Queen, C.M. Brown, F. Grandjean, G.J. Long, A. Dailly, and J.R. Long*, *Chem. Sci.* 2010, 1, 184.