DOE Hydrogen Program

Neutron Characterization in support of the Hydrogen Sorption Center of Excellence

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NIST

National Institute of Standards and Technology

Technology Administration, U.S. Department of Commerce

STP-1

Overview

Timeline

- Project start FY05
- Project end FY09
- 50% complete

Barriers

- Barriers addressed

  Characterization of Hydrogen Physisorption and Chemisorption

Budget

- FY06 $208k
- FY07 $216k
- $FY08_{(req)}$ $225k

NIST has provided over 420 instrument days to date and 2 FTE's/year for the Hydrogen Sorption and MH COEs

Partners

- **HS Center**

  NREL, ORNL, LLNL, Penn State, Duke, CalTech…

- **External**

  UC Berkeley, U. Sydney, Miami University, General Motors

Objectives

Overall: Support the development of hydrogen storage materials by providing timely, comprehensive characterization of Center-developed materials and storage systems using neutron methods. Use this information to speed the rational development and optimization of hydrogen storage materials that can be used to meet the 2010 DOE system goal of 6 wt% and 45 g/L capacities..

- Characterize structures, compositions and adsorption/absorption site interaction potentials for hydrogen in/on several candidate materials.

- **We contribute within the Center and with universities/type-IIs if it furthers the Center goals.**

NIST

Approach

- **Neutron methods:**
  - Elemental compositions of the materials
  - Location and bonding of hydrogen
  - Adsorption sites and binding strength
  - High pressure hydrogen conditions
  - Diffusion mechanisms

NIST

Technical Accomplishment

Non-destructive element analysis with neutrons – characterizing materials from precursors to functional materials

- Boron doped carbons (Penn. State, Mike Chung (plus 5 other samples)

Mass Ratio	B/C	H/C	Cl/C
Sample 1	8.2(9)%	2.0(2)%	0.30(4)%
Sample 2	6.9(2)%	1.9(1)%	51(2)%

- Pt decorated nanohorns (ORNL, new samples)

Before degassing

Mass Ratio	Pt/C	B/C	H/C	Cl/C
O-SWNHs/Pt-CH	20(1)%	0.057(5)%	4.9(4)%	3.1(2)%

After degassing

Mass Ratio	Pt/C	B/C	H/C	Cl/C
O-SWNHs/Pt-CH	21.1(8)%	0.061(3)%	0.159(8)%	1.9(1)%
SWNHs/Pt-LA	17.5(2)%	0.125(2)%	0.271(4)%	N/A

- Pt decorated SWNT (Duke)

Mass Ratio	Pt/C
Pt-SWNT	0.17(1)%

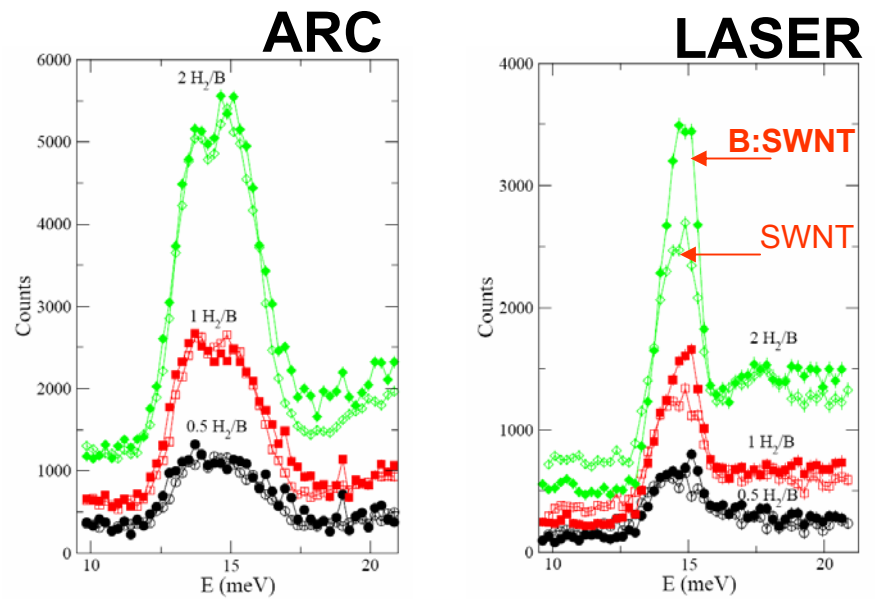
- Parameterize various stage of production for materials of interests to partners.

Technical Accomplishment

Effects of boron substitution on the hydrogen rotational spectrum

- Completed neutron measurements on low B content nanotubes (Blackburn, NREL) *These samples did not show significantly enhanced adsorption (theory predicted) compared to the pristine carbon materials*

- Strong indications that the split rotational peak in arc-produced samples originates from low concentration ***DEFECTS*** and are not intrinsic to the pristine tube/bundle structures.



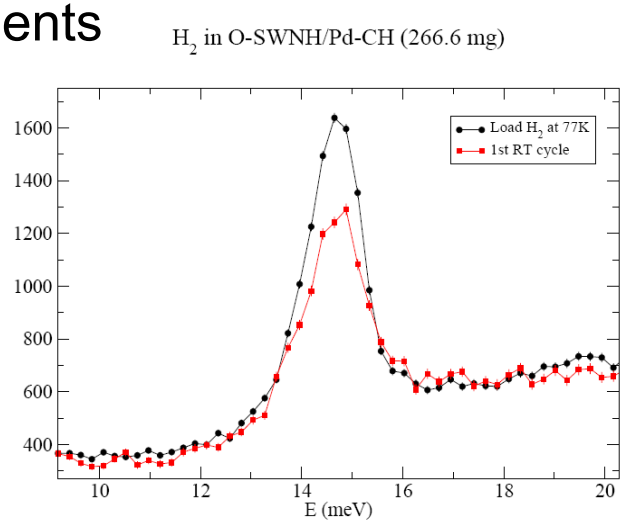
- Using neutrons to probe the hydrogen-substrate interactions (directed by theory).

Technical Accomplishment

Searching for signatures of hydrogen spillover in Pd and Pt-decorated nanohorns (ORNL)

- High incident energy neutron experiments
  - -Inconclusive measurements searching for C-H modes
    - *-Guidance based upon calculations from center theory partners.*
  - -Repeated room temperature cycling experiments
  - -Cycled to 150 K

- TPD experiments with NREL (Blackburn, NREL)
- Repeated performed H_2 isotherm experiments (NIST)



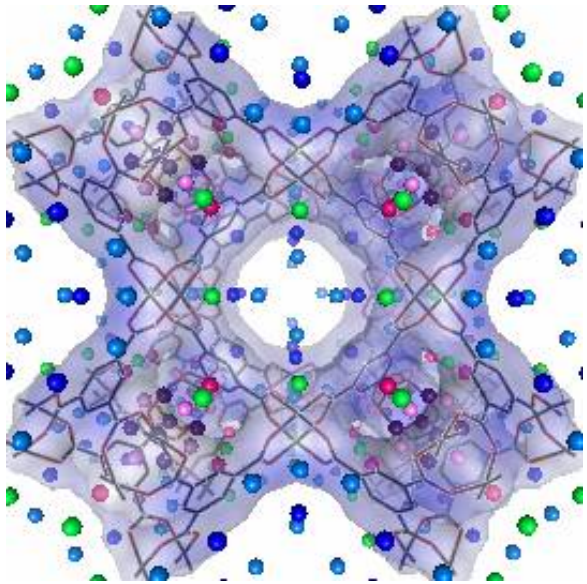
- Using neutrons to probe the hydrogen-substrate interactions (directed by theory).
- Volumetrically, about 0.1 wt.% Hydrogen spills over at room temperature.

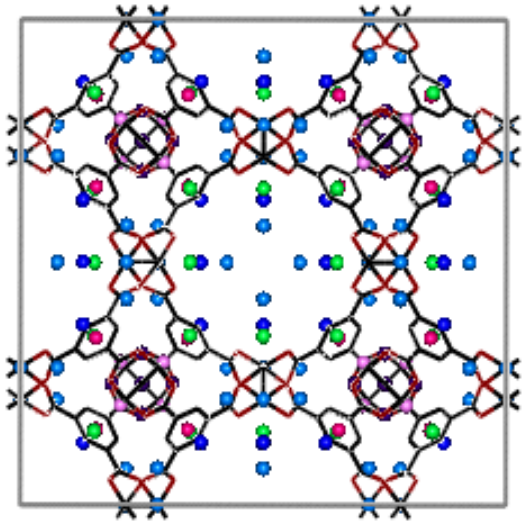
Technical Accomplishment

Metal-hydrogen interactions

- **Cu based HKUST-1 (Kepert, U. Sydney, A.U.)**

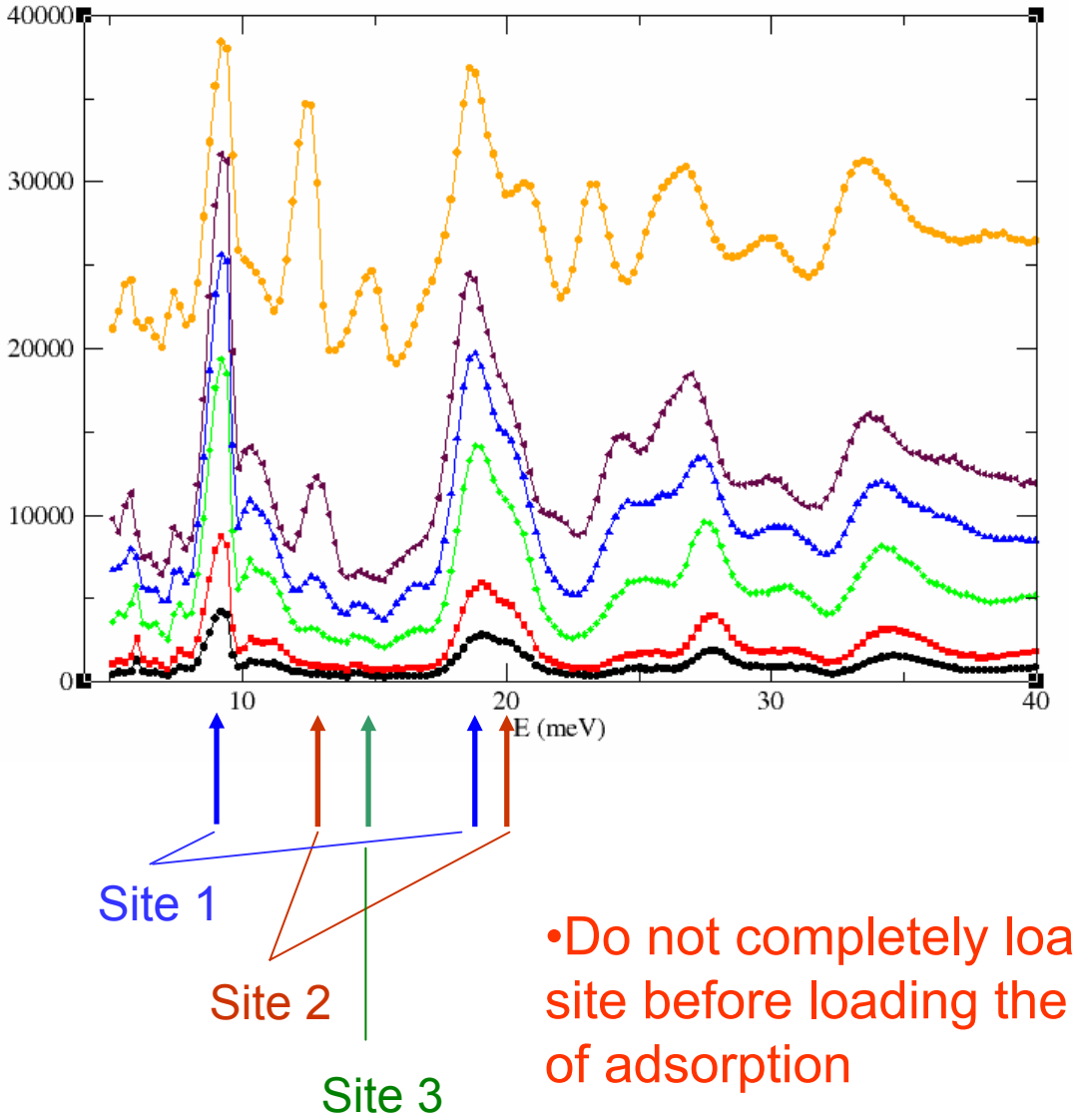
- We can attribute high initial enthalpies of adsorption to the interaction of hydrogen with open metal centers.





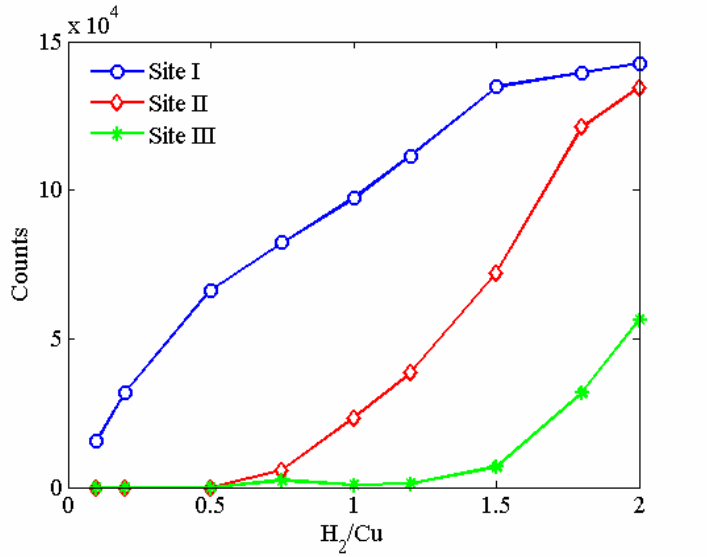
- UNIQUE technique: located 6 hydrogen adsorption sites in HKUST-1
- Hydrogen adsorption occurs in order of
  - open copper site > small 5 Å pore > 5 Å pore window > large ~10 Å pore

Technical Accomplishment



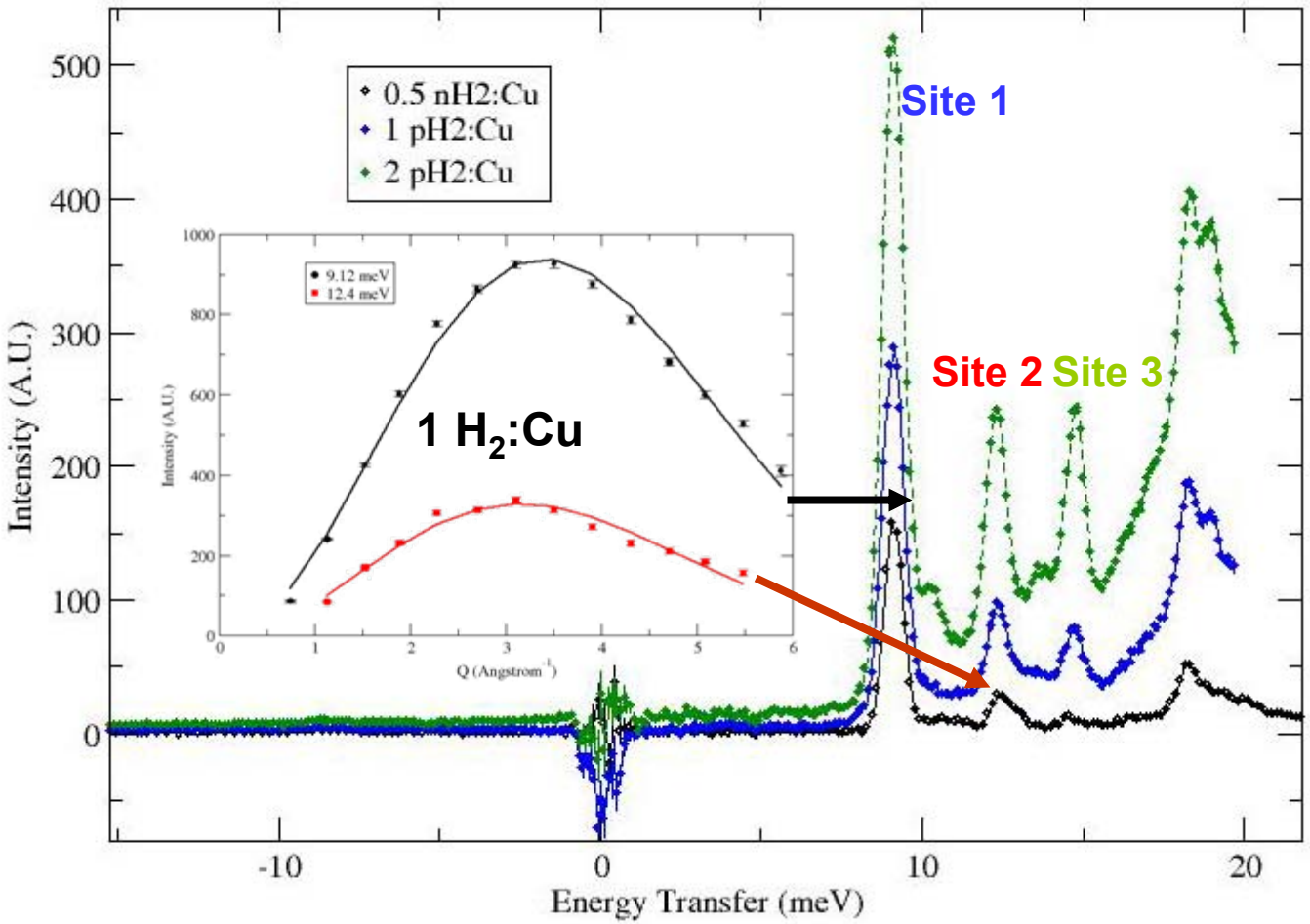
-Rotational spectrum of hydrogen is easily measured by neutrons.
-The large peak downshift from 14.7 meV indicating stronger binding.

Monitor peaks with loading…



•Do not completely load the strongest adsorption site before loading the next strongest. Atomistic view of adsorption

Technical Accomplishment



- Momentum transfer dependence of peaks indicate NO lengthening of H-H bond upon adsorption
  - Not a Kubas-type binding with strong back-bonding

Technical Accomplishment

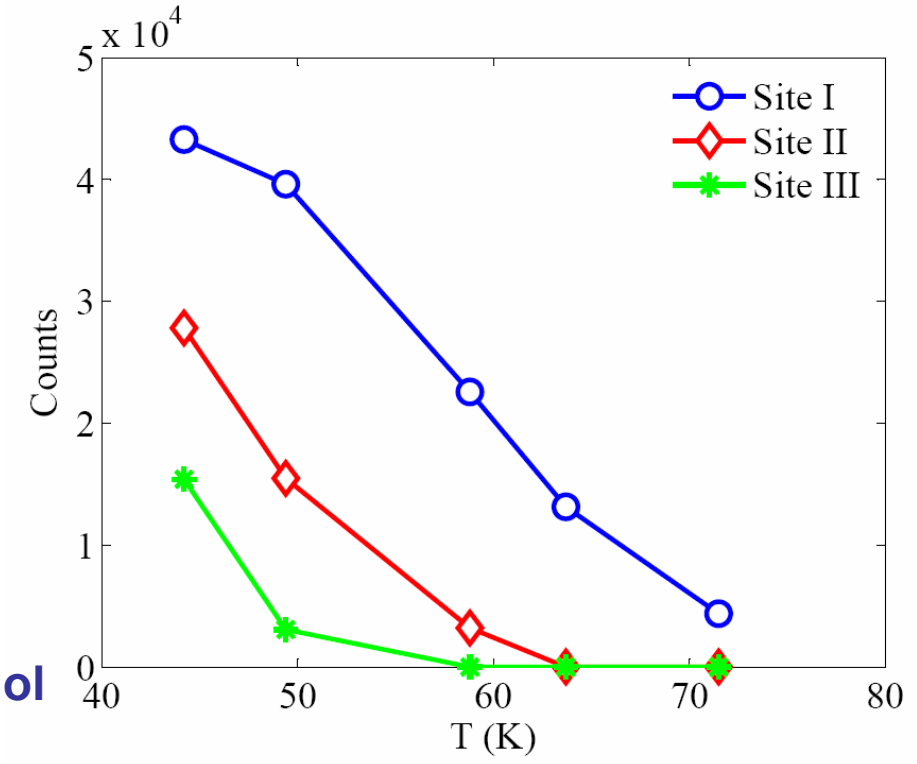
Boil off temperatures → approximate binding enthalpy

Expt. performed by heating sample to known temperature, applying vacuum for ~30 minutes and cooling back to base.

Thermal factors for peak intensities are directly comparable to each other.

There may be site redistribution, but in general, the weakest bound hydrogen boil off first, the strongest last.

Site 1 binding in the range 6 to 10 kJ/mol
Site 2 similar to nanotubes ~5 kJ/mol
Site 3 < 5 kJ/mol



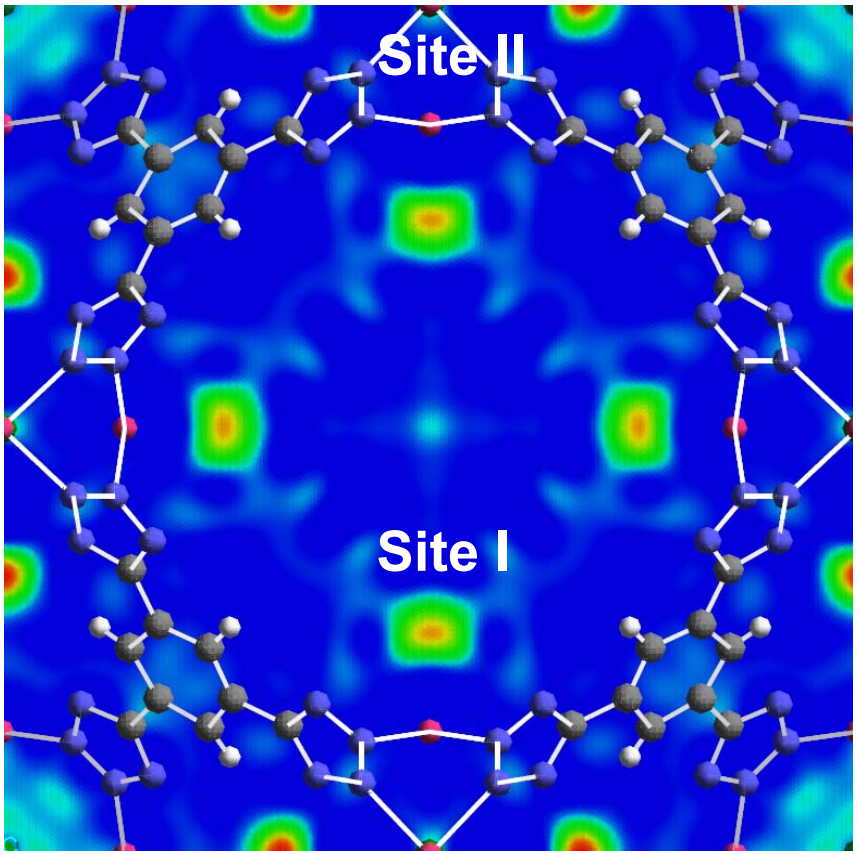
•The technique is not restricted by sample environment and is simpler to interpret than possible optical spectroscopies.

Technical Accomplishment

Metal-hydrogen interactions

– Mn and Cu based tris-tetrazoles (Long, U.C. Berkeley)

10.1 kJmol^{-1}
5.1 wt% excess



D_2 loading Per formula unit	Refinement
6	6.3
12	13.2
24	23.5

Fourier difference scattering-length intensity in the basal plane superimposed with crystal structure to indicate the first two D_2 adsorption sites (red-yellow-green regions).

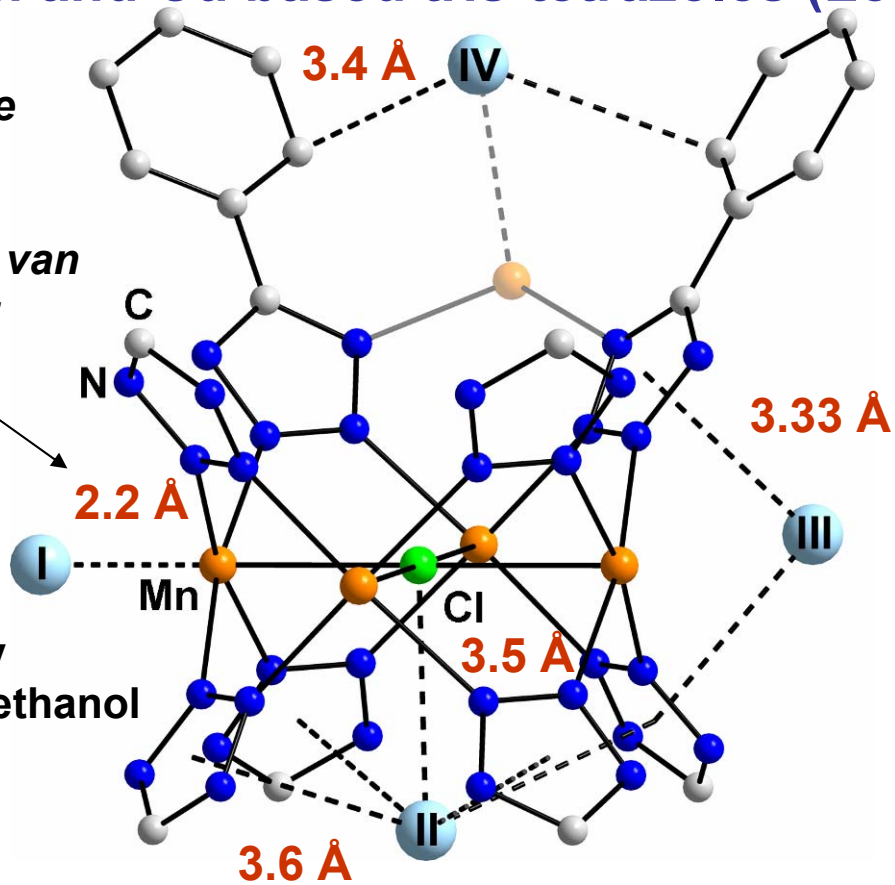
•Determine atomic adsorption sites for molecular hydrogen

Technical Accomplishment

Metal-hydrogen interactions

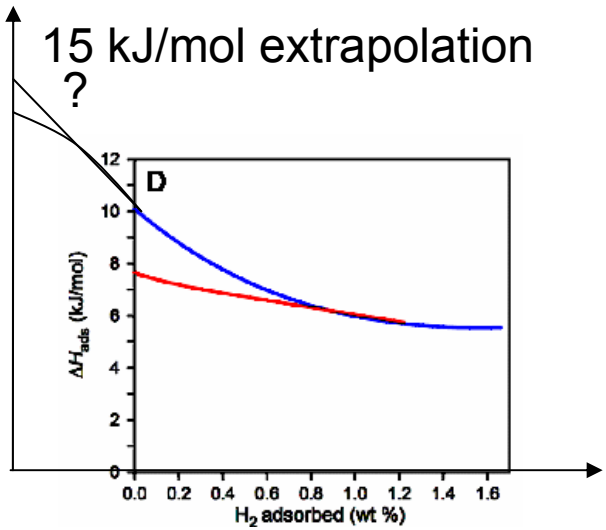
– Mn and Cu based tris-tetrazoles (Long, U.C. Berkeley)

Short distance indicates interactions stronger then van der Waals but weaker than 'Kubas'.



Site 1 partially blocked by methanol ~ 0.5 wt%

10.1 kJmol^{-1}
5.1 wt% excess



- Can we approach ~15 kJ/mol experimentally by exposing more unsaturated metals in MOFs?
- From structure → theory can be used to investigate interactions

Future Work

Remainder of FY 2007:

Continue neutron scattering studies of various adsorbate systems

- Complete analysis of remaining neutron spectroscopy data.
- Expand characterizations to LANL aerogels (samples in hand)
- Initialize characterization of new high adsorption capacity MOFs
- Submit a report on key developments using neutrons to the Steering Committee.

FY 2008:

- Studies aimed at understanding the role of different types of metals and linkers in MOFs. Characterize the dynamics of H_2 strongly interacting with metal sites. Relationships to Kubas-type? →Theory
- Provide thermodynamic measurements of in-situ hydrogen diffusion in select materials of interest to the Center.
- Macroscopic diffusion using neutron imaging when good candidate materials are available (a unique technique)

Summary

Neutron methods provide crucial, non-destructive characterization tools for the Hydrogen Sorption Center of Excellence

Determined that high initial enthalpy of H_2 adsorption arises from interactions with unsaturated metal centers in select MOFs;

- a route to higher temperature adsorption?
- Open questions concerning the type of bonding.

For (B)SWNT, defects give rise to the previously observed hydrogen spectra and it is likely not due to the pristine tube/bundle structures

Volumetric measurements of spillover in Pt-nanohorns ~0.1 wt% H_2