NIST Center for Neutron Research

H_2 Storage Characterization and Optimization Research Effort

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National Renewable Energy Laboratory & National Institute of Standards and Technology

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Overview

Timeline*

Start: October 2015
End: TBD
% complete FY 16: ~65%

*previously a component of NREL's materials development program and supported annually since 2006

Barriers addressed

Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility;
N. Understanding of Hydrogen Physi- and Chemi- sorption;
O. Test Protocols and Evaluation Facilities.

Budget

Funding FY16: $250K*

* cost for scientists in residence at NIST.

Collaborators

PNNL - Tom Autrey, Mark Bowden,
LBNL - Jeff Long, Martin Head-Gordon
HyMARC – LLNL, SNL

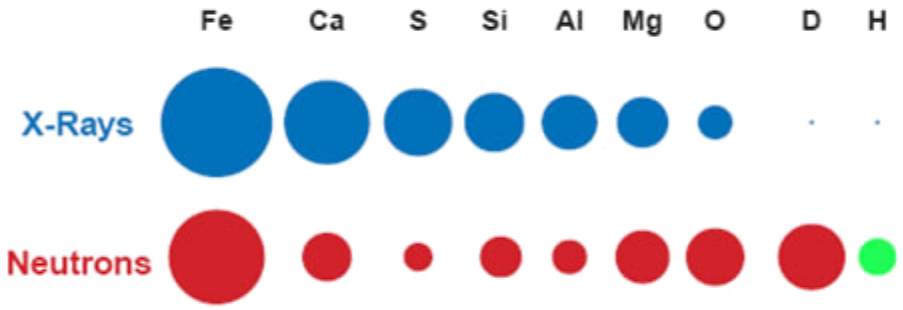
Relevance: Project Objectives

- **NREL leads a collaborative research effort involving NIST, LBNL and PNNL**
  - Seek to employ and develop characterization capabilities at each facility to understand and enhance hydrogen storage media
  - Leverage each institute's unique strengths to jointly validate hydrogen storage claims and design strategies

Relevance: Impact

- **Neutrons provide unique specificity towards determination of hydrogen properties**
  - Enables identification of isotopically-labelled hydrogen location within complex structures
  - Enables identification of hydrogen dynamics within complex structures

Relative comparison of scattering strength for x-rays and neutrons



Approach: Neutron Scattering

- **(FY16) Utilize neutrons to characterize and validate hydrogen storage media**
  - Neutron powder diffraction with precise D_2 loading at T > 4 K and P < 100 bar
    - Elucidate crystal structure of storage materials
    - Harness isotopic sensitivity of elastically scattered neutrons to locate chemi- and physisorption sites of deuterium
  - Inelastic neutron spectroscopy with precise H_2 loading at T > 4 K and P < 100 bar
    - Harness isotopic sensitivity of inelastically scattered neutrons to identify local environment for complex hydrides and chemi- and physisorbed hydrogen

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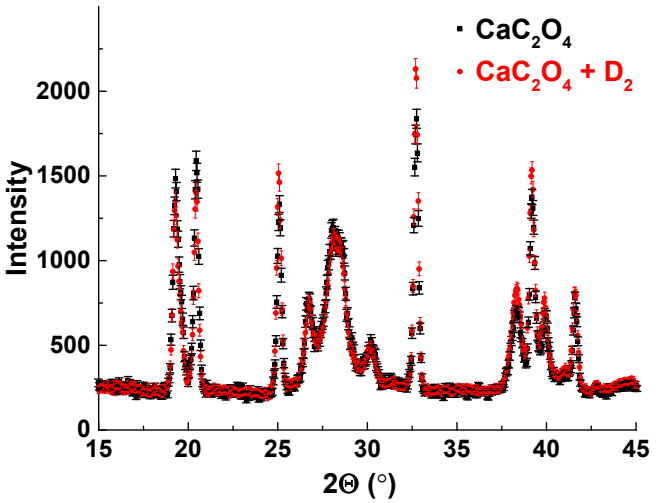
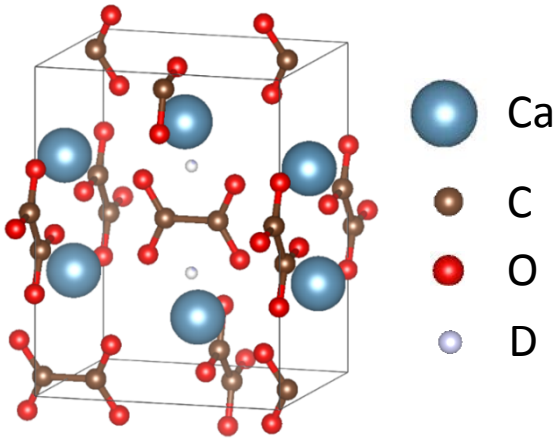
Accomplishments and Progress: Oxocarbons

- **Structure of bare and deuterium-intercalated ultramicroporous calcium oxalate (CaC_2O_4) probed using neutron powder diffraction**
  - Strong correlation identified between D_2 loading pressure and storage capacity
    - Adsorption requires dosing at T > 175 K and P > 250 torr
  - Changes in diffraction pattern upon intercalation consistent with D_2 adsorption between Ca^{2+} and O^{2-} (more work is required to fully understand the data)





Neutrons locate adsorbed D_2 in ultra-micropores

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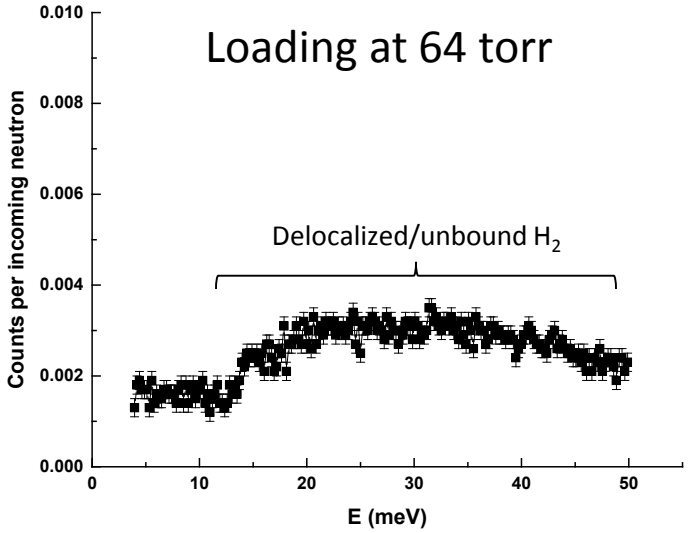
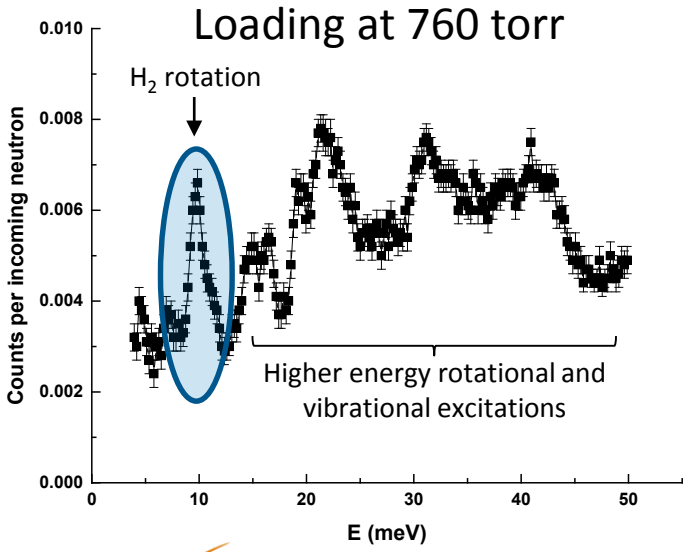
Accomplishments and Progress: Oxocarbons

- **Local dynamics of H_2 adsorbed in CaC_2O_4 probed using inelastic neutron spectroscopy (INS)**
  - Loading at low pressure (<250 torr) leads to weakly bound H_2
  - Loading at atmospheric pressure (760 torr) leads to discrete localized adsorption sites
    - Peak near 10 meV consistent with transition from J=0 to to a sub-level of the J=1 rotational state of H_2
    - More detailed loading dependence and isotopic substitution should help assign remaining peaks to rotation or rotation+phonon coupled peaks





INS indicates adsorption of H_2 in ultra-micropores

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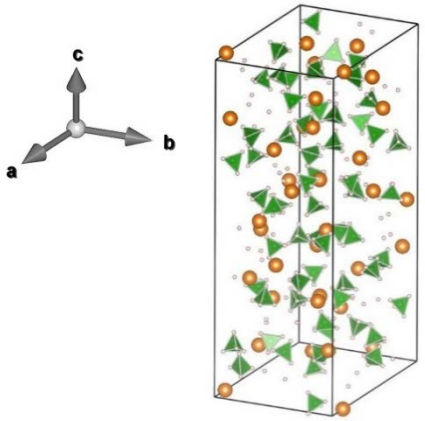
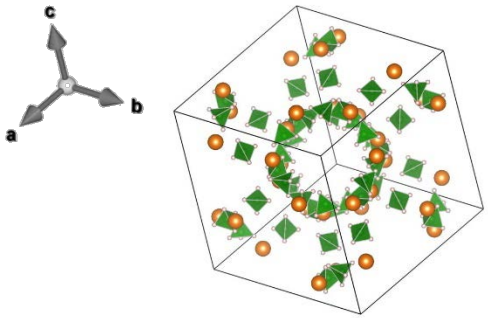
Accomplishments and Progress: Borohydrides

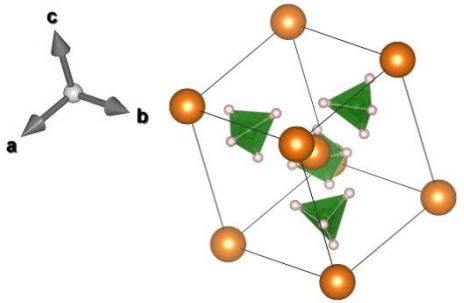
- **Structural and phase dynamics in $Mg(BH_4)_2$ probed with inelastic neutron spectroscopy**
  - Three potential polymorphs identified



α-$Mg(BH_4)_2$
$P6_122$



γ-$Mg(BH_4)_2$
Ia-3d



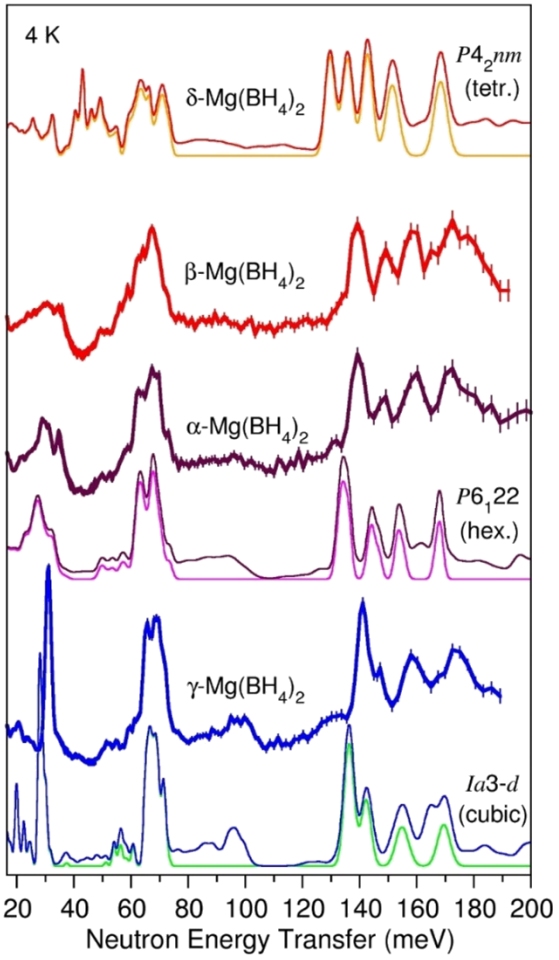
δ-$Mg(BH_4)_2$
$P4_2nm$

Mg B H

Motivation: INS can be used as a fingerprint in non-crystalline environments

Accomplishments and Progress: Borohydrides

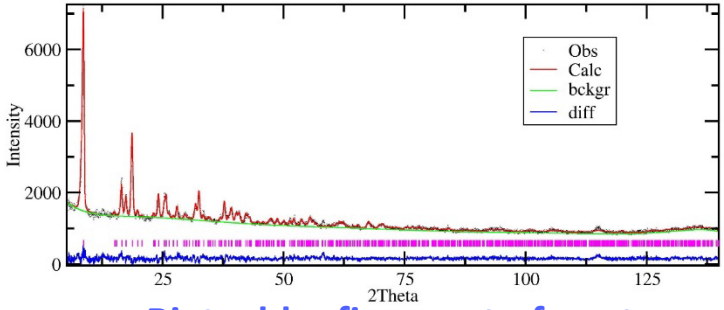
- **Neutron vibrational spectra of different $Mg(BH_4)_2$ polymorphs**
  - Measured at 4 K
  - Agreement established with one-phonon and one+two-phonon densities of states simulated from first-principles phonon calculations of the DFT-optimized structures



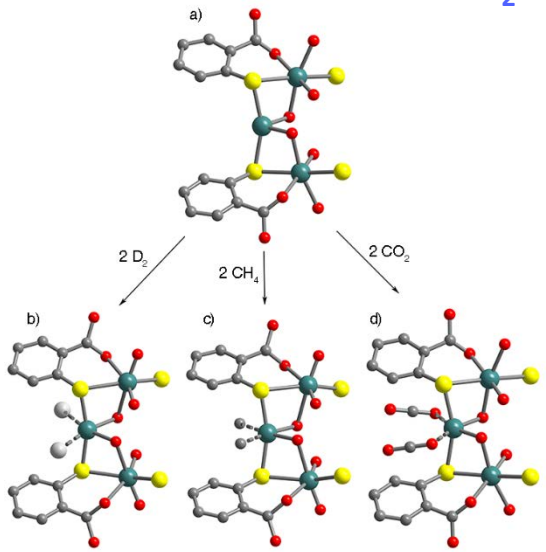
Most intense peaks are due to H-motion: clear signature of different polymorphs

Accomplishments : MOFs (Metal Organic Framework)

- **Identify multiple H_2 binding at a metal site in a MOF**
  - Mn_2(dsbdc)
  - Successful desolvation and activation
  - X-ray and Neutron Diffraction
  - D_2 adsorption sites determined.



Rietveld refinement of neutron diffraction data for 0.75 D_2 : Mn



Mn can bind multiple gas molecules on one metal site

D_2 and other gases have similar binding characteristics. Clear but weak interactions.

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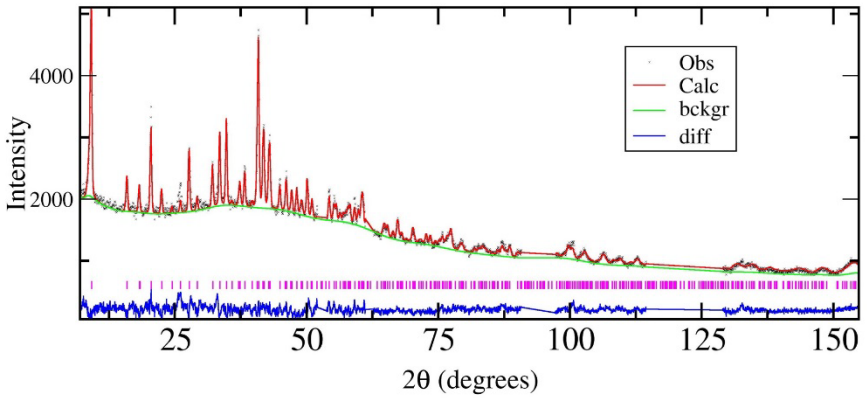
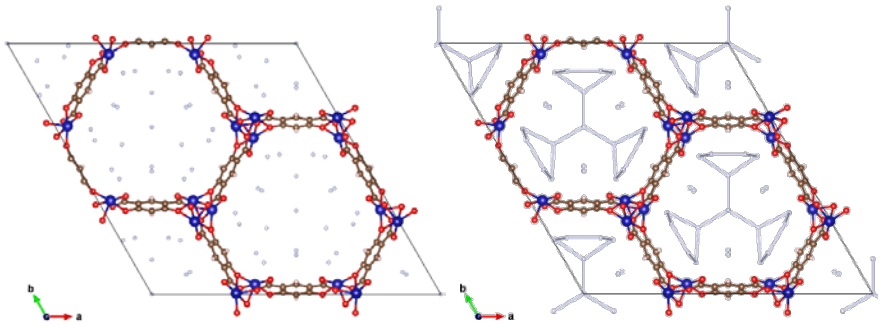
Accomplishments and Progress: MOFs

- **Volumetric capacities at pressure in MOFs**
  - Moderately high pressure neutron diffraction
  - Determine loadings and adsorption distributions in Co_2(m-dobdc) and Ni_2(m-dobdc)
  - Refines to 3.5 D_2:Co

Determine maximum crystallographic volumetric capacities independently from manometry



Rietveld refinement of neutron diffraction data for Co_2(m-dobdc) at 78 bar D_2 pressure



Shorter than bulk D_2-D_2 distances

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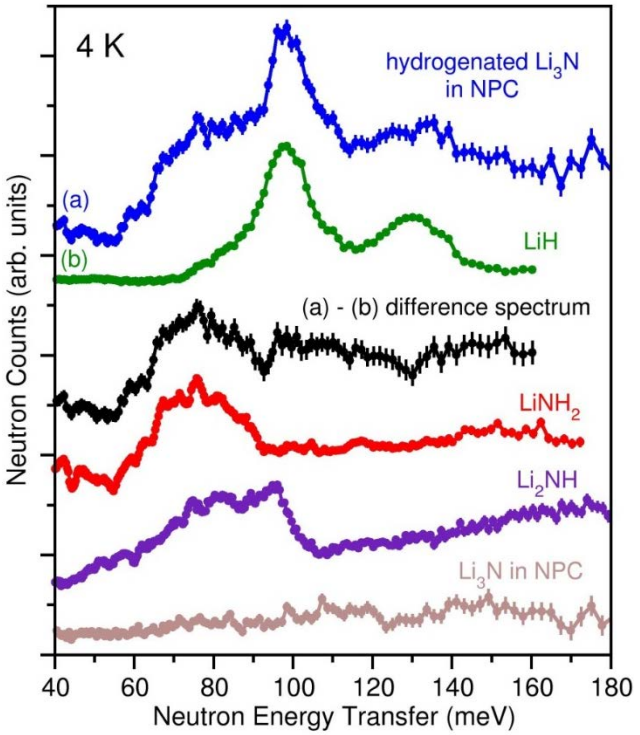
Accomplishments and Progress: Confined phases

- **Determining products of hydrogenated Li_3N in nanoporous carbon**
  - Neutron vibrational spectra associated with hydrogenated Li3N confined in nanoporous carbon (NPC) after 5 desorption/absorption cycles compared to reference spectra indicate that:
  - Relatively little H exists in the dehydrogenated spectrum (Li_3N in NPC)
  - Both $LiNH_2$ and LiH are present in the hydrogenated spectrum
  - Nanoconfinement fundamentally alters both the hydrogenation and dehydrogenation reaction pathways as a direct consequence of solid-solid nanointerfaces

INS used to identify hydrogen-containing phases that cannot be probed easily by other means

Lawrence Livermore National Laboratory

Sandia National Laboratories



Neutron vibrational spectroscopy confirms that both $LiNH_2$ and LiH are hydrogenation products from carbon-nanoconfined Li_3N, with no obvious presence of Li_2NH.

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Collaborations

- **NREL/NIST collaboration**
  - Characterizing ultra-microporous materials using neutron diffraction and neutron spectroscopy
- **NREL/NIST collaboration with LBNL**
  - Characterizing hydrogen adsorption in metal organic framework materials using neutron diffraction and neutron spectroscopy
  - Characterizing various hydrogen storage materials at the Advanced Photon Source
- **NREL/NIST collaboration with SNL**
  - Developing spectroscopic signatures for $Mg(BH_4)_2$
- **NREL/NIST collaboration with LLNL and SNL**
  - Identifying phases for complexes in pores
  - Determining products of hydrogenated Li_3N in nanoporous carbon

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Proposed Future Work

- **Finish work on current projects**
  - Identify precise binding sites for hydrogen adsorbed in ultra-microporous oxocarbons. Establish influence of metal cation on binding distance and hydrogen capacity
  - Complete pressure dependence of volumetric capacities for MOFs
- **Continue to advance the use of neutron scattering to validate materials and concepts**
  - As determined through collaborations and discussion with EERE and HyMarc

Critical Assumptions and Issues

- **Refinement of powder diffraction patterns for oxocarbons complicated by presence of additional phases**
  - Need to determine whether additional phases stem from contaminants or represent polyphases of oxocarbon

Critical Assumptions and Issues

- **Oxocarbons (specifically, CaC_2O_4) exhibit unusual behavior upon thermal cycling**
  - In-situ x-ray diffraction at APS planned to measure structural changes upon activation, thermal cycling, and hydrogen dosing of oxocarbons

Publications

- Outlook and challenges from hydrogen storage in nanoporous materials. D. P Broom, C. J. Webb, K. E. Hurst, P. A. Parilla, T. Gennett, C. M. Brown, R. Zacharia, E. Tylianakis, E. Klontzas, G.E. Froudakis, Th. A. Steriotis, P. N. Trikalitis, D. L. Anton, B. Hardy, D. Tamburello, C. Corgnale, B. A. van Hassel, D. Cossement, R. Chahine, M. Hirscher. *Appl. Phys. A*. 122; 151, 2016.

- Hydrogen Storage in the Expanded Pore Metal-Organic Frameworks M_2(dobpdc) (M = Mg, Mn, Fe, Co, Ni, Zn). Gygi, D.; Bloch, E. D.; Mason, J. A.; Hudson, M. R.; Gonzalez, M. I.; Siegelman, R. L.; Darwish, T. A.; Queen, W. L.; Brown, C. M.; Long, J. R. Chem. Mater. 2016, 28, 1128-1138.

- Dynamics of Pyramidal SiH_3^- Ions in $ASiH_3$ (A = K and Rb) Investigated with Quasielastic Neutron Scattering. C. Österberg, H. Fahlquist, U. Häussermann, C. M. Brown, T. J. Udovic, M. Karlsson, J. Phys. Chem. C 120, 6369, 2016.

- Hydrogen Storage and Selective, Reversible O_2 Adsorption in a Metal-Organic Framework with Open Chromium(II) Sites. Bloch, E. D.; Queen, W. L.; Hudson, M. R.; Mason, J. A.; Xiao, D. J.; Murray, L. J.; Flacau, R.; Brown, C. M.; Long, J. R., Angew. Chem. Accepted.

- Adsorption of Two Gas Molecules at a Single Metal Site in a Metal-Organic Framework. Runčevski, T.; Kapelewski, M. T.; Torres-Gavosto, R. M.; Tarver, J. D.; Brown, C. M.; Long, J. R., submitted.

- Nanointerface-driven Reversible Hydrogen Storage in the Nanoconfined Li-N-H System, B.C. Wood, V. Stavila, N. Poonyayant, T. W. Heo, K. G. Ray, L. E. Klebanoff, T. J. Udovic, J.R. I. Lee, N. Angboonpong, P. Pakawatpanurut, submitted.

Key: NREL, NIST, LBNL, SNL

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Technical Slides: Sample preparation

- Samples activated by slowly heating in tube furnace under dynamic vacuum (~10^{-7} torr)
- Samples transferred to He-filled dry box with < 0.1 ppm H_2O and < 5 ppm O_2 and sealed to copper blocks using an indium o-ring
- Stainless steel tubing connected to copper blocks permits delivery of D_2/H_2 to sealed sample
- Samples mounted onto bottom-loading closed cycle refrigerator and connected to gas delivery manifold of known volume
- Residual He removed using turbo molecular pump

Technical Slides: Neutron Powder Diffraction

- **High resolution neutron powder diffraction data collected at 7 K using a Ge(311) monochromator with an in-pile 60’ collimator**
  - Instrument: BT1
  - Corresponds to λ = 2.078 Å
- **Initial measurements collected on evacuated bare sample**
- **Volumetric dosing of D_2 performed above 20 K with incrementally increasing amounts**
  - Full adsorption ensured by letting pressure fall to zero
- **Sample + adsorbed D_2 cooled to 7 K for measurement**

Technical Slides: Inelastic Neutron Spectroscopy

- **Inelastic neutron spectra collected using the Filter Analyzer Neutron Spectrometer (FANS)**
- **Residual He removed using turbo molecular pump**
- **Spectra collected at 7 K using a pyrolytic graphite (002) monochromator with 20'-20' collimation**
  - Corresponds to energy range of 4.1 – 49.6 meV, resolution of 1.1 meV
- **Volumetric dosing of H_2 performed above 20 K with incrementally increasing amounts**
  - Full adsorption ensured by letting pressure fall to zero
- **Sample + adsorbed H_2 cooled to 7 K for measurement**