Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

Juergen Eckert
University of California Santa Barbara
May 20, 2009

Project ID:
STP_05_Eckert

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
• Project start date: 4/1/2005
• Project end date: 3/31/2010

Budget
• Total project funding
  – DOE share: $1,199,073
  – Contractor share: $299,674
• Funding received in FY08
  $ 320,000 (appr.)
• Funding expected in FY09
  $ ??

Barriers
• Barriers addressed: Hydrogen Storage
  (B) System Weight and Volume
  (F) Efficiency

Partners
• A. K. Cheetham (co-P.I.) Cambridge, UK
• G. J. Kubas, LANL
• University of California, Santa Barbara (host site)

Collaborators
• A. Albinati (U. di Milano, Italy)
• M. Eddaoudi (USF)
• M. Sodupe Roure (UA Barcelona, Spain)
• P. Dietzel (U. of Oslo, Norway)
• P. Forster (UNLV)
Overall Objective

Develop hydrogen storage materials for reversible on-board applications with hydrogen binding energies intermediate between physisorption and (dissociative) chemisorption

• Sorption based storage materials have a several factors* in their favor - but we must Improve Hydrogen Binding - without loss of capacity (but not too much: preserve ease of desorption) to reduce RT operating pressures (but not too low: 2 atm ~ empty)

• Goal is to reach binding energies of 15 - 25 kJ/mol

1. Appropriate thermodynamics (favorable enthalpies of hydrogen absorption and desorption)
2. Fast kinetics (quick uptake and release)
3. High storage capacity (at low temperature)
4. Effective heat transfer
5. Long cycle lifetime for hydrogen absorption/desorption
Path to Sorption-based Material with greater $\text{H}_2$ binding Energy

**Molecular** Chemisorption at Unsaturated (Transition) Metal Binding Sites
(part of the framework, or extraframework)

$\Rightarrow$ binding energies can easily reach $>> 20 \text{ kJ/mol}$

- Density too high?
- Not enough such sites?

Bind Multiple Dihydrogen Ligands

Lighter Metals: alkali, alkaline earth hybrids

Framework Modifications: fluorinated linkers, reduction in pore size, anionic frameworks with cations

Combine two or more of these approaches in one material
Approach

(1) Focus **first** on synthesis of materials, which bind molecular H$_2$ more strongly than most MOF’s, using the following approach:
   (a) Materials with unsaturated metal binding sites combined with
   (b) Framework modifications

(2) Then synthesize analogs with larger surface areas

1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes)

   create porous material with large numbers of unsaturated and accessible metal sites, as part of the framework, or extraframework cations, or post-synthesis insertion

   address ‘weight penalty’ by binding multiple dihydrogen ligands to the open metal sites

   **OR**

   hybrid materials with lighter metals instead of transition metals

*Grellier et al. JACS 127, 17592 (2005)*
Approach

1b. Use fluorinated organic linkers and reduce pore size: increases $H_2$ binding by > 50%

1c. Characterize Binding of Hydrogen by Bulk Measurements and Inelastic Neutron Scattering

1. Adsorption isotherms, porosity, TPD, etc.

2. Structural studies: sorption sites,

3. Computational work (in collaboration)

4. Extensive use of Inelastic Neutron Scattering from the hindered rotations of the sorbed hydrogen molecule: THE most sensitive probe of $H_2$ interactions with host

(BUT: QENS spectrometer w/IPNS/ANL was SHUT DOWN - must use mainly European Neutron Sources in the near term)
Technical Accomplishments
Progress/Results

- Experimental observation of the existence of MOLECULAR chemisorption of hydrogen in several porous materials, including possibly the presence of multiple dihydrogen ligands on one metal site
- Synthesized and characterized structures of a series of hybrid materials using alkaline earths and alkali metals with a highly functionalized organic link
- Synthesized and characterized several novel hybrids with mixed fluorinated and normal organic links
- Demonstrated a ~50% increase in binding energies for fluorinated linkers
- Synthesized an analog of Zn(Im)$_2$: LiB(Im)$_4$ or LiB(C$_3$N$_2$H$_3$)$_4$ with the dense zni structure
- Showed that H$_2$ interactions with extraframework cations are nearly always greater than with “open” metal sites that are part of the framework
- Computational studies on H$_2$ binding at Fe and Cu inserted into ZSM-5 show formation of true dihydrogen coordination, binding energies from 13.5 to 74 kJ/mol
Accomplishment: Synthesis of Hybrid Materials with Alkali Metal Centers and a Highly Functionalized Organic Link:
Cs-Thz, Rb-Thz, K-Thz: 3D structures; Na-Thz is 2-D (H-bonds keep the layers together. K-Thz is anhydrous.
Water molecules in Rb-Thz: coordinating, coordinating/ cation-bridging, and “free” (H-bonded).
Accomplishment: development of novel, partially fluorinated hybrids

- our earlier attempts to make porous perfluorinated hybrids* were unsuccessful
- attempt make partially fluorinated hybrides with open metal sites
- explore this “ligand-metal space”:

```
1,2,4-triazole
2,2’-bipyridine
4,4’-bipyridine

F₄-isophthalate  F₄-terephthalate  F₄-succinate  F₄-hydroxybenzoate
```

Example: Cu(F₄-succinate)(4,4’-bpy)

2-D layered structure
Dimer of Cu²⁺ trigonal bipyramids connects four F₄-succinate ligands

Accomplishment: partially fluorinated structures with 4,4’-bpy

\[ \text{Co(F}_4\text{-succinate})(4,4’\text{-bpy})(\text{H}_2\text{O})_2 \]
\[ (\text{Co/Zn})(\text{F}_4\text{-isophthalate})(4,4’\text{-bpy})(\text{H}_2\text{O}) \]

Structures have same basic connectivity

Pink/blue = 4,4’-bpy
Green = F\(_4\)-succinate or F\(_4\)-isophthalate
Aqua = Metal
Red = Water

Interesting and complicated 3-D structure built up from two different 1-D metal-bpy chains and one 1-D zig-zag F\(_4\)-succ/ipa chain
Accomplishment: partially fluorinated structures with 2,2’-bpy

\[ \text{Cu(F}_4\text{-succinate)}(2,2’\text{-bpy}) \cdot 0.5 \text{H}_2\text{O} \]

- **Polar 3-D structure**
- **Dimer of Cu\(^{2+}\) square pyramids connects to four F\(_4^-\) succinate ligands**
- **Potential for porosity, problem with purity**

\[ \text{Mn(F}_4\text{-isophthalate)}(2,2’\text{-bpy}) \cdot 0.5 \text{H}_2\text{O} \]

- **2-D layered structure**
- **Dimer of Mn\(^{2+}\) trigonal prisms connects through four F\(_4^-\) isophthalate ligands**
Zn-triazolate

layers composed of two hexagonal arrays (left)

Layers connected by F₄-terephthalate to give porous 3-D structure

Desolvated structure contains 4 Å × 7 Å channel; adsorbs 0.4 wt% H₂ at 77 K, 1 atm

Adsorption enthalpy ~ 8 kJ/mol, among highest reported for purely physisorptive interaction

Binding energies increased by more than 50% relative to conventional MOF’s: result of fluorinated surface, small pores

Accomplishment ‘08: Zn₂.₅(1,2,4-triazole)₃(tetrafluoroterephthalate)(H₂O) . 2H₂O

Accomplishment:
Demonstration of the Existence of True Molecular Chemisorption of Molecular Hydrogen with large binding energies

New computational studies of \( \text{H}_2 \) in Fe - and in Cu-ZSM-5:
- binding energies in Fe-ZSM-5 are much lower (13.5 kJ/mol - FeO species) than in Cu-ZSM-5 (70 kJ/mol, Cu(I)).
- Second \( \text{H}_2 \) can bind at Cu site

Follow-up on our previous observations:
- Room temperature \( \text{H}_2 \) isotherms in Cu-ZSM-5
- Hydrogen in Cu-ZSM-5
- THE FIRST observation: Hydrogen adsorbed in “over-exchanged” Fe-ZSM-5
- Unsaturated Ni binding sites in the Nickel Phosphate VSB-5 and in Nickel-5-Sulfoisophthalate

Note: Tunnel splitting in Fe-ZSM-5 >> Cu-ZSM-5 ⇒ Binding energy in Fe-=ZSM-5 lower
Accomplishment: Cluster models for $\text{H}_2$ binding at Fe and Cu sites in ZSM-5

Comparison with Fe-dihydrogen complex (single crystal neutron diffraction)

Fe-H = 1.57, 1.61 Å
H-H = 0.82 Å

Xavier Solans-Montford and Mariona Soodupe Roure, Universitat Autònoma de Barcelona, Spain
Accomplishment: Periodic models for H$_2$ binding at Fe and Cu sites in ZSM-5

\[
\begin{array}{cccc}
\text{(kJ/mol)} & \mathbf{E_{\text{ads}}} & \mathbf{E_{\text{INT}}} & \mathbf{D} \\
\text{(I) Cu} & -15.0 & -7.2 & -7.8 \\
\text{(I) Fe} & -8.7 & -0.7 & -8.0 \\
\text{(IV) Cu} & -69.9 & -58.2 & -11.7 \\
\text{(IV) Fe} & -13.0 & -2.3 & -10.7 \\
\end{array}
\]
Accomplishment: Rotational Barriers for H$_2$ in Fe- and Cu-ZSM-5 - Comparison of Calculations with Experiment

INS results

\[ \omega_t = 1 \text{ cm}^{-1} \]

\[ V_2 \sim 9 \text{ kJ/mol} \]

Calculation

\[ V_2 \sim 13 \text{ kJ/mol} \]

\[ \omega_t = 4 \text{ cm}^{-1} \]

\[ V_2 \sim 4 \text{ kJ/mol} \]

\[ V_2 \sim 6.5 \text{ kJ/mol} \]
Accomplishment: Investigation of the Origin of the Loading dependence of $Q_{st}$ in Cu-ZSM-5

Population of different sites? Binding of multiple $H_2$ ligands?

Second $H_2$ binds only with dispersive forces, $\sim 9$ kJ/mol
Accomplishment: INS studies of $\text{H}_2$ adsorption at “open” metal sites - in-framework vs. extraframework (zeolite) metal sites

Cu in
Cu-ZSM-5 ~0.15 meV
CuNaA ~ 3 meV
Cu-ATC (MOF-11) ~ 8 meV
Cu-BTC (HKUST-1) ~ 9 meV

Ni in
VSB-5 ~ 1.5 meV
NiNaA ~ 2.9 meV
Ni-SIPA ~ 4, 5.5 meV
Ni-CPO-27 ~ 6.6 meV

Why the big differences?
⇒ location, location !! (M-$\text{H}_2$ distance):
2.39 Å in HKUST-1*, ~ 1.7 Å for coordinated $\text{H}_2$

*Smaller value = larger barrier

*V. K. Peterson, Y. Liu, C. M. Brown and C. J. Kepert, JACS 2006, 128, 15578
Accomplishment: INS studies of Li\(^+\) in zeolites

Li\(^+\) is effective for H\(_2\) binding - BUT ONLY when highly undercoordinated and exposed

Li\(^+\) locations are similar as for NaA, except that Site III is not occupied by Li\(^+\)

Instead: One or two cations offset in 8-ring window (site II):

Li\(^+\) in six-ring window (site I) is NOT very effective (~ Na\(^+\), etc.), ~ 8 meV

One or two EXPOSED cations (sites II) make for much stronger interaction: H\(_2\) rot. transition at ~ 1 meV

Accomplishment: Synthesis of Ultra Lightweight ZIFs

I-III Analogues of Zn(Im)$_2$: LiB(Im)$_4$

We have synthesized LiB(C$_3$N$_2$H$_3$)$_4$ with the dense zni structure; DFT calculations show that the sodalite and zeolite-A analogues should also be accessible (SOD recently confirmed by Feng & Bu, Angew. Chem. 2009)
Future Work: Phase 2

• Improvements in Ni-SIPA* to raise binding energies from the current 10-11 kJ/mol
  • use metals other than Ni; will effect pore size as well
  • substitute Li, K, or Rb for Na

• Create highly undercoordinated metal binding sites in MOF’s by insertion
  • use approaches similar to that in ZSM-5 in high-T stable MOF’s (e.g. CuCl vapor)
  • may require prior modification of surface to bind metal, metal-oxide

• Fluorinated linkers in hybrid materials
  • synthesize materials with open metal sites other than Zn
  • achieve greater porosity (larger links - see below)
  • demonstrate the expected increase in H$_2$ binding to well above 10 kJ/mol

* Initial result: zinc, 1, and tetrafluoroterephthalate

* our first hybrid to exceed 10 kJ./mol binding energy
Summary

- Demonstrated the Presence of True Molecular Chemisorption of Hydrogen in a number of porous materials ⇒ higher binding energies than physisorption
  - from 10 kJ/mol (Ni-SIPA), to 13.5 kJ/mol (Fe-ZSM-5) to well over 70 kJ/mol (Cu-ZSM-5)

- Synthesized a large number of new hybrids with mixed fluorinated and organic linkers and decreased pore size
  - binding energies increase by some 50% vs. typical MOF’s

- Utilization of INS on the H$_2$ hindered rotor: most sensitive technique for the study of H$_2$/host interactions at specific binding sites

- Open metal sites must very closely accessible by H$_2$; this is much more likely at extra-framework metal sites, and difficult for in-framework “open” metal sites

- Transition metal sites in porous materials ⇒ weight penalty may be addressed by
  - Use of lightweight frameworks
  - Investigated the possibility of binding multiple dihydrogen ligands
    - requires highly undercoordinated metal sites

- Combination of the above should make it possible to reach ~ 20 kJ/mol or better

- Practical materials of this type need increased surface area