Hydrogen Storage Materials with Binding Intermediate Between Chemisorption and Physisorption

A. K. Cheetham and J. Eckert
Materials Research Laboratory UC Santa Barbara
G. J. Kubas, C- Division, LANL

This presentation does not contain any proprietary or confidential information

Project ID
STP50
Evolution of Open Framework Materials

Can this type of material be designed to strongly bind a large amount of hydrogen?
Nanoporous Nickel Phosphates

• VSB-1:
  – \( \text{Ni}_{18}(\text{HPO}_4)_{14}(\text{OH})_3\text{F}_9(\text{H}_3\text{O}^+,\text{NH}_4^+)_4 \cdot 12 \text{H}_2\text{O} \)
  – Synthesized under acidic conditions with \( \text{F}^- \)

• VSB-5
  – \( \text{Ni}_{20}[(\text{OH})_{12}(\text{H}_2\text{O})_6][(\text{HPO}_4)_8(\text{PO}_4)_4] \cdot 12 \text{H}_2\text{O} \)
  – Synthesized under basic conditions without \( \text{F}^- \)


Porosity of VSB-5

Guillou et al, Angew. Chemie, 40, 2831 (2001)
Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials

H$_2$ uptake (77K) on the basis of weight

H$_2$ adsorption, cm$^3$/g

- VSB-5
- ZSM-5
- Activated Carbon
- VSB-1
Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials

H₂ uptake (77K) on the basis of volume

H₂ adsorption, cm³/cm³

VSB-5
ZSM-5
Activated Carbon

H₂ pressure (torr)
Adsorption of Molecular Hydrogen in microporous Ni(II) phosphate VSB* materials

Removal of water in VSB-5 creates unsaturated metal binding sites

VSB-5 $\text{Ni}_{20}[\text{(OH)}_{12}(\text{H}_2\text{O})_6][(\text{HPO}_4)_8(\text{PO}_4)_4]12\text{H}_2\text{O}$

$\text{H}_2$ rotational tunneling transition at $\sim 1.5\text{ meV}$ - $1/10$ of that in carbons!!!!

Rotational Tunneling Spectra by Inelastic Neutron Scattering - VSB-5 at 10 K

![Graph showing rotational tunneling spectra](image)

- Tight bound $\text{H}_2$
- Loaded, 1 $\text{H}_2$/ formula unit
- Unloaded VSB-5

Energy Transfer/ meV
Hydrogen Adsorption in VSB-5

- All the evidence points to molecular chemisorption of H₂ at low loadings, followed by physisorption at higher ones.
- Hydrogen probably binds to pentacoordinated nickel sites that are exposed following dehydration.
- Can we make systems that contain more of these sites?

Water lost on dehydration?
Hydrogen Storage for Mobile Applications: lower operating pressures?

Can we tune the guest-host interaction of the hydrogen molecule into the range between physisorption and (dissociative) chemisorption – i.e. that of the molecular hydrogen complexes? (10-20 kJ/mol) – AND make materials with enough of these sites??

(1) Create highly porous material with many (unsaturated) metal binding sites (Cheetham et al.: Ni-5sulfoisophthalate, below right)
(2) Support metal-(multiple-)dihydrogen complexes in porous material (Kubas)

\[ \text{NaNi}_3(\text{SIPA})_2(\text{OH})(\text{H}_2\text{O})_5.\text{H}_2\text{O} \]


Objectives:

- Primary goal is to synthesize and characterize new lightweight materials for storage of hydrogen as molecular hydrogen ($H_2$) at the interface of physisorption and chemisorption, i.e. where $H_2$ binds moderately strongly yet reversibly.

- The ability to sorb and desorb $H_2$ rapidly and reversibly using only moderate pressure and/or temperature swings without accompanying chemical reactions is a critical factor in the design and application of these materials.

$X, Y, Z =$ light main-group atoms:

e.g. Li, Be, B, C, N, O, F

$X$ could also be transition metal such as iron embedded in framework and capable of binding multiple $H_2$

$H_2$ gas rapidly diffuses in and out; dissociation pressure ~1-100 atm

Reversible molecular hydrogen binding in $W(CO)_3(P-i$-$Pr_3)_2(H_2)$ discovered by Kubas and coworkers. Over 500 metal–$H_2$ complexes are now known.
Molecular Chemisorption of Hydrogen

ZSM-5: largest surface area among zeolites (~500 m²/g)

Hydrogen (1/Fe) adsorbed (at 70K) in “over-exchanged” Fe-ZSM-5
INS data collected on NEAT at Hahn-Meitner Institut, Berlin, Germany

Observation:
Two pairs of peaks, (+/-) 4, 8 cm⁻¹
Much lower energy than (e.g.) NaA
Comparable with H₂ bound in Fe complexes
Example: FeH₂(η²-H₂)(PEtPh₂)₃

Figure 4. Rotational tunneling spectrum of the H₂ ligand in Fe(H)₃
(H₂)(PEtPh₂) obtained at 1.5 K on the INS spectrometer at the ILL.
Challenges and Technical Approach

- Weight% $H_2$ too low in $M-H_2$ complexes; need to increase
- Temperature/pressure ranges and limits to reversibly adsorb $H_2$ need to be studied
- New supramolecular materials as well as molecular metal compounds binding multiple $H_2$ will be synthesized and tested for $H_2$ adsorption.
- “Naked” transition metal cations are capable of binding up to six $H_2$ molecules in the gas-phase, e.g. $[Fe(H_2)_n]^+$. We will investigate synthesizing such hydrogen-rich species in the condensed phase, e.g. in ionic liquids, and embed in MOF structures.

$$MCl_2 + 2Ag^+ \xrightarrow{\text{ionic liquid}} H_2 [M(H_2)_n]^{2+} + 2AgCl$$

Also likely to form: $[MH_2(H_2)_n]$ $[M(\text{anion})_2(H_2)_n]$

Bimetallic bridging halide species $M-Cl-Ag$

A better route may be:

$$M(R)_2 + 2H^+ \xrightarrow{\text{ionic liquid}} H_2 [M(H_2)_n]^+ + 2RH$$

- Sieverts apparatus designed at LANL will be used to measure $H_2$ adsorption and desorption on gram amounts of solids at pressures of 0-27 atm at 4-700 K.
A Thermally Stable Nickel 5-Sulfoisophthalate
5-Sulfoisophthalate

Weight loss (%) vs. Temperature (°C)

- Water
- Acetonitrile
- Ethanol
- Methanol
Rotational tunneling spectra of H$_2$ in Nickel 5-Sulfoisophthalate
(QENS, IPNS(ANL), April 2005)

Spectra (shown as a function of H$_2$ loading) reveal several well-defined binding sites with strong guest-host interaction
( $>>$ than carbons or MOF-5)
Acknowledgements

• Funding: DOE
• Neutron Scattering Facility: IPNS/ANL
• Collaboration:
  Prof. Gérard Férey (Versailles)
  Dr. Nathalie Guillou (Versailles)
  Dr. Qiuming Gao (Versailles/UCSB)
  Dr. Marc Nogues (Versailles)
  Dr. Jong-San Chang (UCSB/KRICT)
  Dr. Sang-Eon Park (KRICT-Taejon))
  Dr. Paul Forster (UCSB; now SUNY-SB)
  Brandon Heiken (UCSB)