Neutron Characterization in support of the Hydrogen Sorption Center of Excellence

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May 18-22th 2008 STP_35_Neumann

Overview

Timeline

- Project start FY05
- Project end FY10
- 80% complete

Budget

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

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**
  - Caltech, NREL, ORNL, LLNL, Penn State, Texas A&M
- **External**
  - UC Berkeley, U. Sydney, Monash Uni., Uni. Nottingham, General Motors, ORNL, 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)

- **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)

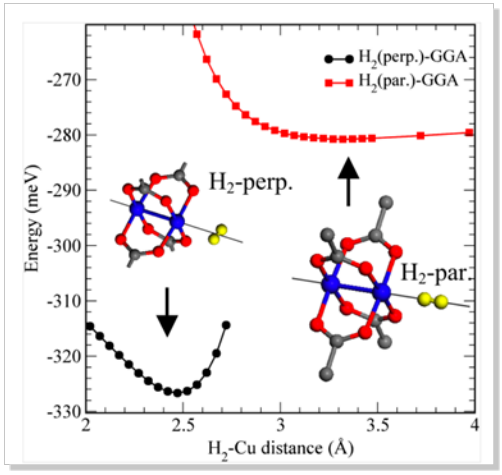
Approach – Milestones

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

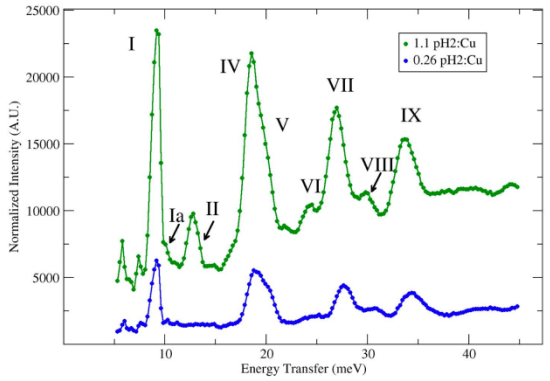
Month/Year	Milestone or Go/No-Go Decision
Apr-08	Survey of materials of interest to the Center. Continue isothermal gas loading, inelastic neutron scattering, neutron powder diffraction, and prompt gamma hydrogen content measurements (status: met).
Dec-08	*Detailed neutron studies*. Evaluate the effects of controlled synthesis on materials such as MOFs and metal decorated materials (status: met). Structural and isothermal characteristics of M-MOF74 (mg, Ni, ZN..) - Measured hydrogen diffusion in Mg-MOF74 - Measured INS at higher energies for Pt-SWNHs and Pd-nanofibers
May-09	*Detailed neutron studies in support of the Center's go/no-go analysis*. A thorough analysis as needed of the materials that have favorably passed the Phase 1 go/no-go decisions and show the most promise to the center's goals of achieving the 2010 targets (status: continuing). -Performed go/no-go analysis of materials -Commencing measurements of go-materials. -AX-21, B-carbons, Ni-composites,

Technical Accomplishment

Understanding binding of H_2 in Cu-paddlewheel MOFs – (Kepert, U Sydney)

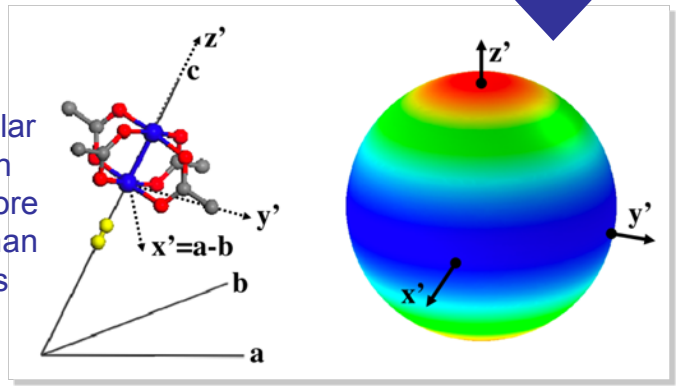


Brown, et al.
Nanotechnology (in press)



Excellent agreement when compared to inelastic neutron data

Calculate energy of H_2 as a function of orientation in HKUST-1



Perpendicular orientation -78 meV more favorable than along axis

Solve rotational Schrodinger eqn.

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
6	-5.64	55.82	J=2, M=+/-1
7	-5.53	55.93	J=2, M=-/+2
8	9.95	71.41	J=2, M=0

Classical Harmonic Phonon Frequencies for a fixed H_2 orientation (H_2 perp)

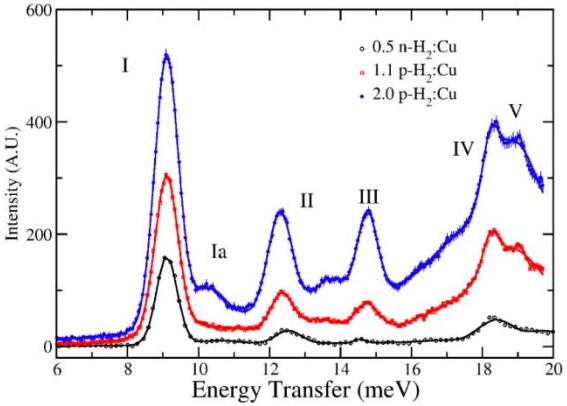
ω (x') = 9.56 meV ω (y') = 13.44 meV ω (z') = 22.87 meV

- Size and shape of Coulomb potential determines inelastic neutron scattering features. Spectra composed of rotations and multiple rotation-phonons

Technical Accomplishment

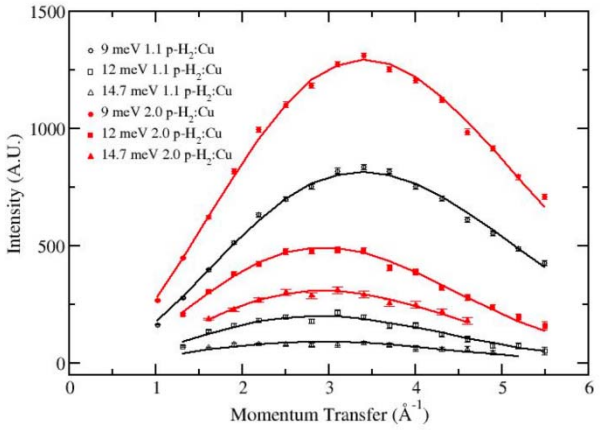
Understanding binding of H_2 in Cu-paddlewheel MOFs – (Kepert, U Sydney)

Brown, et al.
Nanotechnology (in press)



Measure Q-dependent Inelastic neutron scattering (INS) of H_2 in HKUST-1.

Extract data for rotational lines only.



	1.1 *p*-H_2:Cu			2.0 *p*-H_2:Cu		
	9.1 meV Peak I	12.3 meV Peak II	14.7 meV Peak III	9.1 meV Peak I	12.3 meV Peak II	14.7 meV Peak III
$\langle U^2 \rangle$ (Å^2) INS	0.175(1)	0.28(1)	0.28(2)	0.171(1)	0.26(1)	0.26(1)
U^2 (Å^2) diffraction	0.146	0.24	-	0.152	0.255	0.3

Fit data to freely rotating H_2 model, compare to diffraction.

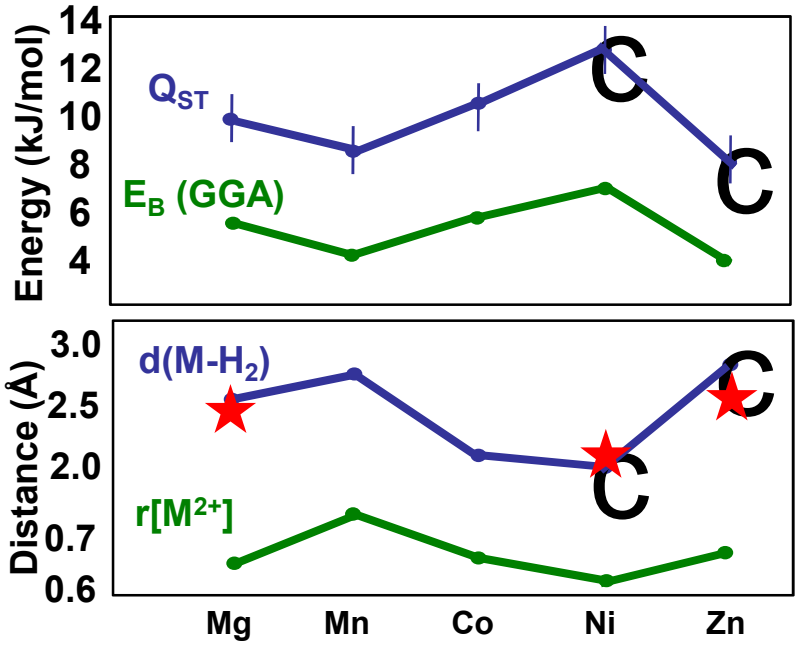
Parameters:
d_e: H_2 bond length
$\langle U \rangle^2$: mean-squared displacement/ Debye-Waller factor

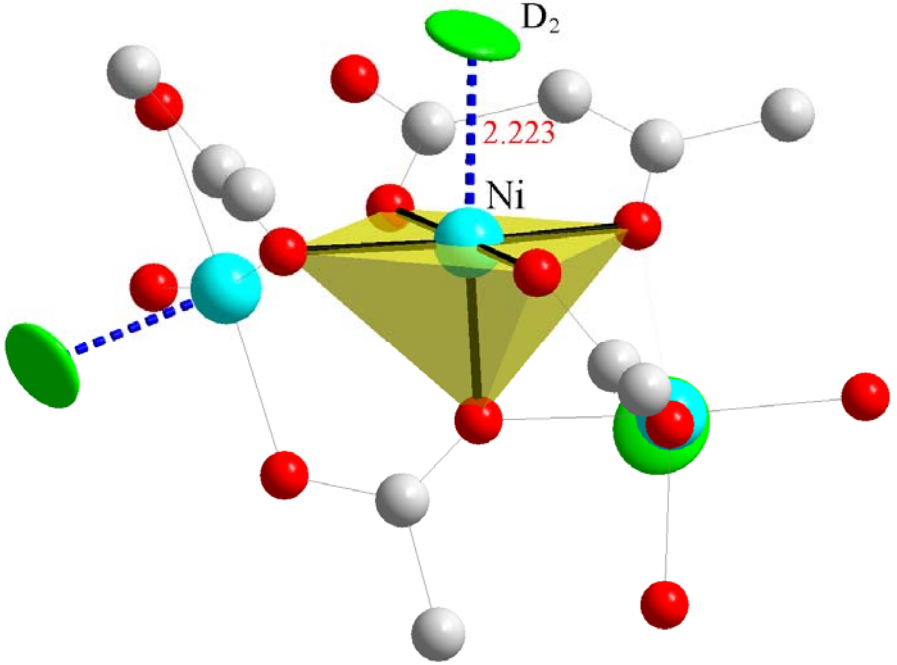
- H_2 Debye-Waller factors agree between INS and diffraction
- No need to have an elongated hydrogen to explain the spectra.

→Not 'Kubas' : Helps define direction of Research cluster 3.

Technical Accomplishment

Effect on transition metal on H_2-M interactions
– (Long/Morris, Berkeley/U. St. Andrews)





Graph from W. Zhou et al. (JACS, 130, 15268, 2008)
Expt data (red star) this work. Zn^{2+} data from last year.

- Experiment confirms theory; points to Irving-Williams series (Ionic size) being responsible for Metal-D_2 distance and ΔH : Refines research path of RC3

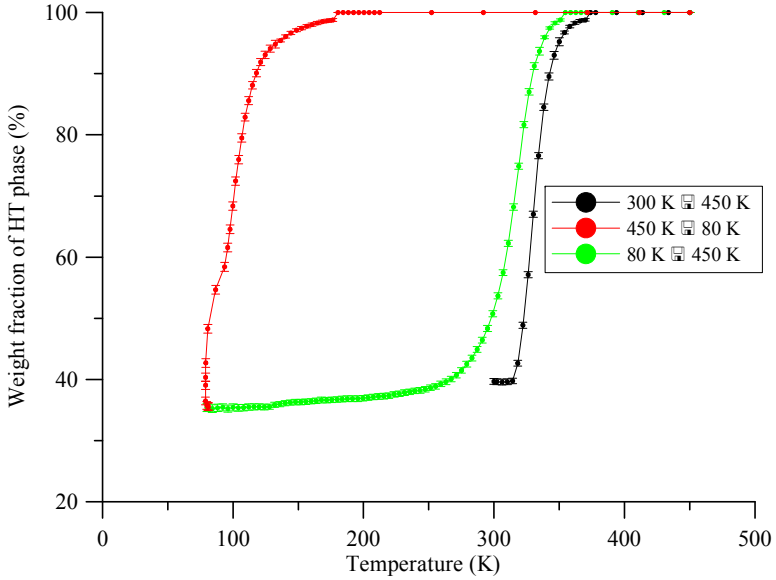
Technical Accomplishment

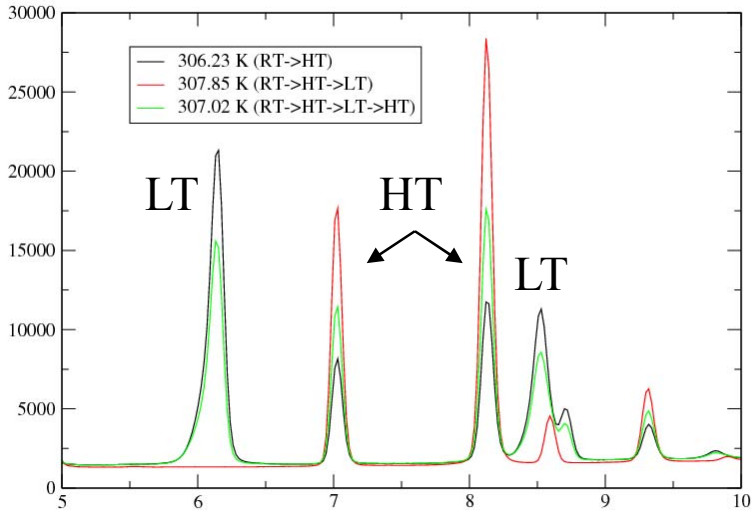
Thermal hysteresis of MIL-53

– (Dailly, G.M., van Beek, ESRF)

- Large thermal hysteresis of MIL-53 (Al)

  better defined using synchrotron X-ray powder diffraction



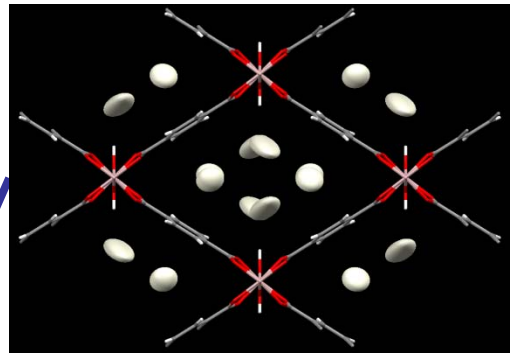


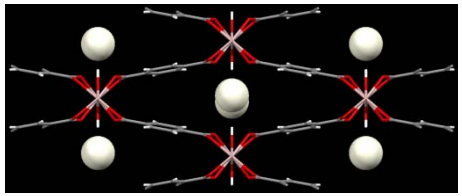
- Large variation in history-dependent unit cell volume must be taken into account for any sorption experiments.

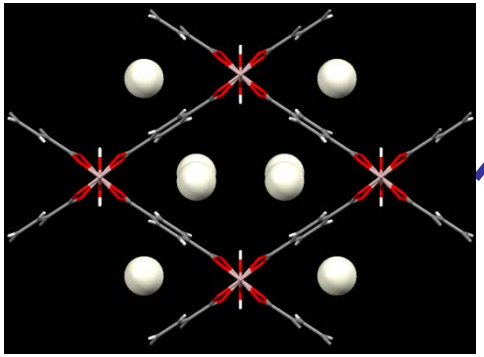
Technical Accomplishment

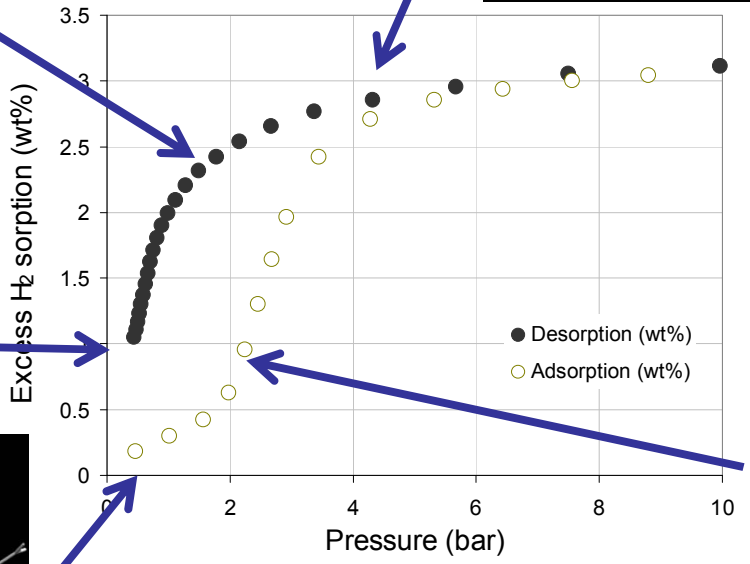
Hydrogen adsorption in MIL-53 – (Dailly, G.M.)

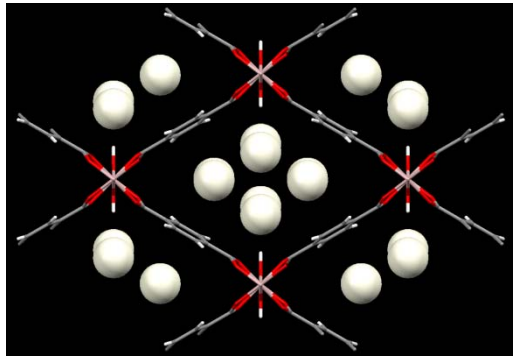
Hydrogen becomes disordered upon desorption











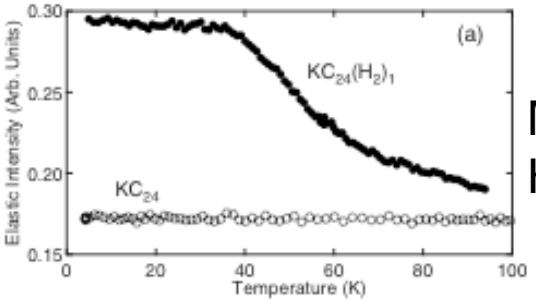
- Hydrogen forces open the pore upon adsorption
- H_2 remains in closed pore even when pumping at 100 K! : Refines research path of RC1 – are dynamic frameworks useful for go-no go decisions?

Technical Accomplishment

Hydrogen diffusion in graphite intercalation system

– **(Ahn, Cal Tech)** Quasielastic neutron scattering of $KC_{24}(H_2)_1$

Purewal, et al. Phys. Rev. B. (in press)



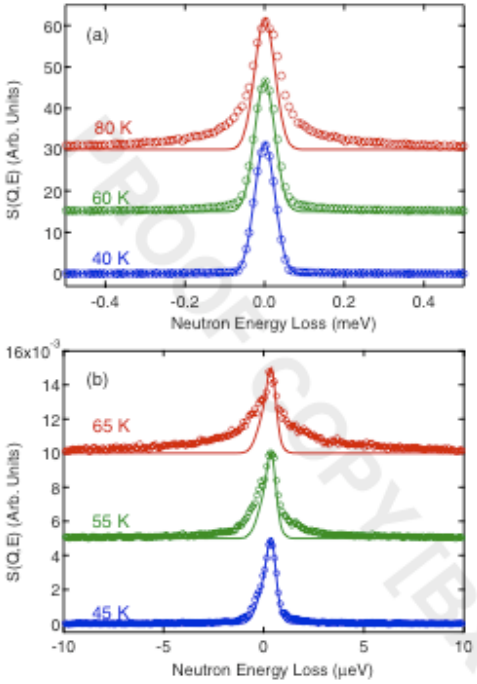
Melting of stage-2 H_2 at 35 K

Higher loadings melt > 60 K

ΔH= 8.5 kJ/mol

Residency times:
τ_0=1.0(1) ps

Activation energy
E_a=156(5) K

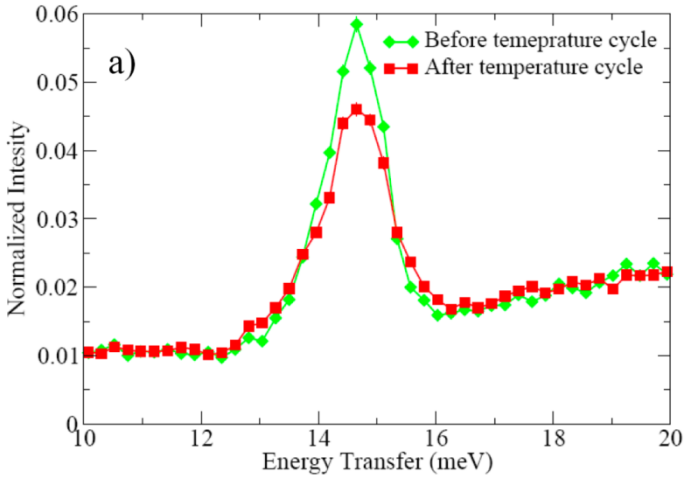


τ_0=21(2) ps
E_a =189(5) Kçç

- Two different time-scales of H_2 motion beyond melting. Characteristic residency times between jumps, τ. Arrhenius dependence of both motions
- H_2 randomly diffuses (fast); Follows jumping K^+ ions (slow).

Technical Accomplishment

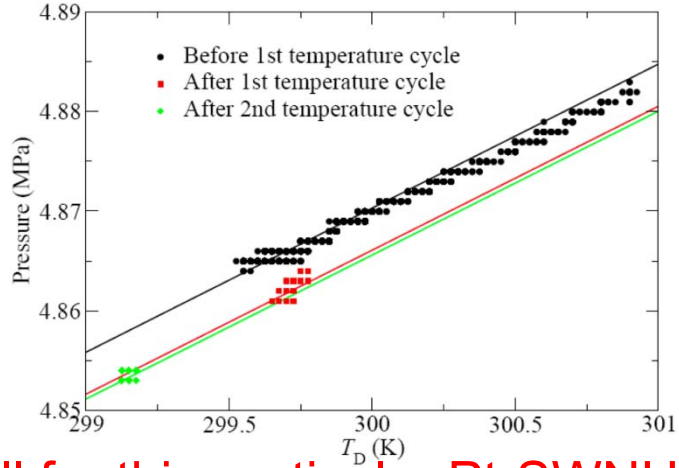
Spillover on Pt-nanohorns – (NIST/ORNL)



We knew previously (from INS) that only 0.17 wt% molecular H2 was lost during spillover at room temperature and ~5 bar

In a closed volume system:
Cycle temperature from 77 K to RT.
Monitor pressure vs. time and temperature of dosing volume (T_D)

Pressure drop → only 0.08 wt% of H_2 spillover

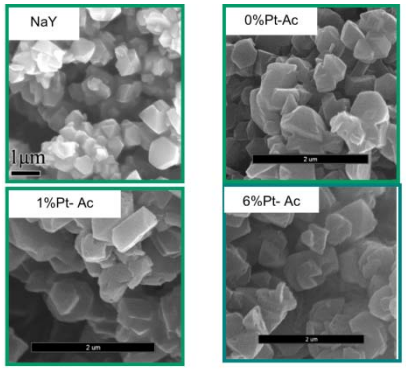


- Confirmed that spillover is indeed small for this particular Pt-SWNH Sample : Provides additional experimental procedures and confirmation of spillover amount for RC4.

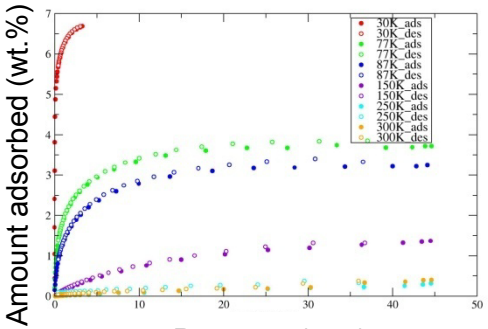
Technical Accomplishment

Hydrogen adsorption in templated Carbons

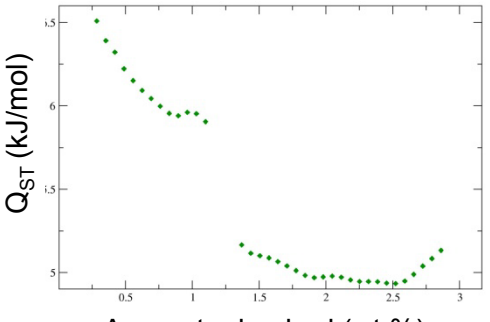
– **(Webley/Yang, Monash)** Yang, et al. ACS Division of Fuel Chemistry, Preprints, vol. 53(2), (2008).



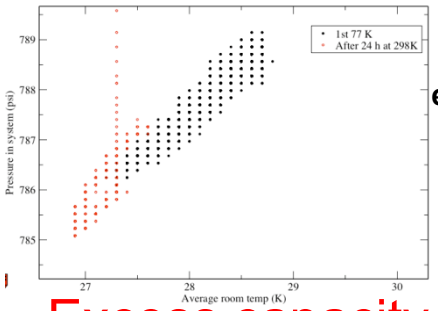
Templated carbon



Templated carbon

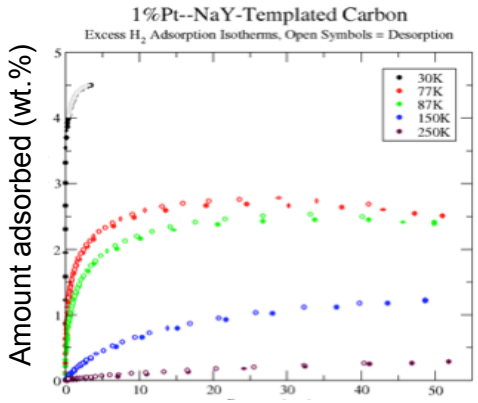


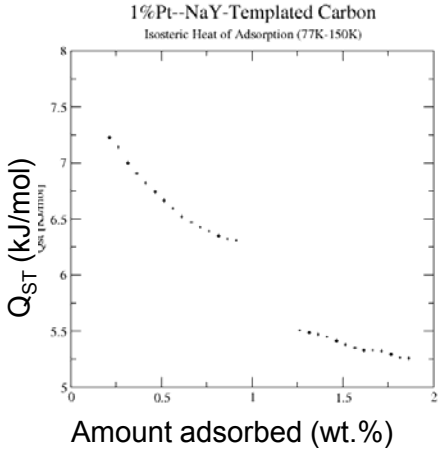
	BET (m^2/g)	Excess (20 bar, 77K)	Q_{ST} (kJ/mol)
Carbon	1300*	3.7 wt.%	6.5
1%-Pt	1200	2.65 wt.%	7.2



Isotherm spillover expt. on 1%-Pt does not indicate any spillover.

Same result after baking in air.





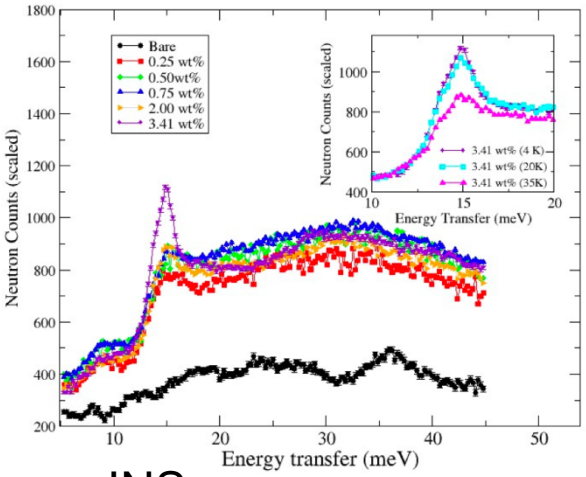
*less than the 3200 m^2/g 6.9 wt%, by Yang JACS 2007

- Excess capacity small, reduced with added Pt. Surface area retained
- No spillover through this preparation method: input to RC4

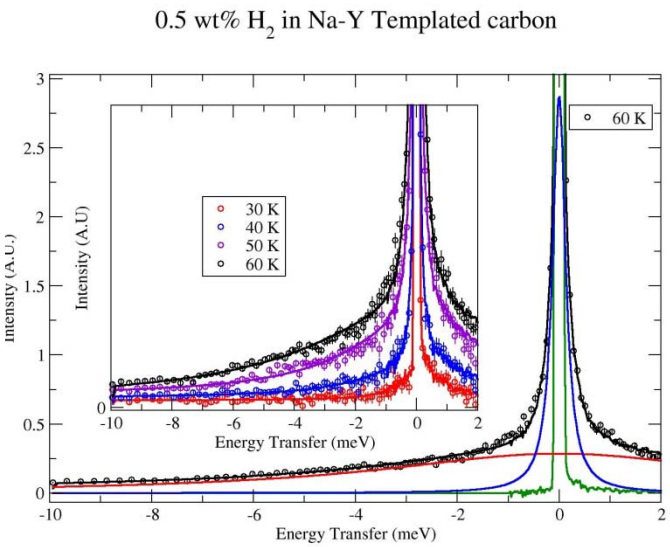
Technical Accomplishment

Hydrogen adsorption in templated Carbons

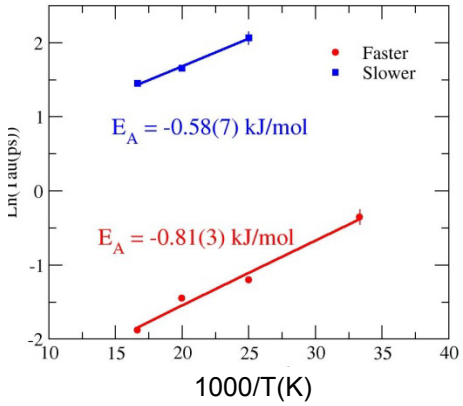
– **(Webley/Yang, Monash)** Yang, et al. ACS Division of Fuel Chemistry, Preprints, vol. 53(2), (2008).



INS
→Unusual broad recoil
→fluid-like H_2



Fast surface diffusion and slower bulk-like diffusion …



Arrhenius activation energies…

Compare 'fast' E_A to:
Nanotubes = -0.37 kJ/mol
Solid H_2 = -1.9 kJ/mol
Liquid H_2 = -0.37 kJ/mol

- Narrow, low dimensional pores give rise to liquid-like hydrogen
- Surface diffusion is fast with larger activation energy than on nanotubes
- Understanding the adsorbed hydrogen state and diffusion is good for all clusters

Collaborations

Partners:

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

U. Nottingham (University) Neutron measurements on high capacity MOFs

Monash Uni. (University) Adsorption in templated carbons and spillover

St. Andrews (University) Neutron measurements on Ni-MOF-74 variant

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

Rice (University/HSCoE) Calculations of vibrational modes of spillover H_2

U. Sydney (University) Hydrogen interactions in MOFs.

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

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

ORNL (Federal) Neutron and H_2-adsorption measurements on spillover candidates

G.M. (Industry) Understanding hydrogen adsorption in flexible MOFs

Ford (Industry) Structure of complex hydrides.

Air Products (Industry/HSCoE) Structural characterizations of C_5N

ESRF (European Synchrotron) X-ray powder diffraction and Raman spectroscopy

Future Work

Remainder of FY 2009:

Neutron scattering studies of various adsorbate systems

- Validation measurements of H_2 adsorption on B-substituted carbons (NREL)
- Validation measurements on exposed TM systems with high ΔH (NREL)
- Neutron scattering of H_2 in polymers (ANL)
- Assessing alternative mechanism for producing porosity in boron-carbon systems

FY 2010:

- Focus on down-selects; select metal decorated materials for validation in Research Cluster 3.
- Continue supporting measurement needs of Center
- Commence neutron imaging of physisorption storage beds.

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.

Determined structures and locations of H_2 in key MOFs with CUMCs.

Determined that there is an intrinsic phase breathing mode in MIL-53. The mechanistic impact on the adsorption isotherms was measured.

Determined hydrogen diffusion characteristics at relevant temperatures in various media. Information has impact on assumptions of ΔS and determination of ΔH for isotherms

Determined spillover is low or negligible in select systems.