Neutron Characterization in Support of the Hydrogen Sorption Center of Excellence

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Overview

NIST

Timeline

- Project start FY05
- Project end FY10
- 100% complete

Budget

FY	HSCoE	MHCoE
FY05	$130K	$125K
FY06	$208K	$156K
FY07	$216K	$276K
FY08	$225K	$287K
FY09	$234K	$298K
FY10	$234K	$298K

NIST provides access to neutron facilities and FTEs for the HSCoE and MHCoE

Barriers

- Barriers addressed
  - Characterization of Hydrogen Physisorption and Chemisorption

Partners

- **HS Center**
  - Caltech, NREL, ORNL, LLNL, Penn State
- **External**
  - UC Berkeley, U. Sydney, Monash Uni.,General Motors, ISIS (U.K.)

Objectives and Relevance

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)
- Relevance
- Neutron scattering on a great variety of new hydrogen storage materials for various research groups contributes to a focusing on technical barriers

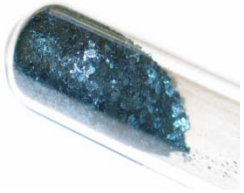
- **We contribute within the Center and with external partners.**

Approach

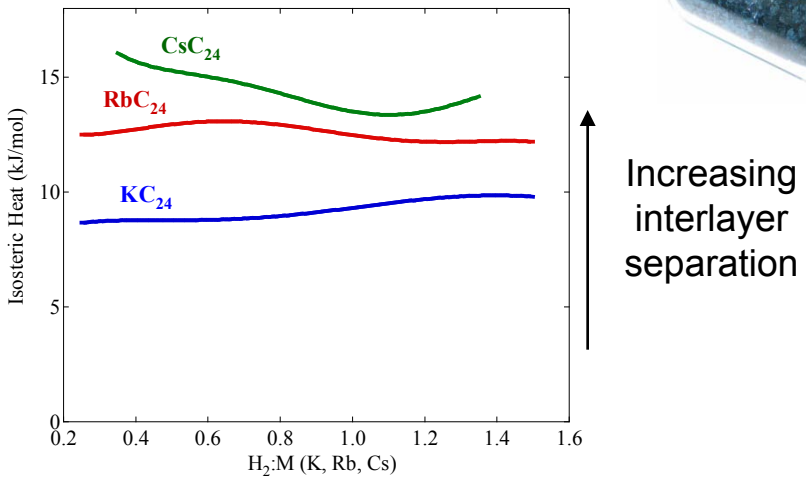
- **Neutron methods**
  - –determine elemental compositions of materials (prompt-γ activation analysis)
  - –determine location of H and crystal structures of materials (neutron diffraction superior to XRD for locating light elements)
  - –determine bonding of absorbed H (unlike IR and Raman, neutron 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)

Technical Accomplishment

Graphite Intercalation Compounds (Ahn, Caltech)



We seek to understand hydrogen interactions with metal ions and focus on the rational synthesis of sorbents that can strongly bind di-hydrogen ligands for vehicular hydrogen storage



Problem

- Graphene slit-pore structure not stable
- Need a "spacer molecule" to prop open layers

Strategy

- Insert alkali-metal (AM) atoms between graphite layers
- Nomenclature: "Graphite intercalation compounds"
- Pore-width controlled by size of AM atom

- Correlation between interlayer spacing and H_2 adsorption enthalpy
- H_2 adsorption reversible at low temperatures (< 150 K); H_2 reacted chemically at higher temperatures (~195 K).

Graphite Intercalation Compounds	***Isosteric Heat$_{ave}$ (kJ/mol)***	***Adsorption$_{max}$ (wt%)***
$KC_{24}(H_2)_x$	9.2	1.24
$RbC_{24}(H_2)_x$	12.6	1.03
$CsC_{24}(H_2)_x$	14.9	0.85

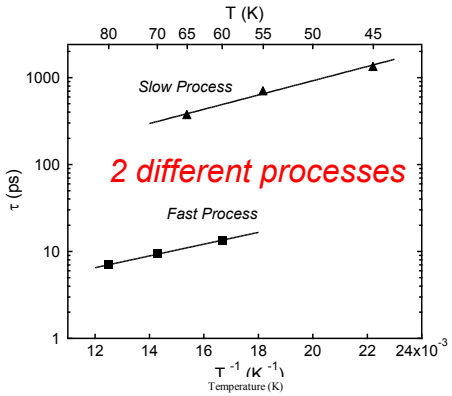
Technical Accomplishment

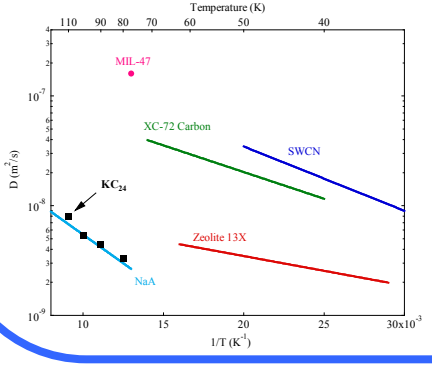
Graphite Intercalation Compounds (Ahn, Caltech)

Problem

- How does hydrogen bind in these systems?
  - Can we apply this to GO/Graphene pores?
- In-plane structure of $KC_{24}(H_2)_{0.5}$ not well-known:
  - makes computation difficult

QENS: Diffusional Dynamics

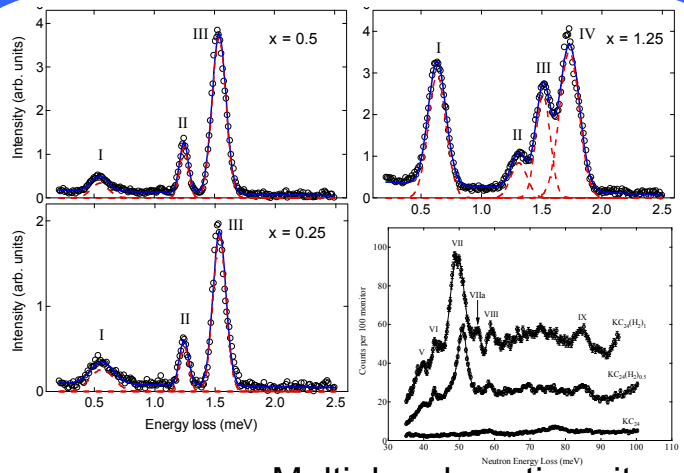




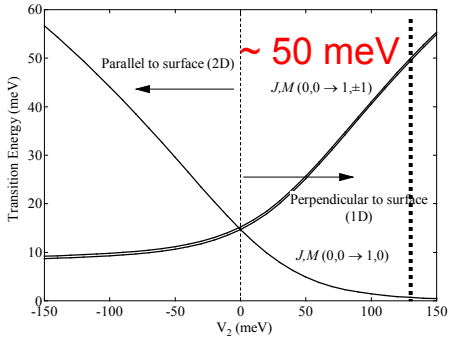
The rate of H_2 diffusion in KC_{24} is slower than in other types of carbon adsorbents.

Reduction of H_2 diffusion at larger concentration: site-blocking and correlation

INS: Neutron spectroscopy



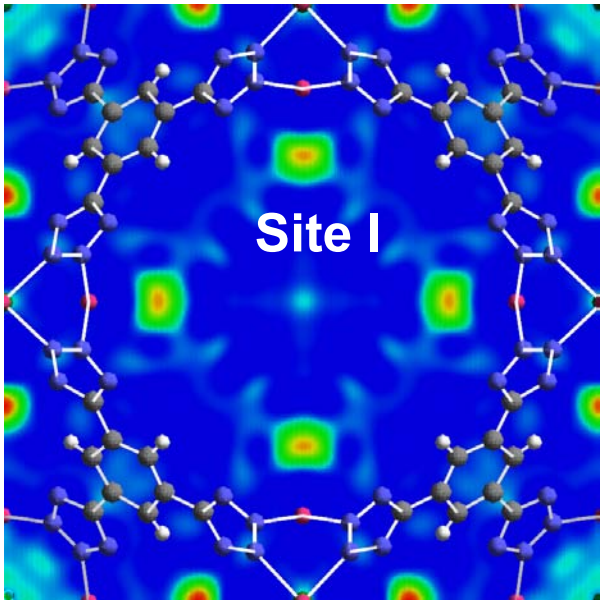
- Multiple adsorption sites
- Strong rotational barrier (~130 meV)
- H_2-H_2 interactions
- Change in structure

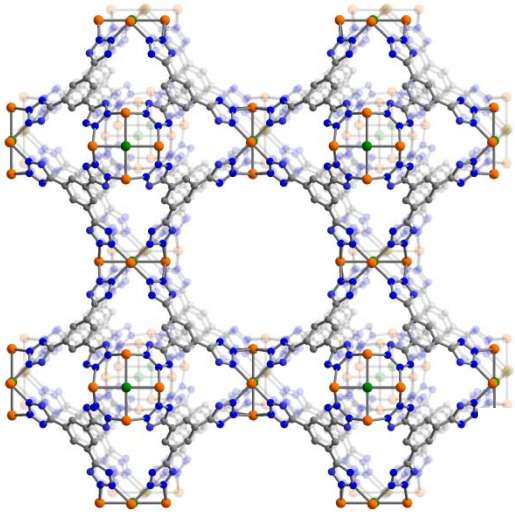


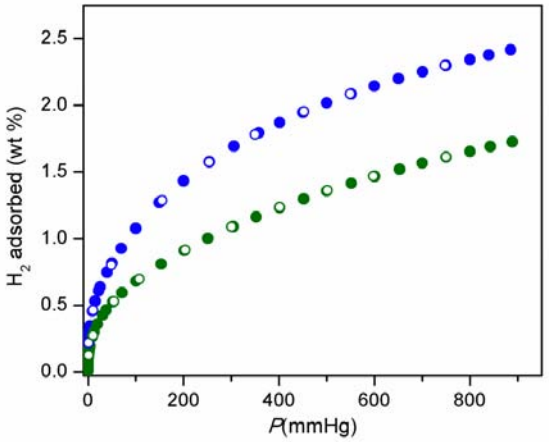
Technical Accomplishment

Effect on transition metal on H_2-M interactions (Long U.C. Berkeley)

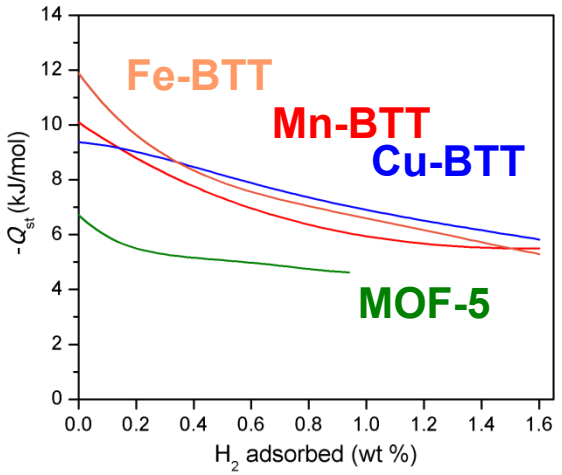
We previously used neutron diffraction to locate hydrogen binding sites in TM-benzenetristetrazole frameworks (TM= **Mn**, **Cu**).
- Initial high enthalpy of adsorption due to TM:H_2 interaction







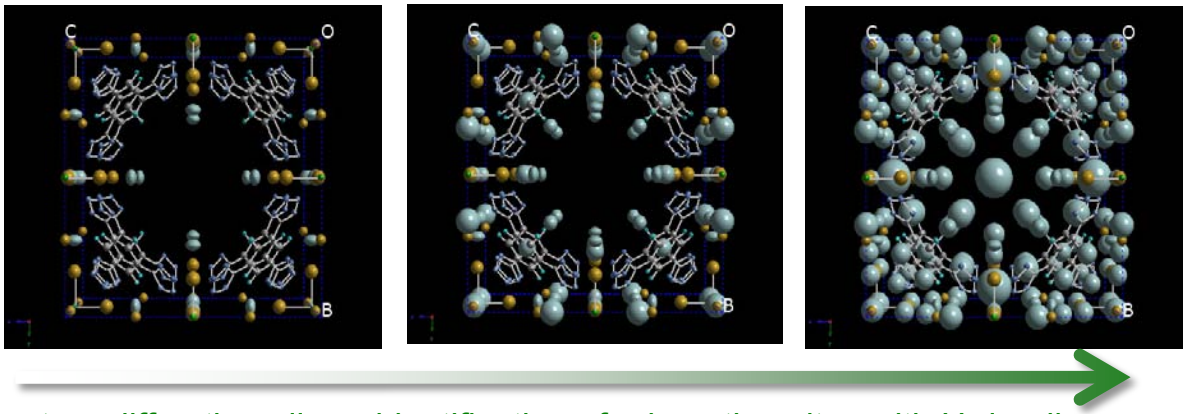
Combinatorial search for reaction conditions allows new Fe^{2+}-BTT to be characterized at U.C. Berkeley

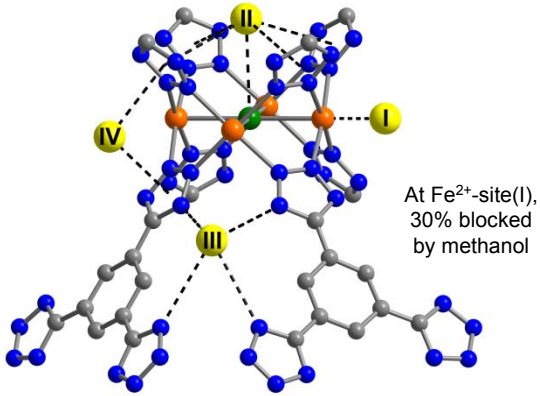


Excess 3.7 wt% 30 bar; total: 4.1 wt% 95 bar
35 g/l (Crystal ρ); 2100 m^2/g :
(lower values than for Mn-BTT)

Technical Accomplishment

Effect on transition metal on H_2-M interactions (Long U.C. Berkeley)



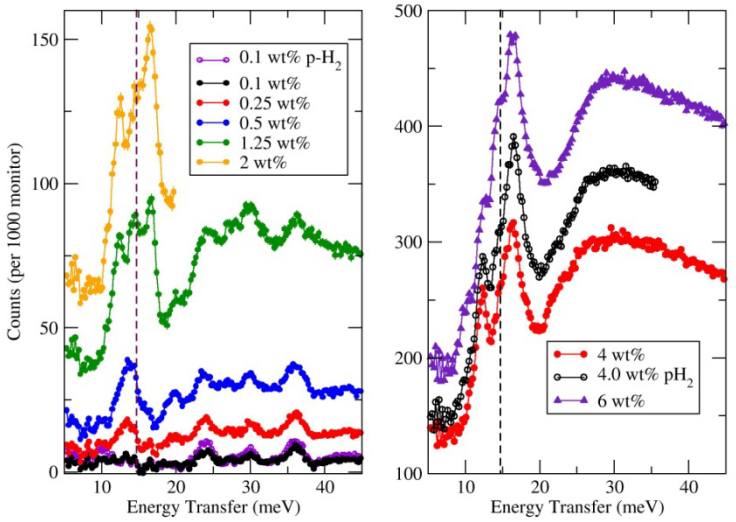


Neutron diffraction allows identification of adsorption sites with H_2 loading

Correlation of adsorption strength: $Fe^{2+} > Mn^{2+} > Cu^{2+}$
with TM-H_2 distance: $Fe^{2+} < Mn^{2+} < Cu^{2+}$
[2.17(5)< 2.27 < 2.47 Å]
but not ionic radius*: $Mn^{2+} > Fe^{2+} > Cu^{2+}$

- Primary adsorption sites @TM have highest enthalpy
  - Shortest TM-D_2 distance found so-far is in Fe-BTT
- INS consistent with strong H_2:Fe interaction at low loading
- Fe^{2+} site catalyzes hydrogen conversion to para-H_2 (complete at low loading, partially at high loading)

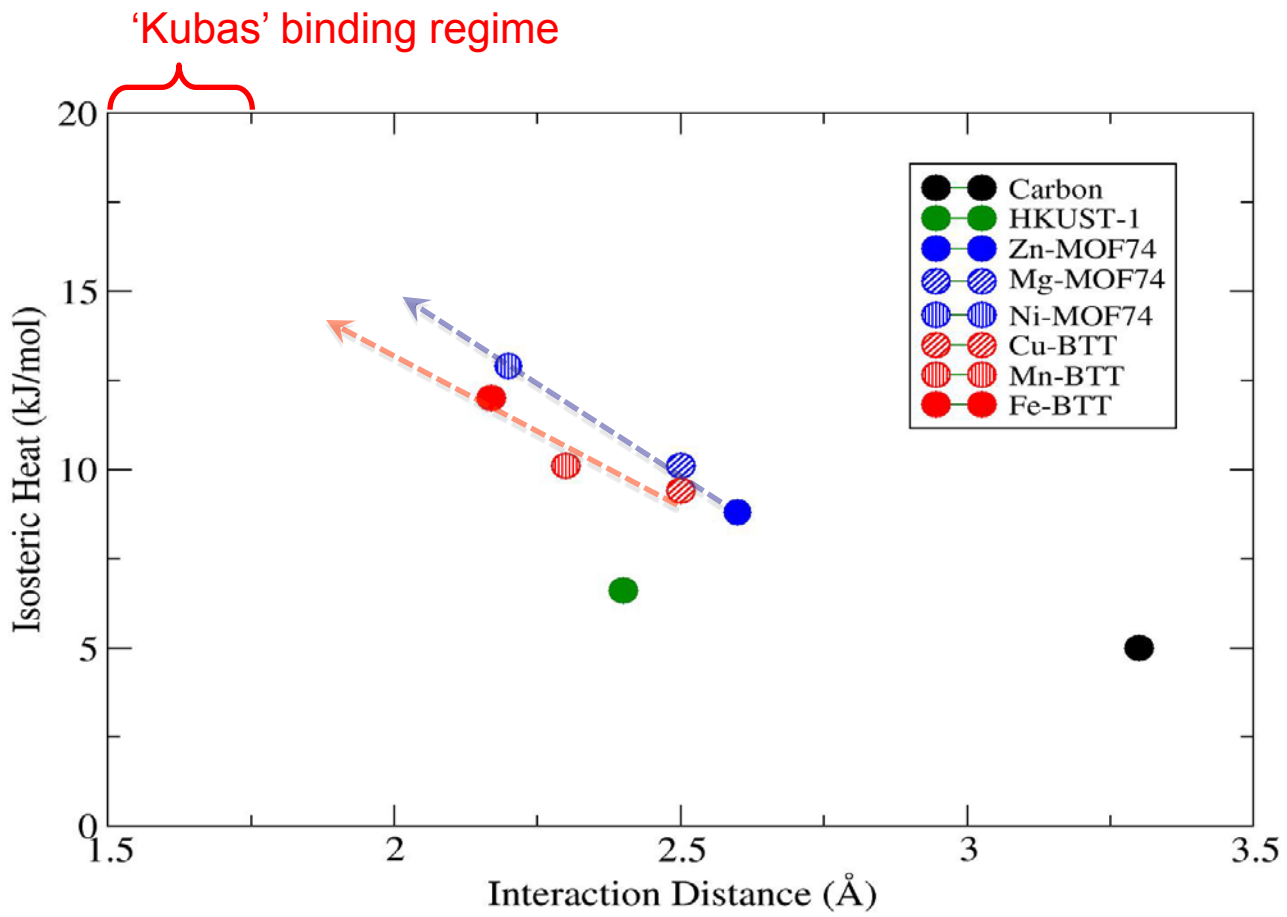
INS: H_2 rotational spectra



*MOF-74 isostructural series has been predicted to have ΔH(TM-H_2) distance varying ~PROPORTIONAL (INVERSE) with ionic radius. Zhou et al. JACS, 130, 15268, 2008

Technical Accomplishment

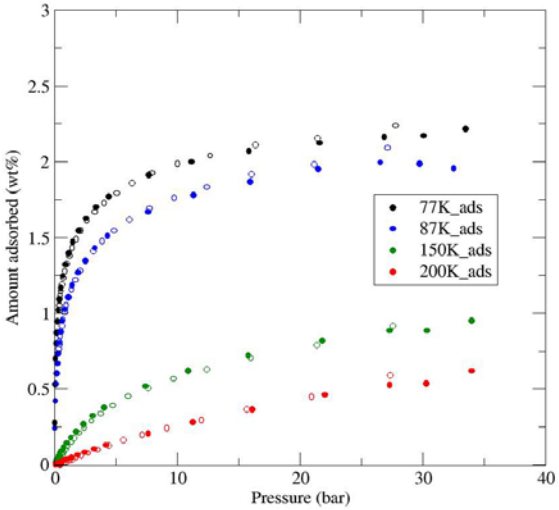
What are the limits on ΔH in MOFs?



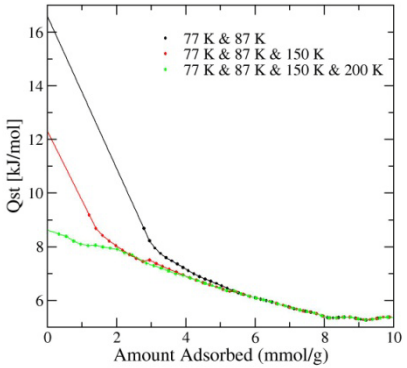
Neutron diffraction and INS indicate electrostatic origins of interaction, no discrete orbital bonding-back bonding observed in character or strength.

Technical Accomplishment

Boron substituted carbons (M. Chung, Penn State Uni.)

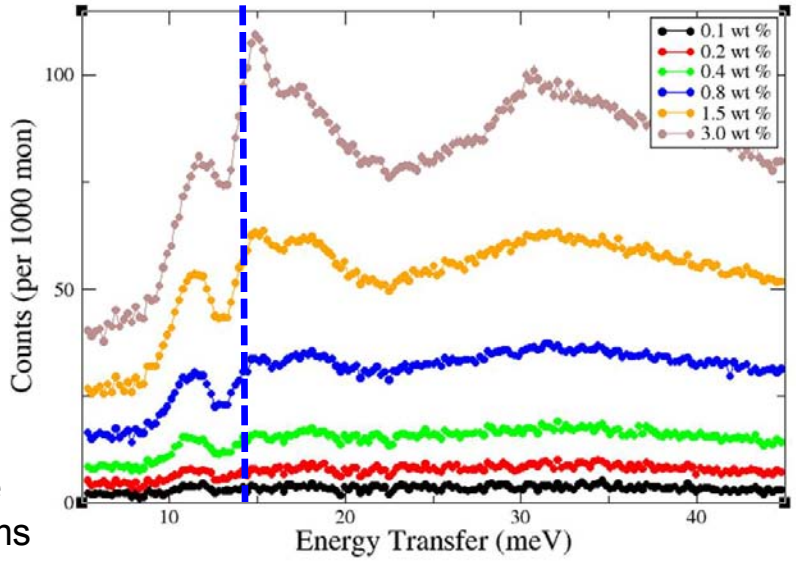


Variable temperature, high pressure isotherms →



Clearly demonstrate the need to include isotherms at a range of temperatures to obtain robust ΔH values.

Bulk H_2 rotation



Consistent with a model of hindered H_2

H_2 lies ll

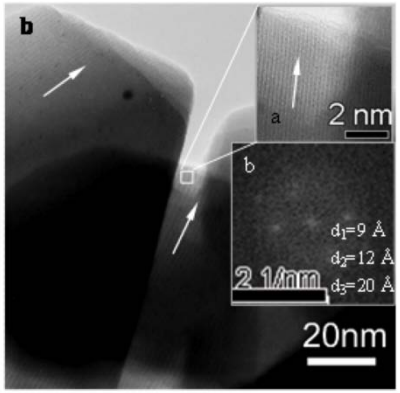
rotation barrier ~13 meV

NMR indicates 6 at% B:C

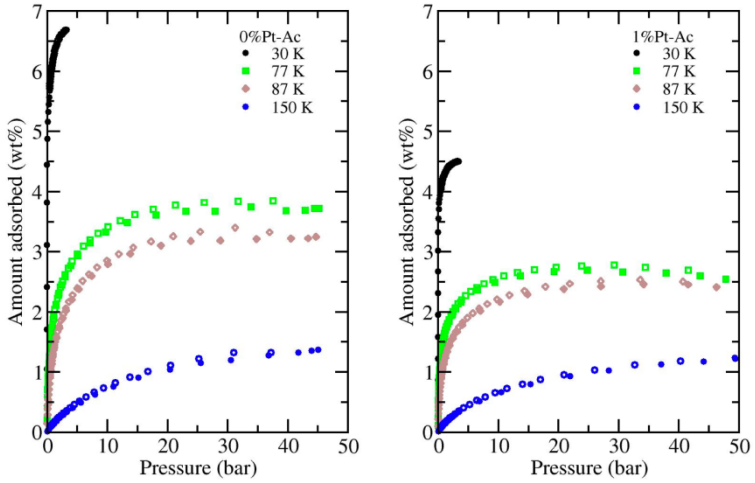
- INS data shows, *for the first time*, a large rotational splitting indicative of enhanced H_2 interactions in a substituted carbon.

Technical Accomplishment

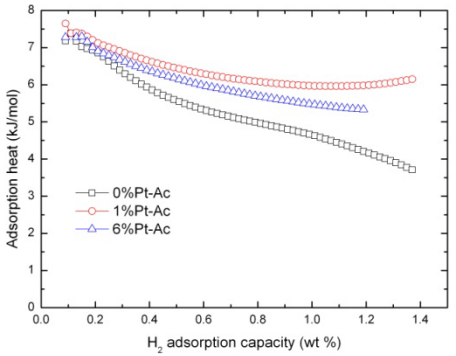
Hydrogen diffusion in templated carbons (Webley, Monash Uni.)



TEM image of 1%Pt loaded activated carbon



Excess hydrogen adsorption for bare carbon and 1%Pt-Ac



Isosteric Heats

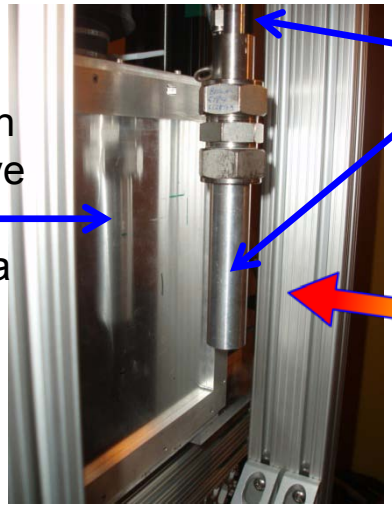
Samples	Pt loading wt%	BET specific surface area m^2/g	Pore volume cm^3/g		H_2 uptake 77 K and 1 bar wt%	H_2 uptake at 87 K and 1 bar wt%
			Vmicro	Vmeso		
0%Pt-Ac	0	2200	0.94	0.27	1.7	1.5
1%Pt-Ac	1	2087	0.87	0.19	2	1.4
6%Pt-Ac	6	1930	0.8	0.15	1.6	1.2
40%Pt-Ac	40	912	0.43	0.05	- *	- *

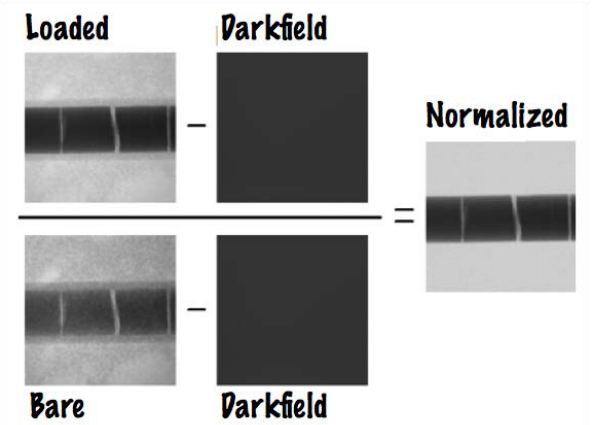
- Platinum loading decreases surface area, excess adsorption
- Pore structure well defined (TEM and BET pore size analysis)
- Surface chemistry (XPS) and ΔH differs on Pt loading

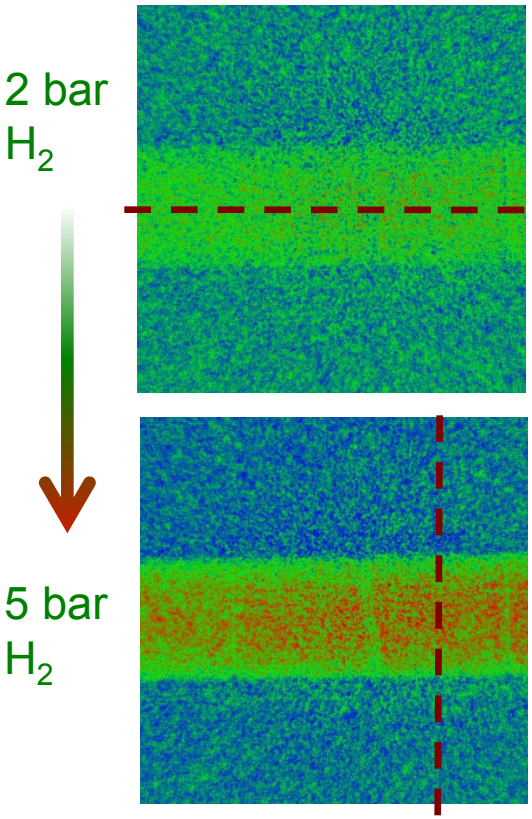
Technical Accomplishment

NIST

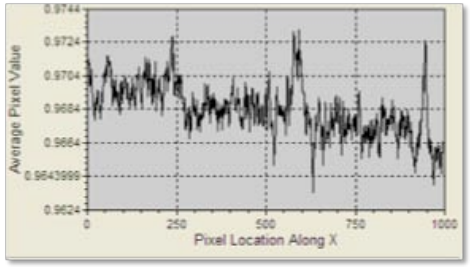
Imaging H_2-adsorption in an activated carbon– Pfeifer, U Missouri



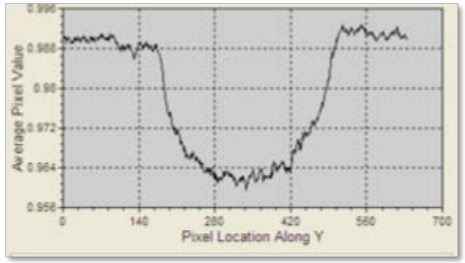




Hydrogen scatters neutrons reducing intensity where adsorbed



Profile shows cylindrical profile of briquettes



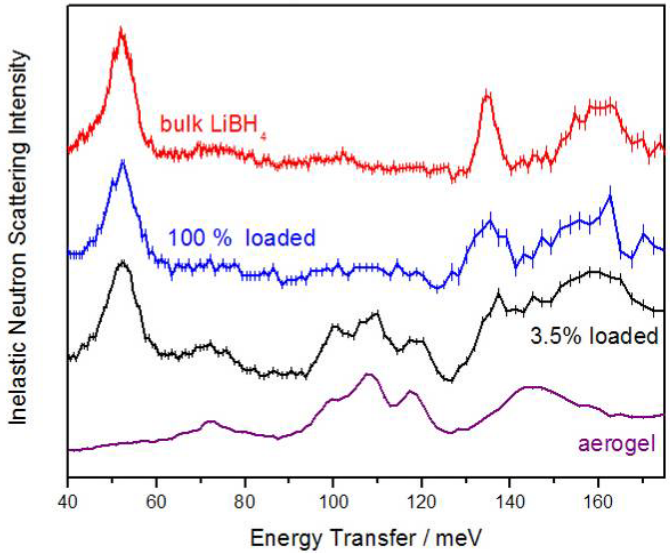
- Real-time observation of loading profiles as a function of pressure
- Quantitative information

Characterization of Nanoconfined Systems

Technical Accomplishment | Collaboration with HRL, Lawrence Livermore, Maryland, and Michigan

Motivation: to characterize the properties of nanoconfined $LiBH_4$

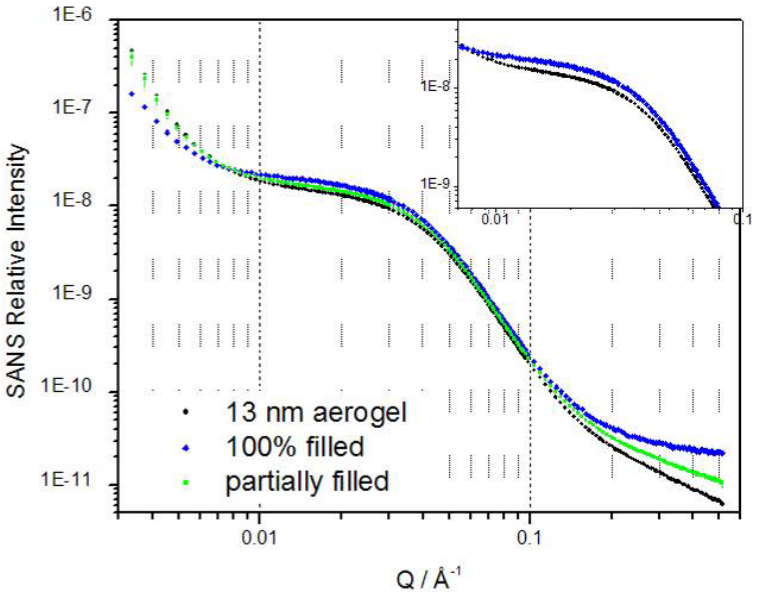
NV spectra of $LiBH_4$ in 13 nm carbon aerogels



$LiBH_4$ vibrational modes in the carbon aerogel exhibit a minor (~10%) broadening compared to bulk $LiBH_4$ modes

SANS suggests that the smallest pores fill first, and there is no change in apparent mesopore geometry with filling

Small-angle neutron scattering (SANS) data



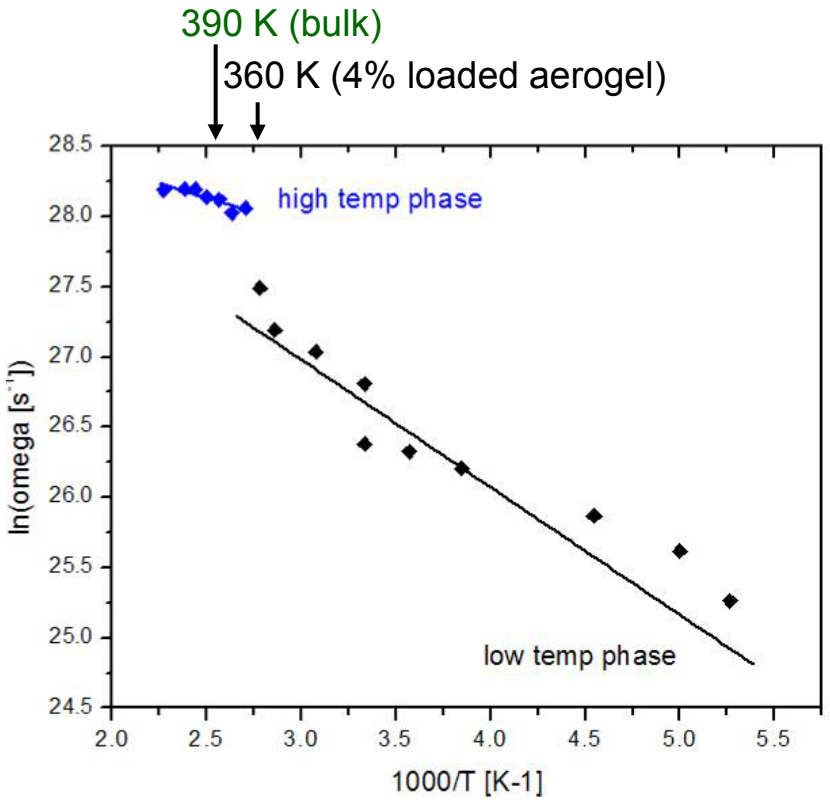
* We need to understand the relationship between pore morphology and filling behavior of nanoconfined storage materials.

Characterization of Nanoconfined Systems

Technical Accomplishment | Collaboration with HRL, Lawrence Livermore, Maryland, and Michigan

Motivation: to investigate borohydride dynamics perturbations in carbon aerogels

- Bulk $LiBH_4$ undergoes a phase transition at 390 K
- Under conditions of confinement, we observe indications of a phase transition at 360 K
- Low-temperature dynamics due to hydrogen reorientation appear on the nanosecond timescale at 200 K in the bulk and fully-loaded aerogel
- This temperature is decreased by 75 K in the partially-loaded carbon aerogel



T dependence of BH_4^- rotational jump frequency for nanoconfined $LiBH_4$ (4% loading in carbon aerogel)

* Nanoconfinement appears to perturb the bulk thermodynamic properties

Collaborations

Partners:

CalTech (University/HSCoE, joint) Alkali intercalated graphite, high surface area MOFs

Monash Uni. (University, primary) Dynamics of H_2 in templated carbons

U. C. Berkeley (University, primary) Neutron measurements on various MOFs

Penn. State (University/HSCoE, primary) Composition and H_2 interactions in B-substituted carbons

NREL (Federal/HSCoE, primary) Neutron measurements on candidates for 'strong interactions' and B-substituted carbons

Missouri (University/HSCoE, primary) Imaging of storage media

ISIS (U.K. central facility, primary) INS measurements in MOFs

Future Work

NIST

This was the final year of the HSCoE. See the final Center report for key achievements and areas requiring further study.

Summary

NIST

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.

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 understanding of the local adsorption potential is obtained from the current INS data.

For the first time we have observed a significant perturbation of the hydrogen rotational levels in a high surface area B: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.