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

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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 Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure 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 HSCoE.

Accomplishments

- Determined bulk elemental compositions of materials of interest to the HSCoE. These include metal decorated carbon based materials, metal organic frameworks (MOFs) and boron-infused carbon materials.
- Determined the location of hydrogen binding in several crystalline materials.
- Illustrated the site-specific hydrogen adsorption strength in MOF materials.

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Introduction

DOE goals for hydrogen storage are unlikely to be attained in their timeframes through mere trial-and-error testing of materials. Thus, there must be some focus upon 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 (NCNR) is currently the leading facility in the USA for studying these materials

Approach

NIST provides important materials characterization for HSCoE 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 HSCoE partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine the fundamental issues that need to be addressed.

Results

Enhanced Physisorption

HSCoE-directed research aimed at improving the adsorption enthalpy of physisorbed hydrogen has numerous directions. One effort is to modify the local electronic structure around heteroatoms included in carbon frameworks such as the substitution or inclusion of boron in the carbon framework. We completed neutron spectroscopy measurements on low boron content nanotubes in collaboration with NREL. Figure 1 shows the neutron rotational spectra of hydrogen adsorbed in small amounts on arc-produced and laser-produced pristine and boron-substituted single-walled nanotubes (SWNTs) [1]. These particular samples did not show the theoretically predicted enhanced adsorption compared to pristine carbon materials and the characteristics of the local hydrogen rotational spectra reflected that of the parent carbon material. These results indicate that the split rotational peak in arc-produced samples originates from low concentration defects or disorder resulting from the production method and are not intrinsic to the pristine tube/bundle structures. While the current boron content in these materials is relatively small and potentially inaccessible to the hydrogen, we have used prompt-gamma activation analysis to show that the alternative preparation methods used at Pennsylvania State can be used to obtain much larger total boron content materials, exceeding eight mass percent relative to carbon.

Hydrogen Spillover

Due to the interest in using carbon as a support for hydrogen that has been catalytically associated with the surface, allowing stronger interactions than pure physisorption, we have been working with a number of the HSCoE members who are actively producing materials with the desired characteristics. Working with Oak Ridge National Laboratory, we have measured some of the characteristics of hydrogen associated with opened and opened metal-decorated single-walled nanohorns (SWNH). For the neutron spectroscopy, we are using the molecular rotational peak as a gross measure of the total number of physisorbed hydrogen molecules. In order to be sure that spillover will not occur and that we will then be able to measure the hydrogen rotational peak, hydrogen is loaded into the system at temperatures below 55 K. Upon temperature cycling the closed system up to room temperature and waiting between 12 to 48 hrs, we observed reductions in the intensity of the rotational peak and hence a change in the amount of hydrogen molecularly. For opened SWNHs, there is essentially no change in the magnitude of the rotational peak after waiting up to 12 hours at room temperature (Figure 2). However, when performing the same experiment with platinum-SWNTs there is a marked reduction in the intensity of the rotational peak, as shown in Figure 3. Repeated measurements ensure that the systems are leak-tight and that we are measuring a consistent phenomenon. We assume that this is a measure of the spill-over hydrogen and, from the reduction in peak area, the effect is on the order of 5% in 12 hours, though this increases with equilibration time. Using the same sample to volumetric measure the amount of spillover hydrogen on chemically opened Pt-SWNHs with a simple cycling of temperature from 77 K to room temperature results in only ~0.1 mass% hydrogen uptake in excess of the physisorbed hydrogen.

Metal Organic Frameworks

MOFs are composed of metal ions or metal clusters linked via organic ligands to form porous three-dimensional scaffolds. Evacuation of guest molecules typically results in a high-surface area material capable of adsorbing hydrogen. However, only weak

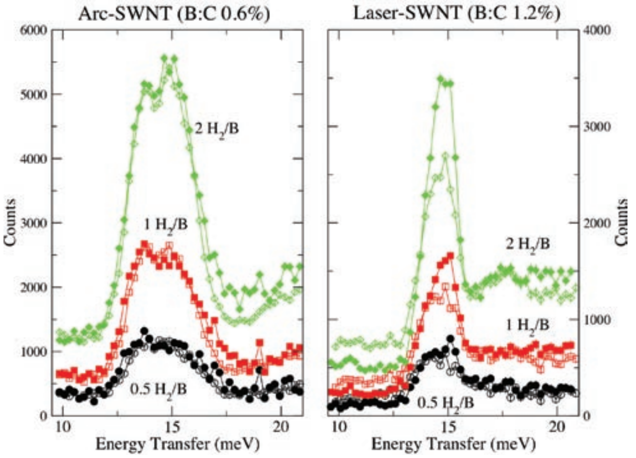

FIGURE 1. Neutron Rotational Spectra of Hydrogen Adsorbed on SWNTs (empty symbols) and B-Substituted SWNTs (filled symbols) (Left panel shows data with increasing hydrogen loading for arc-produced materials. The B-substitution level is 0.6 % B/C. Right panel displays the same information for laser produced materials where the B-substitution level is 1.2 % B/C.)

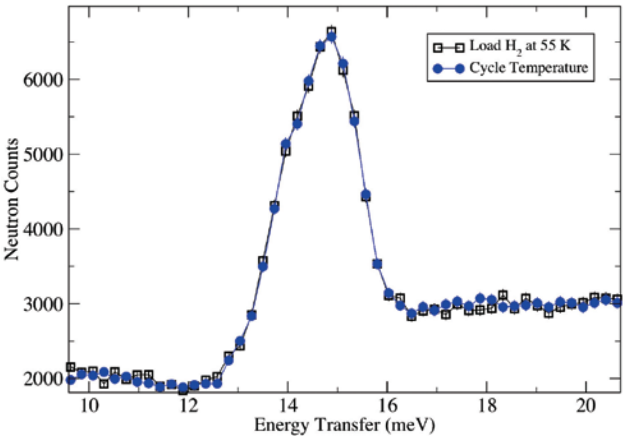

FIGURE 2. Neutron Rotational Spectrum of Hydrogen Adsorbed at Low Temperatures on Opened SWNHs (open squares) and After Cycling the Temperature of the Closed System to Room Temperature for 12 Hours (filled circles)

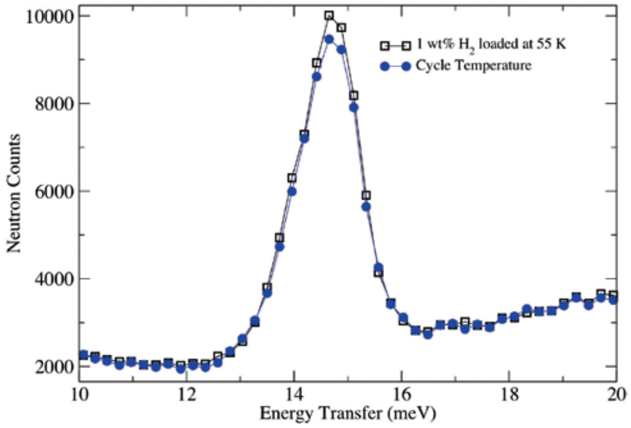

FIGURE 3. Neutron Rotational Spectrum of Hydrogen Adsorbed at Low Temperatures on Opened-Pt-SWNHs (Open Squares) and After Cycling the Temperature of the Closed System to Room Temperature for 12 Hours (Filled Circles)

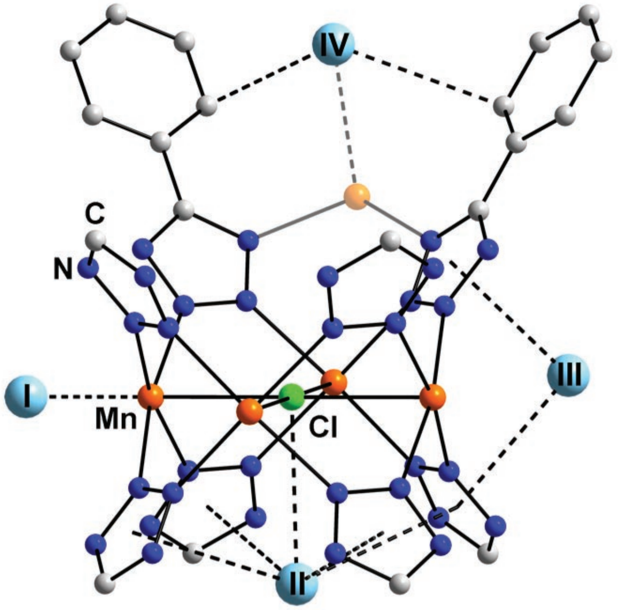

FIGURE 4. Initial D_2 adsorption sites within the Mn-based MOF. Light blue spheres represent D_2 centroids, while the transparent orange sphere shows the position of a partially-occupied, extraframework Mn^{2+} ion site. Sites are labeled I to IV in order of the observed adsorption sites.

interactions are observed between the poorly polarizable H_2 molecules and the pore walls, such that cryogenic temperatures are required to observe significant H_2 uptake. Frameworks exhibiting stronger binding interactions are needed to facilitate H_2 adsorption at higher temperatures, and, indeed, a binding energy of 15 kJ/mol has been predicted to maximize the amount of adsorbed H_2 accessible at 298 K and up to 20 bar [2].

Along with collaborators at U.C. Berkeley, we have used neutron powder diffraction to demonstrate that the highest observed maximum isosteric heat of adsorption (10.1 kJ/mol) observed for a MOF is directly related to H_2 binding at coordinatively unsaturated Mn^{2+} centers within the framework (Figure 4) [3]. Additional work also revealed the replacement of Mn^{2+} ions with Cu^{2+} ions in the sodalite-type metal–organic framework provides a material that can be fully desolvated to give a higher density of exposed coordination sites for H_2 binding [4].

Expanding on the concept of open coordination sites, we have shown that the initial hydrogen binding site in a dehydrated Cu_3(1,3,5-benzenetricarboxylate)$_2$ (HKUST-1) material is also at the unsaturated copper site with similar Cu-H_2 interaction distances (~2.4 Å), as found in the sodalite-type MOF [5]. The key difference between the two copper-based MOFs is that the maximum enthalpy of adsorption is somewhat lower in the HKUST-1 material compared to the sodalite-like material. We performed a series of inelastic neutron scattering (INS) investigations of hydrogen adsorbed in activated HKUST-1. The distinct inelastic features in the spectra show that there are three binding sites that are progressively populated when the H_2 loading is less than 2.0 H_2:Cu and is consistent with the result obtained from our neutron powder diffraction experiments. The temperature dependence of the INS spectra reveal the relative binding enthalpies for H_2 at each site and compare well with the site-averaged volumetric adsorption values.

Conclusions and Future Directions

Significant efforts have been expended characterizing materials produced by the HSCoE partners. We have used non-destructive elemental analysis, neutron powder diffraction, small-angle neutron scattering, vibrational spectroscopy and quasi-elastic spectroscopy in efforts to understand the fundamental hydrogen-material interactions and identify useful paradigms to extend the hydrogen storage capacity in both amounts and increasing the temperature for adsorption. This work will continue into the coming year. In particular we will:

- Perform neutron scattering measurements on high concentration boron-substituted carbons to identify strongly bound hydrogen.
- Perform additional crystallographic and spectroscopy studies on MOF materials that show promise to the HSCoE or that advance concepts for new hydrogen storage mechanisms.
- Continue efforts to use neutron scattering to probe spillover hydrogen effects and characteristics on HSCoE-produced materials.

FY 2007 Publications/Presentations

1. "Observation of CuII-H_2 Interactions in a Fully-Desolvated, Sodalite-Type Metal-Organic Frameworks," M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, and J. R. Long, *Angewandte Chemie Int. Ed.*, 2007, 46,1419.

2. Neutron diffraction and neutron vibrational spectroscopy studies of hydrogen adsorption in the Prussian Blue analogue $Cu_3[Co(CN)_6]_2$, M. R. Hartman, V. K. Peterson, Y. Liu, S. S. Kaye and J. R. Long, Chem. Mater., 2006, 18, 3221.

3. "Inelastic Neutron Scattering of H_2 Adsorbed in HKUST-1," Y. Liu, C. M. Brown, D. A. Neumann, V. K. Peterson, and C. Kepert, accepted *J. Alloys Compounds*.

4. "Inelastic Neutron Scattering of H_2 Adsorbed on Boron Substituted Single Walled Carbon Nanotubes," Y. Liu, C. M. Brown, J. L. Blackburn, D. A. Neumann, T. Gennett, L. Simpson, P. Parilla, A. C. Dillon and M. J. Heben," accepted *J. Alloys Compounds*.

5. "Hydrogen Storage in a Microporous Metal-Organic Framework with Exposed Mn^{2+} Coordination Sites," M. Dinca, W. S. Han, Y. Liu, A. Dailly, C. M. Brown, and J. R. Long, *J. Am. Chem. Soc.*, 2006, 128, 51, 16876.

6. Neutron powder diffraction study of D_2 sorption in $Cu_3(1,3,5\text{-benzenetricarboxylate})_2$, V. K. Peterson, Y. Liu, C. M. Brown and C. Kepert, J. Am. Chem. Soc., 2006, 128, 15578.

7. C. M. Brown, "Applying Neutron Scattering to the Quest for Hydrogen Storage Materials", ASM Education Series Seminar, Apr. 18th 2007, Oak Ridge, TN.

8. Y. Liu, C. M. Brown, D. A. Neumann, M. Dinca, J. Long, A. Dailly, V. Peterson, C. J. Kepert, "Hydrogen Molecule Binding to Unsaturated Metal Sites in Metal-Organic Frameworks Studied by Neutron Powder Diffraction and Inelastic Neutron Scattering," American Physical Society Meeting, Denver, CO (Mar. 2007).

9. C. M. Brown, Y. Liu, D. A. Neumann, "Understanding Hydrogen Storage Materials through the Use of Neutron Scattering," Dynamics in Molecules and Materials Workshop, Jan 30th-Feb 2nd 2007, Grenoble, France.

10. C. M. Brown, "Applying Neutron Scattering to the Quest for Hydrogen Storage Materials," SNS Seminar, Nov. 17th 2006, Oak Ridge, TN.

11. C. M. Brown," "Applying Neutron Scattering to the Understanding of Potential Hydrogen Storage Materials," ISIS Seminar, Nov. 7th 2006 ISIS, Chilton, OXON, U.K.

12. D. A. Neumann, "Hydrogen Storage and Neutron Scattering at NIST," University of Delaware, Newark, DE, (March 2007).

13. D. A. Neumann, "Hydrogen Storage and Neutron Scattering at NIST," 31st Annual Condensed Matter and Materials Meeting, Wagga Wagga, Australia, (Feb. 2007).

14. D. A. Neumann, "Hydrogen Storage and Neutron Scattering at NIST," Department of Chemistry, University of Sydney, Australia, (Jan. 2007).

15. Y. Liu, C. M. Brown, D. A. Neumann, "Characterization of Hydrogen Structure and Dynamics by Neutron Scattering," Nuclear Science and Engineering Department, MIT, Cambridge, MA (Nov. 2006).

16. Y. Liu, C. M. Brown, D. A. Neumann, M. Dinca, J. R. Long, A. Dailly, "Direct Observation of Hydrogen Binding to Unsaturated Metal Sites in Metal-Organic Frameworks," Material Research Society, Boston, MA (Nov. 2006).

17. C. M. Brown, Y. Liu, D.A. Neumann, V. Peterson, K. Kepert, "Inelastic Neutron Scattering of H_2 Adsorbed in HKUST-1," Metal Hydrides 2006, Oct. 1–6 2006, Kahului, Hawaii.

18. C. M. Brown, Y. Liu, J. L. Blackburn, D. A. Neumann, T. Gennett, L. Simpson, P. Parilla, A. C. Dillon and M. J. Heben, "Inelastic Neutron Scattering of H_2 Adsorbed on Boron Substituted Single Walled Carbon Nanotubes," Metal Hydrides 2006, Oct. 1–6 2006, Kahului, Hawaii.

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