IV.C.1o NIST Center for Neutron Research in Support of the Hydrogen Sorption Center of Excellence (HSCoE)

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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 Storage section (3.3) 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 Center 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

- Determined bulk elemental compositions of materials of interest to the Center. These include metal-decorated carbon-based materials, MOFs, and Boron-infused carbon materials. This understanding helps to speed sample development and material synthesis aimed at reaching the DOE goals of specific energy (1.8 kWh/kg) and energy density (1.3 kWh/L).
- Determined the location of hydrogen binding in several crystalline materials. Provides atomistic understanding of how hydrogen is adsorbed and confirms newly developed theories.
- Illustrated the site-specific hydrogen adsorption strength in MOF materials. The overall appreciation of this determines the isosteric heats of hydrogen adsorption. The size and shape of the Coulomb potential determines inelastic neutron scattering features. Spectra are composed of rotations and multiple rotation-phonon transitions.
- Confirmed that spillover is small for a particular Pt-single-wall nanohorn (SWNH) sample using multiple techniques.

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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

Enhanced Physisorption

NIST and the National Renewable Energy Laboratory (NREL) co-lead this development effort within the HSCoE focused on understanding interactions with metal ions and focuses on the rational synthesis of sorbents that can strongly bind multiple di-hydrogen ligands. Di-hydrogen ligands may be bound to a single metal atom with binding energies in a desirable range for vehicular hydrogen storage. The synthesis of materials that have open, isolated metal sites exhibiting moderate H_2 binding energies, with interactions potentially similar to those observed in Kubas-type complexes, are explored and optimized by the appropriate Cluster members. Key issues are balancing the reactivity of the hydrogen sorption sites with their stability and hydrogen capacity given a 2 bar delivery pressure.

MOFs exhibiting stronger binding interactions are needed to facilitate H_2 adsorption at higher temperatures, and, indeed, a binding energy of 15-20 kJ/mol has been predicted to maximize the amount of adsorbed H_2 accessible at 298 K and up to 20 bar [1]. We have previously used neutron powder diffraction to demonstrate that the highest (at the time) observed maximum isosteric heat of adsorption (10.1 kJ/mol) observed for a MOF was directly related to H_2 binding at coordinatively unsaturated Mn^{2+} centers within a framework [2]. This observation also held for other MOFs with coordinatively unsaturated metal centers (CUMC) of different metal ions [3-5] and also speculation of the Kubas binding nature of the hydrogen [6].

The first evidence for CUMC–H_2 interactions [7] came from low-temperature infrared spectra of a

nanostructured MOF, HKUST-1 [8]. This revealed at least three distinct binding sites with induced red-shifts in the vibrational mode frequencies attributed to site-specific binding energies ranging from (2.5 to 4) kJ mol^{-1} with the molecule undergoing relatively free rotation. Powder neutron diffraction experiments located the hydrogen adsorption sites and conclusively verified that initially D_2 binds to the unsaturated coordination sites of the Cu^{2+}–carboxylate paddle-wheel building units [9], followed by filling of the small cages before the Cu^{2+} site is fully saturated [9,10]. Filling of the larger pores followed along with some structural rearrangement of the dihydrogen molecules in the smaller pore. The distance between the metal and the centroid of nuclear deuterium scattering is 2.39(1) Å, a much-reduced distance from that typical of van der Waals interactions. This interaction should also be compared to the range of M–H distances from ca. 1.7 to 1.9 Å found in the well-known organometallic 'Kubas' compounds where there is evidence for electron donation from the dihydrogen to transition metal and elongation of the H–H bond through back bonding [11].

To address this issue further, we used inelastic neutron scattering (INS) and first-principles computer simulations to gain additional insight into the framework structure of HKUST-1 and to provide a detailed understanding of the local potential of para-hydrogen (p-H_2) adsorbed at the primary metal adsorption site (Figure 1). The form-factors of the three main rotational peaks follow that expected for a free hydrogen molecule with a regular H–H intra-molecular bond distance and provide evidence against a Kubas-type interaction. The form-factors associated with the individual adsorption sites are characterized by differing Debye–Waller factors reflecting the strength of the site-specific adsorption strengths. Based on our calculated potentials using the density functional theory formalism and generalized gradient approximation (GGA) functional, we can assign all the features observed in the INS data for hydrogen adsorbed in HKUST-1 (Table 1). We find that the orientational potential is slightly two-dimensional and dominated by a small Coulombic term, hence there is a tendency for the H_2 to lie in a plane perpendicular to the Cu–Cu bond. The in-plane rotation is almost free and unhindered. The features observed at 9.1, 12.75 and 14.0 meV with increasing H_2 loading are due to rotational transitions from J = 0 to 1, M = ±1. The other features observed in the data are due to rotation-rotation or rotation-phonon excitations.

Engineered Nanospace

Although the crystal structures of MOFs are typically composed of rigid frameworks, they can demonstrate significant structural distortions upon adsorption/desorption of guest molecules. An extreme aspect of this type of distortion occurs as a "breathing"
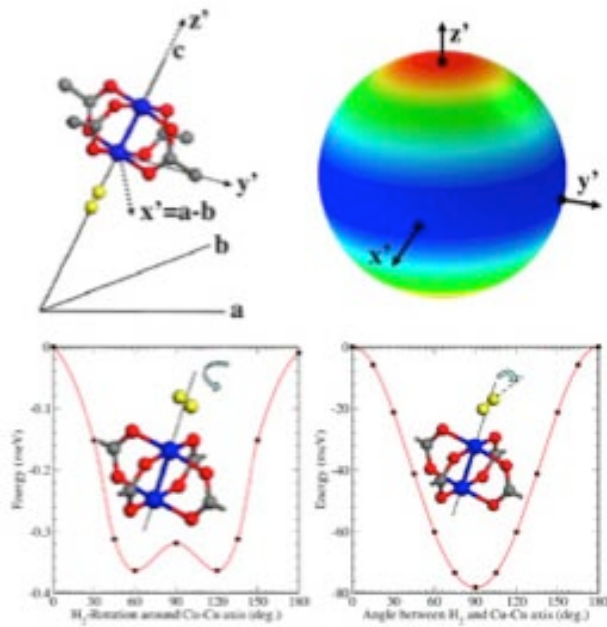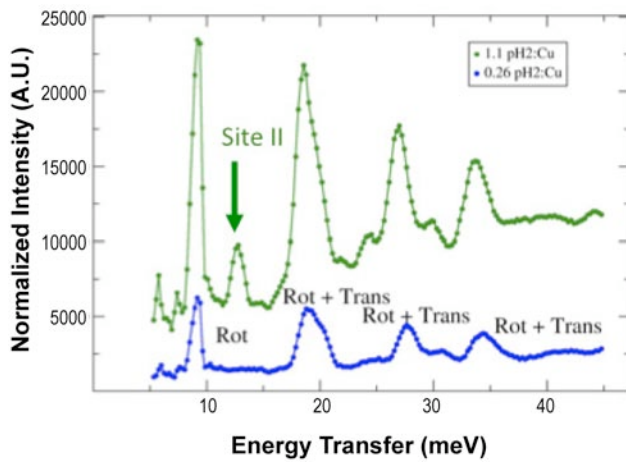
TABLE 1. Orientational potential obtained from GGA calculations and the corresponding rotational levels. The calculated classical harmonic H_2 phonons for a fixed H_2 orientation perpendicular to the Cu-Cu bond are $\omega(x') = 9.56$ meV, $\omega(y') = 13.44$ meV and $\omega(z') = 22.87$ meV. The coupling of phonons with rotational transitions explains the observed INS spectra.

H_2 rotational levels for an orientational potential: $V(\Omega) = V_0 + \sum_{lm} A_{lm} Y_{lm}(\Omega)$ $V_0 = -53.3$ meV, $A_{20} = 82.0$ meV, $A_{22} = 0.2$ meV, $A_{40} = 3.0$ meV, $A_{60} = 1.0$ meV			
State #	Energy (meV)	$E_i - E_0$ (meV)	Major JM
0	-61.47	0	J=0, M=0
1	-51.85	9.61	J=1, M=+/-1
2	-51.71	9.76	J=1, M=-/+1
3	-25.39	36.08	J=2, M=+/-2
4	-25.39	36.08	J=2, M=-/+2
5	-24.20	37.27	J=1, M=0

FIGURE 1. (Upper) Difference inelastic neutron scattering spectra of p-H_2 loaded HKUST-1 and the bare substrate measured on FANS. The displayed spectra result from p-H_2 scattering only and peaks of significant intensity are labeled as either rotations (Rot) or combination rotation and transition (Trans). Ratios of p-H_2 to copper are 0.26 (blue circles, adsorption at Cu site only) and 1.1 (green circles, adsorption at Cu site and 2nd site). (Lower) The orientational potential of H_2 located at the (x,x,0) adsorption site in HKUST-1. Top-left panel shows the primitive lattice vectors (a,b,c) and the local coordinate system (x',y',z') which was taken to describe the H_2-orientation. Top-right panel shows the contour-plot of the potential mapped on a sphere representing the H_2-orientation θ-ϕ. The potential maximum is at θ = 0° (H_2 parallel to z-axis) (z'-pole(red), zero of energy) and the potential minimum is at the θ = 90° (x'-y' plane (blue), -78 meV). The left-bottom panel shows how the potential changes as the H_2-molecule is rotated around Cu-Cu axis. The right-bottom panel shows the variation of the potential with θ for fixed ϕ = 0.

the applicability of this mechanism to achieving the hydrogen storage goals associated with developing high specific surface area materials with optimized pore geometries.

The coarsely defined hysteresis of MIL-53(Al) observed under varying temperature [12] was better defined using synchrotron X-ray radiation. We further undertook several neutron studies aimed at describing the adsorbed hydrogen structures not only at low temperatures (4 K), but also through a complete hydrogen adsorption/desorption isotherm at 77 K. At low loading the hydrogen resides in the residual open-pored phase and gradually forces open the closed-pores upon further adsorption with multiple adsorption sites being occupied to saturation. Upon desorption, there comes a situation where there is no residual pressure in the system, but the framework traps ≈1 wt% of the hydrogen in the closed-pores. The H_2 remains in closed pore even when pumping under high vacuum to well over 100 K (Figure 2).

Substituted Materials

NIST has contributed to the efforts of developing materials with high concentrations of substituted atoms (e.g., B on graphene structures) using non-destructive bulk elemental determination from prompt-gamma activation analysis (PGAA) of Center synthesized samples. The results of the PGAA analysis has been successful in steering synthetic approaches of the Center members interested in optimizing the dopant contents of micro- and nano-porous carbons. Continued efforts in small-angle neutron scattering and INS measurements on nano-porous carbons have been used to gain insights into the morphology of the pore structure and how hydrogen is adsorbed into these materials with several Center members (Blackburn, NREL; Ahn, Caltech;
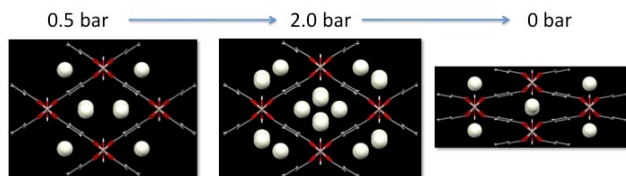
effect that is typically associated with a large change of the internal pore volume. Last year's report detailed our initial results on the MIL-53 system (collaboration with General Motors Corporation) aimed at evaluating

0.5 bar ⟶ 2.0 bar ⟶ 0 bar

FIGURE 2. Sequential adsorption of D_2 in MIL-53 at 77 K. D_2 (0.5 bar) initially occupies the un-transformed open-pore crystal phase and gradually forces open the majority closed-pore phase (2 bar). The D_2 adsorption sites are saturated at ≈4 bar D_2 pressure after which we reduce the pressure also whilst monitoring the neutron powder diffraction patterns. The natural tendency for the framework to 'close' at 77 K results in some trapping of the hydrogen that is then difficult to remove without extensive heating and application of high-vacuum.

Pfeiffer, University of Missouri). Detailed INS of the hydrogen rotational spectra in BC_8 materials prepared by NREL showed similar characteristics compared to a similarly prepared carbon material though the hydrogen is more apparently rotationally hindered through the entire adsorption range in BC_8 than for the pure carbon. However, desorption studies with temperature, indicate that both materials retain similar amount of hydrogen between 60 K and 85 K.

Spillover Materials

NIST has continued efforts to indentify the final state of spillover hydrogen in several Center produced materials, though clear results have been elusive. Parallel efforts to use gas adsorption apparatus to produce a one shot determination of spillover amounts have been successful, with the observation of ≈ 0.08 wt% hydrogen spillover in a Pt-SWNH (Oak Ridge National Laboratory) sample, that corresponds well to the 0.17 wt% determined from INS on the same sample (previously measured by us). Additionally, we have working with collaborators from Monash University (Australia) to attempt to observe the spillover and general hydrogen dynamics in zeolites-templated microporous carbons. Despite several attempts at synthesis and platinum incorporation, the isosteric heat of adsorption for hydrogen remains around 7 kJ/mol with no additional indicators from spillover apparent. Apparently, the pore structures in the templated carbon are such that the INS of the hydrogen spectra are broad and liquid-like and there seems to be two types of hydrogen diffusing on two different timescales at 77 K as determined by quasi-elastic neutron scattering. Further work is needed to fully understand these developments.

Conclusions and Future Directions

The main conclusions of this years work can be summarized as follows:

- Determined that open metal centers in MOF materials do not exhibit to any H-H bond elongation upon adsorption and hence are not Kubas-type complexes.
- Determined the temperature dependence of the structural transition in a flexible framework material, MIL-53 with precision.
- Determined the structural dependence of MIL-53 throughout the isotherm cycle and that the natural tendency for the framework to close at 77 K causes some trapping of ≈1 wt% hydrogen.
- Determined characteristic rotational spectra with adsorption for several nano-porous substituted and pure carbon materials.
- Zeolite-templated carbons exhibit liquid like hydrogen recoil, even at low coverage, and there are two timescales for hydrogen diffusion at 77 K.

Currently, only a few MOFs exhibit the capacity to adsorb multiple H_2 per metal center. We will look at the most promising materials that could exhibit this behavior to determine the viability of this approach given the non Kubas-type adsorption we have observed. We will continue to aid the other Center partners in characterizing their materials aiming to understand the fundamental characteristics that improve hydrogen storage capabilities.

Special Recognitions & Awards/Patents Issued

1. Jae-Hyuk Her: winner of the 2009 Sigma-Xi NIST Chapter Postdoctoral Poster Prize.

FY 2009 Publications/Presentations

Publications

1. *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. Kepert, Nanotechnology (Accepted 2009).

2. *Adsorption and melting of hydrogen in potassium-intercalated graphite*, J. Purewal, J.B. Kieth, C.C. Ahn, B. Fultz, C.M. Brown and M. Tyagi, Phys. Rev. B 79, 054305 (2009).

3. C.M. Brown, Y. Liu, H. Kabbour, D.A. Neumann, and C.C. Ahn, "Denser than Solid Hydrogen: Improving Hydrogen Storage," in *2008 NIST Center for Neutron Research Accomplishments and Opportunities, NIST Special Publication 1089 (R.L. Cappelletti, ed.), U.S. Government Printing Office, Washington, D.C., p. 30 (2008).*

4. *High Capacity Hydrogen Adsorption in Cu(II) Tetracarboxylate Framework Materials: The Role of Pore Size, Ligand Functionalization, and Exposed Metal Sites*, X. Lin, I. Telepeni, A.J. Blake, A. Dailly, C.M. Brown, J. Simmons, M. Zoppi, G.S. Walker, K.M. Thomas, T.J. Mays, P. Hubberstey, N.R. Champness and M. Schroder, J. Am. Chem. Soc. 2009, 131, 2159.

5. *Detection of Hydrogen Spillover in Palladium-Modified Activated Carbon Fibers During Hydrogen Adsorption*, C.I. Contescu, C.M. Brown, Y. Liu, V.V. Bhat and C. Gallego, J. Phys. Chem. 2009, 113, 5886.

6. *Hydrogen Adsorption in a Highly Stable Porous Rare-Earth Metal-Organic Framework: Sorption Properties and Neutron Diffraction Studies*, J. Luo, H. Xu, Y. Liu, Y. Zhou, L.L. Daemen, C.M. Brown, T.V. Timofeeva, S. Ma and H.-C. Zhou, J. Am. Chem. Soc. 2008, 130, 9626.

7. *A reversible structural transition of MIL-53 with temperature hysteresis*, Y. Liu, J.-H. Her, A. Dailly, A.J. Ramirez-Cuesta, D.A. Neumann and C.M. Brown, J. Am. Chem. Soc. 2008, 130, 11813 .

8. *Quasielastic neutron scattering experiments of orthorhombic ammonia borane*, N.J. Hess, M.R. Hartman, C.M. Brown, E. Mamontov, A. Karkamkar, D.J. Heldebrant, L.L. Daemen, and T. Autrey, Chem. Phys. Letts. 2008, 259, 85.

9. *Hydrogen Storage on Ordered Microporous Carbon Molecular Sieves Containing Dispersed Platinum Nanoparticles*, Y. Yang, J. Schalch, Y. Liu, J.-H. Her, J. Simmons, C.M. Brown, P.A. Webley A.L. Chaffee, American Chemical Society National Meeting, Philadelphia, ACS Division of Fuel Chemistry, Preprints, vol. 53(2), (2008).

10. *Hydrogen Adsorption in MOF-74 Studied by Inelastic Neutron Scattering*, Y. Liu, C.M. Brown, D.A. Neumann, H. Kabbour, and C.C. Ahn, in Life Cycle Analysis for New Energy Conversion and Storage Systems, edited by V.M. Fthenakis, A.C. Dillon, and N. Savage (Mater. Res. Soc. Symp. Proc. Volume 1041E, Warrendale, PA, 2008), 1040-R2_03.

11. *Neutron Powder Diffraction of Metal-Organic Frameworks for Hydrogen Storage*, C.M. Brown, Y. Liu and D.A. Neumann, PRAMANA J. Physics 2008, 71, 755.

Presentations

1. C.M. Brown, "From metal hydrides to physisorbed H_2-systems: what we are learning with neutrons", Metal Hydrogen-Metal Systems Gordon Conference, July 2009, Lucca, Italy. *Invited*

2. J.-H. Her, Y. Liu, C.M. Brown, M. Yousufuddin, T.J. Udovic, and D.A. Neumann, "Structural Studies on Various hydrogen Storage Materials: MIL-53, $K_2Zn_3[FE(CN)_6]_2$ and $LI_2B_{12}H_{12}$" named Outstanding Poster Presentation in Materials category at the 16th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD, Feb. 2009.

3. J.-H. Her, " Structural Studies of MIL-53, A Potential H2 Storage Material, as a Function of Temperature and Gas Loading.", American Conference on Neutron Scattering, Santa Fe, 2008.

4. Y. Liu, "Hydrogen adsorption properties in metal-organic frameworks", Department of Physics, The Chinese University of Hong Kong, Hong Kong, China, Feb. 2009.

5. Y. Liu, "Probing Hydrogen in Storage Materials Using Neutron Scattering Techniques", The 2nd US-China Workshop on Scientific & Industrial Applications Using Neutron, Muons & Protons, 2008, Dongguan City, Guangdong Province, China, Nov. 2008. *Invited*

6. Y. Liu, "Applications of Neutron Scattering Techniques for Materials Science Research", Institute of Chemistry, Chinese Academy of Science, China, Nov. 2008. *Invited*

7. D.A. Neumann, "Hydrogen storage and neutron scattering at NIST", Caltech, Pasadena, CA, Feb. 2009.

8. J.-H. Her, "Powder diffraction studies of hydrogen storage materials", HANARO, Korea Atomic Energy Research Institute, July 2009.

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11. G.J. Kubas, *Chem. Rev*., **2007**, 107, 4152.

12. Y. Liu, J.-H. Her, A. Dailly, A.J. Ramirez-Cuesta, D.A. Neumann and C.M. Brown, *J. Am. Chem. Soc*. **2008**, 130, 11813.