Neutron Characterization in support of the Hydrogen Sorption Center of Excellence

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STP6

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Overview

Timeline

- Project start FY05
- Project end FY09
- 70% complete

Budget

FY	HSCoE	MHCoE
FY05	$130K	$125K
FY06	$208K	$156K
FY07	$216K	$276K
FY08	$225K	$287K

NIST continues to provide access to neutron facilities and FTEs for the HSCoE and MHCoE

Barriers

- Barriers addressed

  Characterization of Hydrogen Physisorption and Chemisorption

Partners

- **HS Center**

  Cal Tech, NREL, ORNL, LLNL, Penn State, U. Miami

- **External**

  UC Berkeley, U. Sydney, Monash Uni., Uni. Nottingham, 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..

- Provide Calphad calculations of phase relationships of potentially promising hydrides. (MHCoE only)

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

NIST

Milestones

NIST

Detailed neutron studies in support of the Center's go/no-go analysis

Month/Year	Milestone or Go/No-Go Decision
Apr-07	Milestone: Evaluate structural and bonding properties of new materials selected through discussions with the leadership of the Center. Formation of Research Clusters to focus team efforts on specific targets.
Sep-07	Milestone: A thorough analysis as needed of the materials that are the most promising in terms of meeting the Phase 1 go/no-go decisions. Formalizing of Research cluster directions. (Continuing interest in, e.g., carbon nanohorns, metal decorated systems, MOFs)
Apr-08	Milestone: Evaluate structural and bonding properties of new materials selected through discussions with the leadership of the Center. Current systems of interest are MOFs with unsaturated metal centers, 'breathing' MOFs for kinetically hindered storage, materials capable of generating higher enthalpy and multiple binding sites.
Sep-08	Milestone: A thorough analysis as needed of the materials that have favorably passed the Phase 1 go/no-go decisions and show the most promise of achieving the DOE 2010 targets (e.g., other carbon-based materials and MOFs).

Approach

- **Neutron methods**
  - –determine elemental compositions of materials (prompt-γ activation analysis)
  - –determine location of H and crystal structures of materials (neutron diffraction superior to XRD for locating light elements)
  - –determine bonding of absorbed H (unlike IR and Raman, neutron vibrational spectroscopy “sees” all H vibrations for straightforward comparison with first-principles calculations)
  - –elucidate H diffusion mechanisms (faster dynamics timescale of neutron quasielastic scattering complements NMR; transport mechanisms gleaned from momentum transfer dependence. Has not been used extensively in this project)

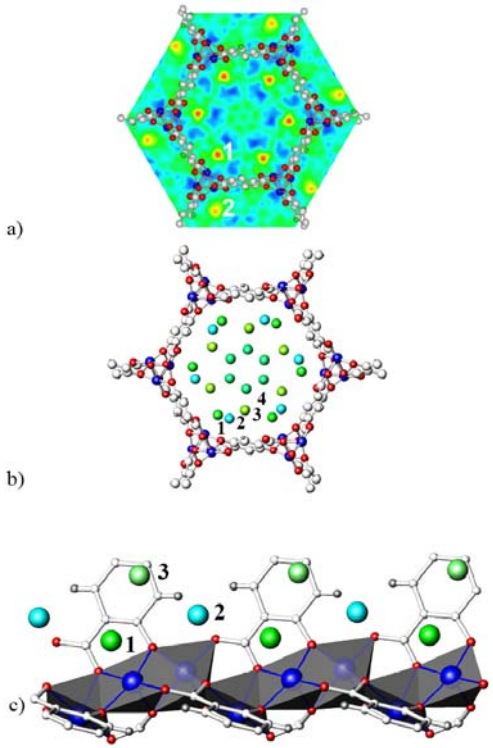
NIST

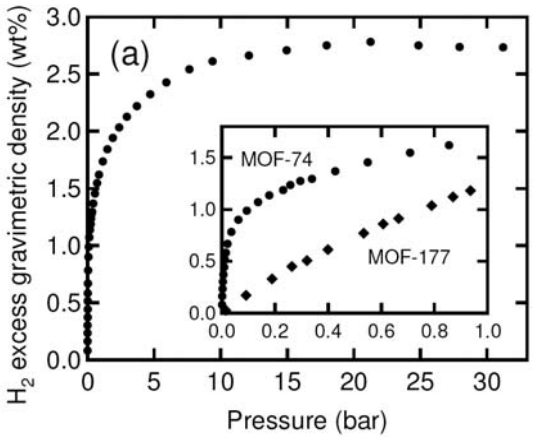
Technical Accomplishment

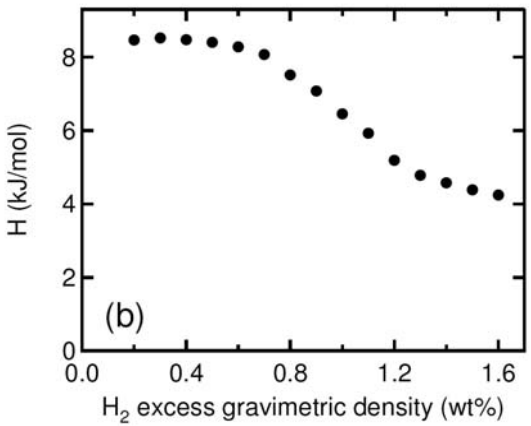
Increasing the density of adsorbed Hydrogen

– **Zn based MOF-74 (Ahn, Cal Tech)**

- We can attribute high initial enthalpies of adsorption to the interaction of hydrogen with CUMCs (Coordinatively Unsaturated Metal Centers) (Zn-H_2 2.6 Å).
- First observation of denser than hydrogen monolayer!







- Site 1 to 2: ~ 2.9 Å
- Site 1 to 3: ~ 2.85 Å

(Nearest neighbor distance of solid D_2: ~ 3.6 Å)

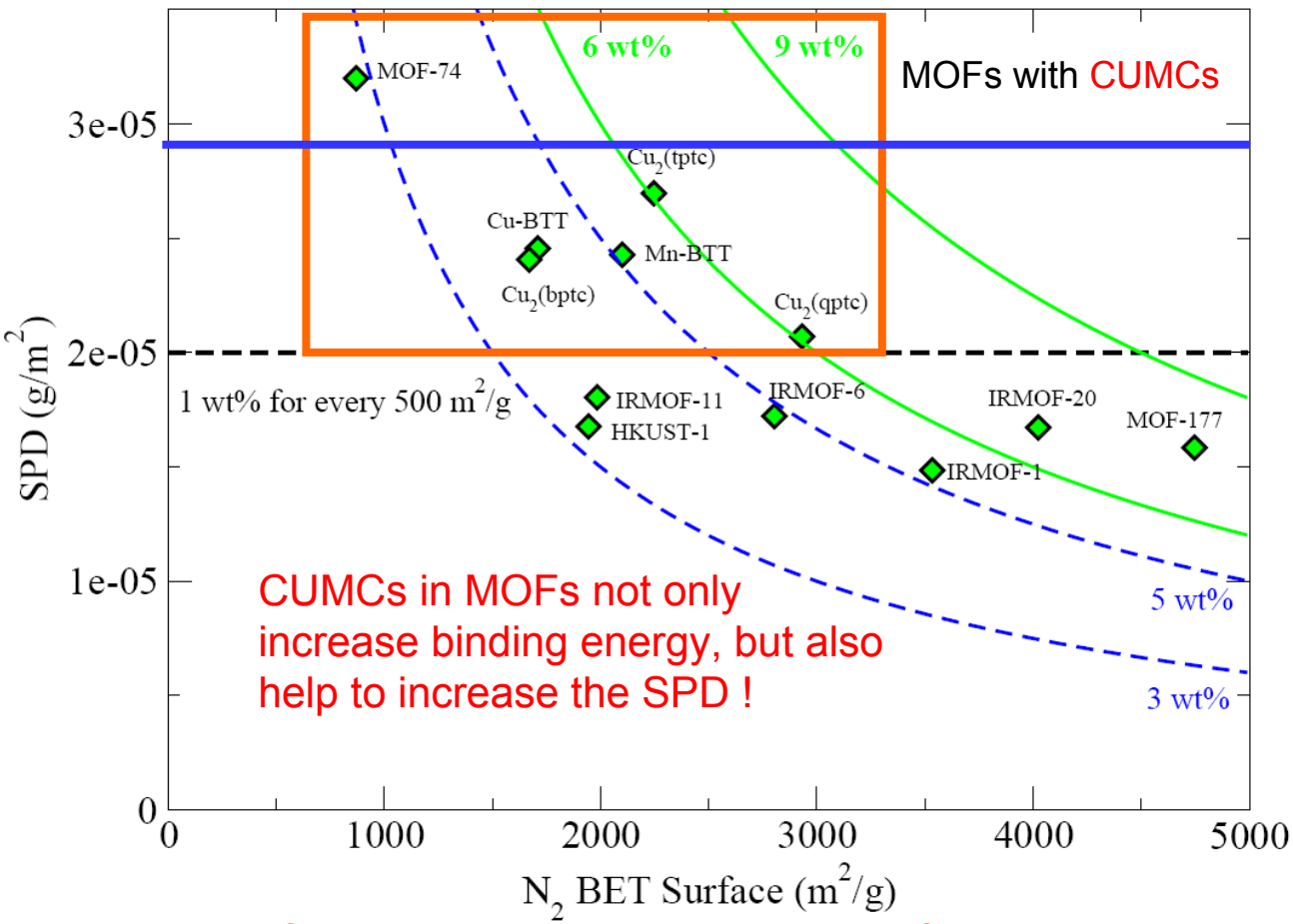
Liu et al., Langmuir (2008) online

- UNIQUE technique: located 4 adsorption sites in MOF-74
- Inelastic neutron scattering indicates no elongation of H-H bond: not 'Kubas'

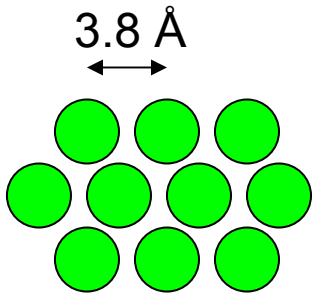
Technical Accomplishment

Increasing the density of adsorbed Hydrogen

$$\text{SPD} \approx \frac{\text{Saturation Excess Adsorption}}{\text{BET Surface Area}}$$



SPD:~2.8×10^{-5} g/m^2



Nearest neighbor distance of solid H_2 : 3.8 Å.

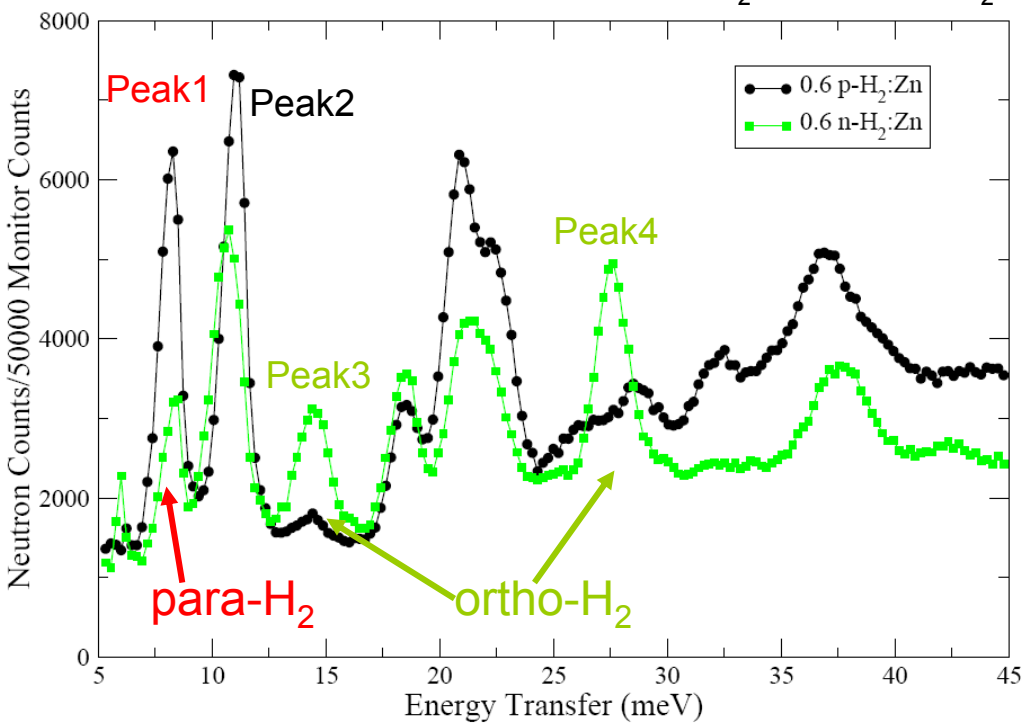
Liu et al., Langmuir (2008) online

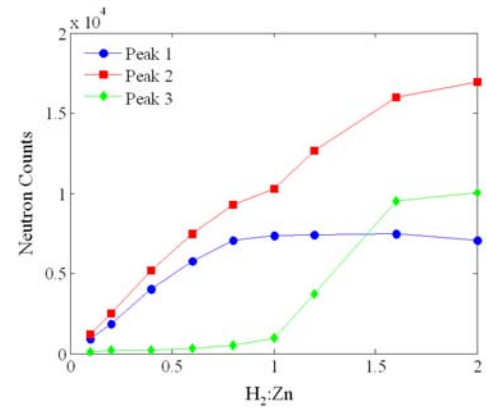
- Density of hydrogen adsorbed at surface greater than in solid H_2!

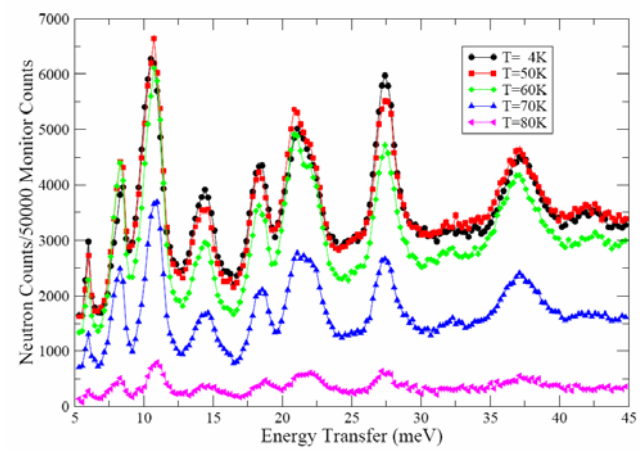
Technical Accomplishment

Hydrogen binding in MOF-74

p-H_2: pure para-H_2
n-H_2: 75% ortho-H_2







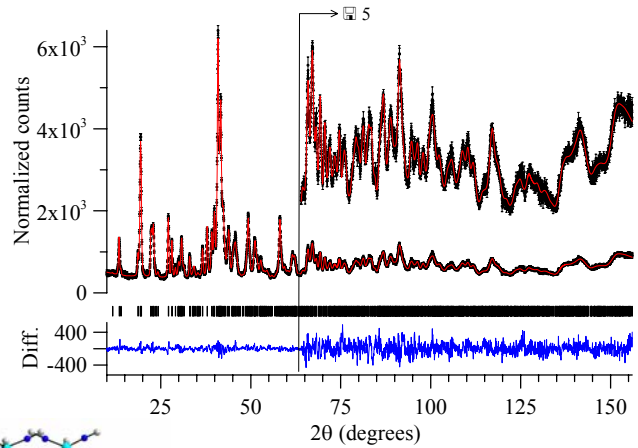
Liu et al., MRS proc. (2008)

- Zn site is first fully populated before other weaker binding sites are occupied
- Hydrogen molecules at the Zn sites are still very strongly bound at 60 K
- Temperature dependence shows binding strength of *ortho* and *para* H_2 are similar

Technical Accomplishment

Metal-hydrogen interactions

– **Alkali Metal Iron Cyanides (Long, U.C. Berkeley)**



Qst = 9->8 kJmol^{-1} 1.2 wt% @ 1atm

Kaye Chem. Comm. 486 (2007) [prior work]

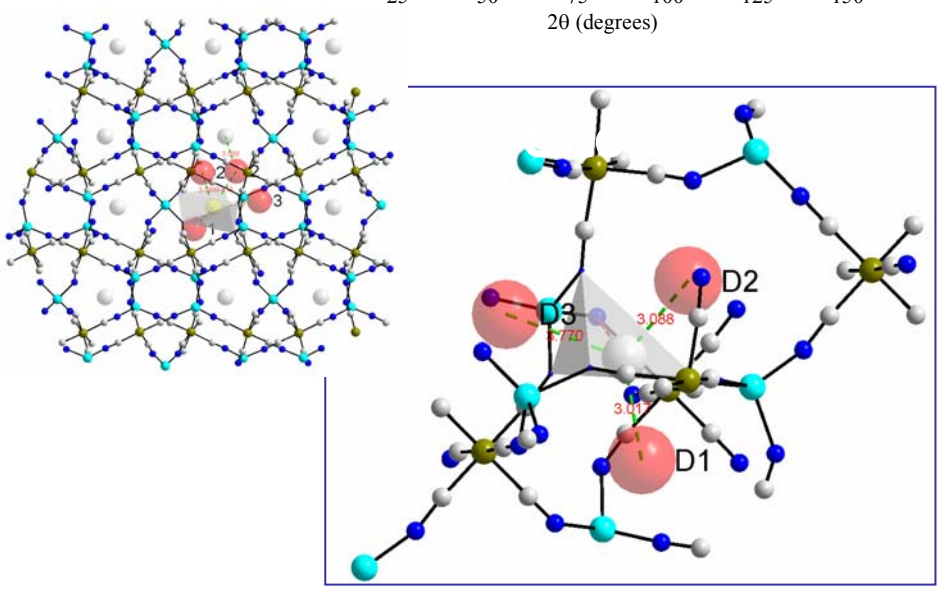
Upon desolvation, *R-3c* → *C2/c*

Structure solved using simulated annealing

K^+ in center of pore, coordinated by 5 nearest N of cyano-group, (ave. dist. = 3.03 Å) forming strongly distorted pyramidal structure.

3 Deuterium sites close to the K+ ion (3.02 Å, 3.1 Å to 3.41 Å, 3.77 Å)

Other pores unfilled!

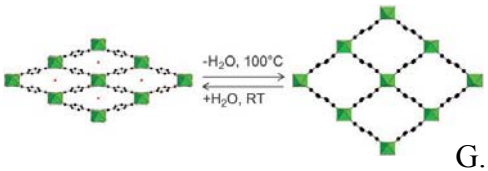


•Determine atomic adsorption sites for molecular hydrogen

Technical Accomplishment

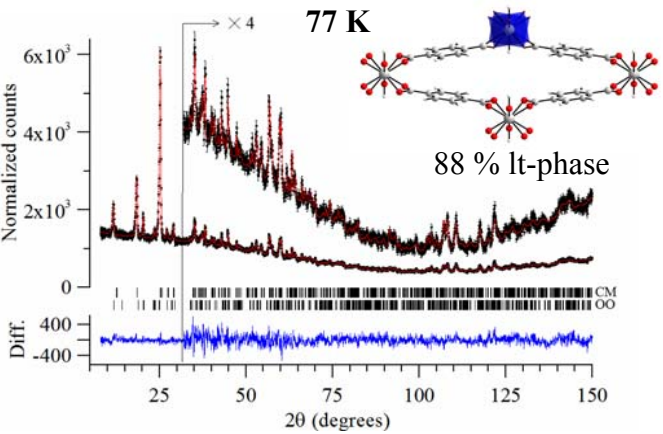
Adsorption of hydrogen in a 'breathing' MOF

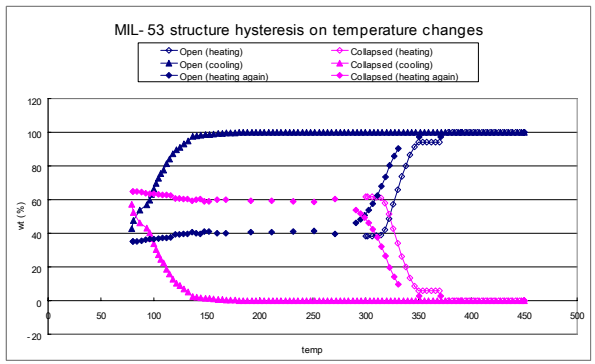
– MIL-53

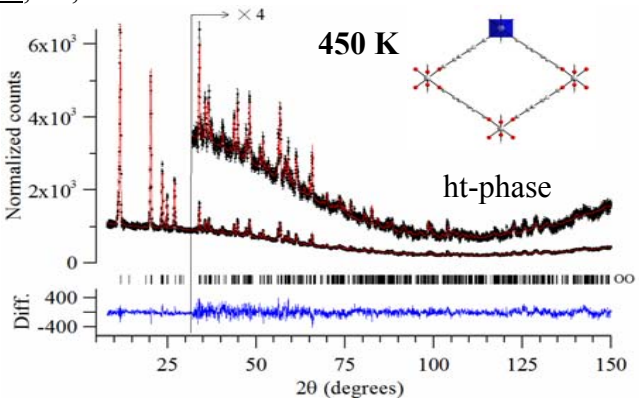


- "Breathing" effect – structural change of MIL-53 by loading solvent molecules.
- Hysteresis observed upon the various gas adsorption/desorption cycles, due to the structural breathing phenomenon

G. Férey *et al.*, *Chem. Commun.*, 2003, 2976, C. Serre *et al.*, *J. Am. Chem. Soc.*, 2002, **124**, 1351, P. L. Llewellyn *et al.*, *Angew. Chem. Int. Ed.*, 2006, **45**, 7751.





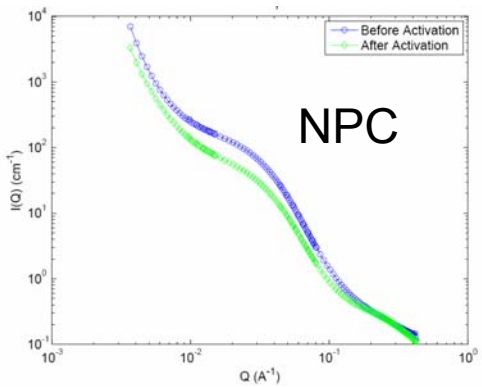


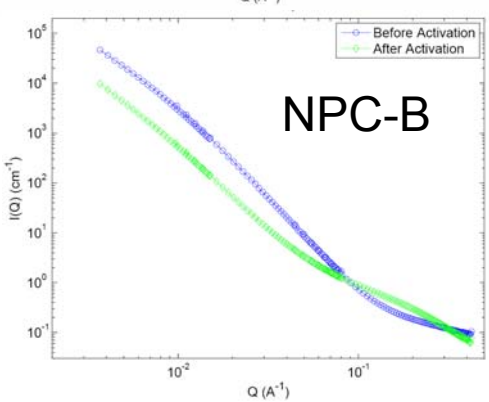
- Shown that the 'breathing' effect is *independent* of adsorbates
- Large structural hysteresis identified Since isotherm experiments rely on the empty volume measurement (correction) at R.T. , this temperature dependent unit cell volume change must be taken into account.

Technical Accomplishment

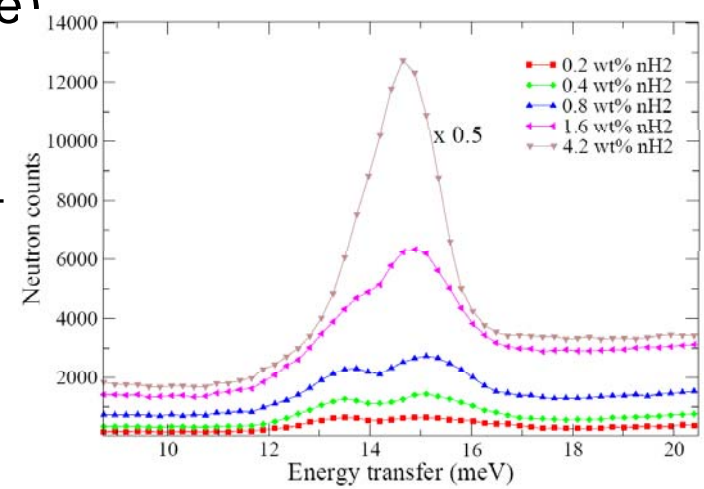
Effects of boron inclusion on the structure and hydrogen adsorption properties of nano-porous carbons

- Completed small angle neutron scattering measurements and hydrogen rotations on series of nanoporous carbons (NPC) and boron included NPC-Bs (Foley/Rajagopalan, Penn State)





- Activation in general helps to open the structure at the nano-scale (a few nm pores).
- NPC sample has a much more well-defined pore structure around 100 nm compared with boron incorporated sample.



- Hydrogen first adsorbed into nano-pores with diameters of around 1 nm

- Structure and hydrogen spectroscopy useful in correlating expt. differences in H_2 adsorption

Technical Accomplishment

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

Nano-porous Carbons (Penn. State Foley, Rajagopalan (plus 8 other samples)

B/C mass ratio

Identifier	Before activation	After activation
NPC (Carbon)	0.0042(2)%	0.029(1)%
B:NPC	0.87(7)%	5.4(3)%

(Numbers in parentheses estimate statistical uncertainty in the preceding digit)

Boron Doped Carbons (Penn. State Mike Chung (14 samples in July, 2007))

Sample number	1	2	3	4	5	6	7
Mass Ratio (B/C)	5(2)%	N/A	N/A	2.1(3)%	1.8(3)%	8.4(8)%	0.56(1)%

Sample number	8	9	10	11	12	13	14
Mass Ratio (B/C)	2.0(2)%	2.6(2)%	8(1)%	1.4(1)%	2.3(3)%	1.9(2)%	1.5(1)%

(Other elements, such as Cl, N, H and Na, have been characterized for samples simultaneously.)

Another 13 samples in March, 2008

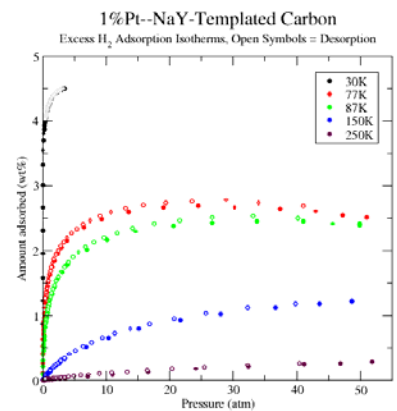
Parameterize various stage of production for materials of interests to partners.
This technique does not distinguish structural incorporation of boron

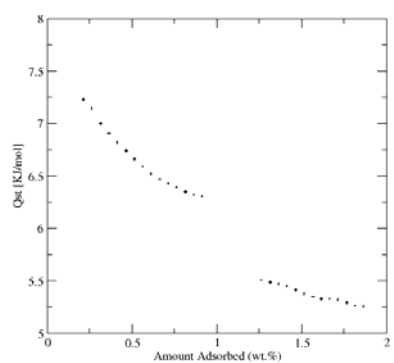
Technical Accomplishment

H_2 ON ORDERDED MICROPOROUS CARBON MOLECULAR SIEVES CONTAINING DISPERSED PLATINUM NANOPARTICLES

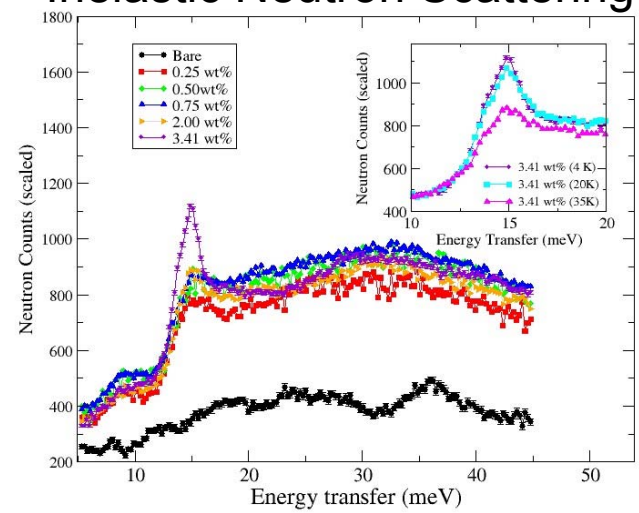
-P. Webley, Monash Uni

Attempt to synthesize ordered microporous carbon molecular sieves containing well dispersed Pt nano-particles by a templating approach using Pt impregnated NaY. An enhanced homogeneous adsorption heat of 11 kJ/mol had previously been observed. Yang, Y-X, et al. Micro. Meso. Maters (submitted)





Inelastic Neutron Scattering



The hydrogen adsorption potential is unusually very flat bottomed (uniform) as a function of loading in this material.

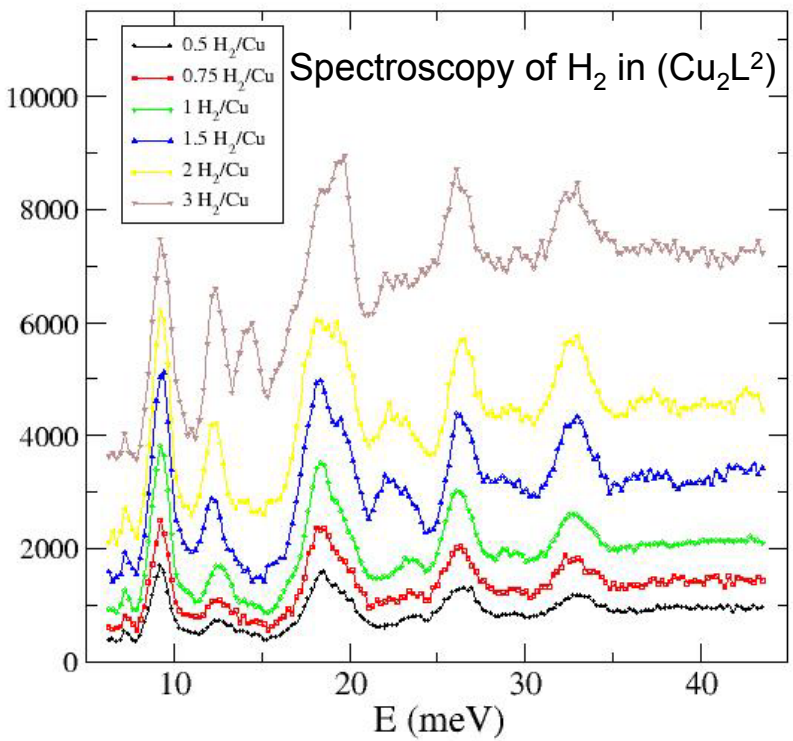
- Low adsorption capacity 2.4 wt% at 35 bar.
- Heat of adsorption lower than previously obtained.

Technical Accomplishment

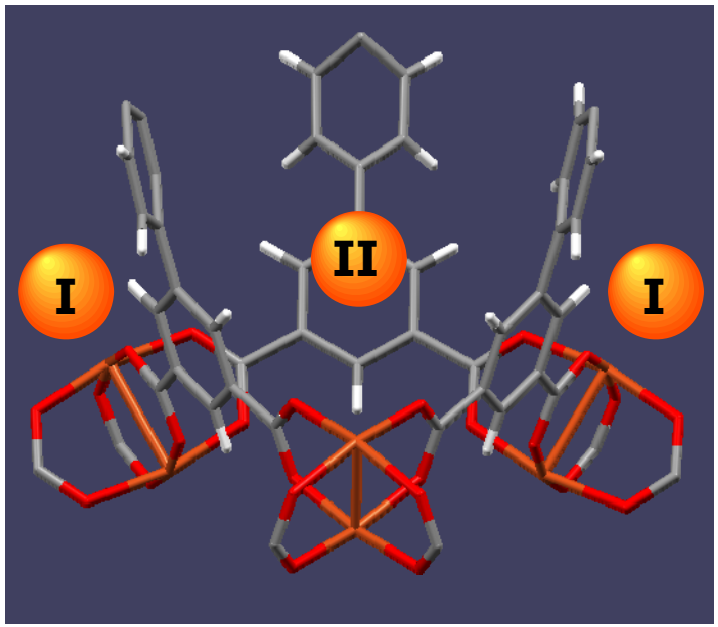
Adsorption sites and binding in copper paddlewheel MOFs

H-C. Zhou (U. Miami) and M. Schroder (U. Nottingham)

We understand that MOFs containing CUMCs have a better capacity for adsorption than pure carbons. This work adds to our knowledge of these systems



Adsorption sites in Cu(tptc) (Cu_2L^2)



- Obtaining atomic positions and adsorption sites.
- Probing the site specific potential of the adsorption sites. Similar to HKUST-1

Future Work

Remainder of FY 2008:

Continue neutron scattering studies of various adsorbate systems

- Complete analysis of remaining neutron spectroscopy data.
- Measure hydrogen diffusion in MOFs
- Characterize effect of hysteresis on H_2 adsorption in MIL-53: is this a useful mechanism for storage?
- Expand on small angle scattering studies to elucidate morphology of non-crystalline materials
- Initialize characterization of new high adsorption capacity MOFs

FY 2009:

- 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
- Extend collaborations to search for MOFs capable of binding multiple hydrogen per metal site.
- 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

We have continued our primary task of performing various neutron characterization measurements in support of other HSCoE members.

Determined structures and locations of H_2 in key MOFs with CUMCs. It is possible to adsorb monolayer hydrogen at densities above the solid close-packed layer.

Determined that there is an intrinsic phase breathing mode in MIL-53. The impact on the adsorption isotherms is relevant to understanding the adsorption mechanism.

Determined bulk composition, morphology and hydrogen adsorption characteristics for a series of NPC and B-NPC upon synthesis and activation