DOE Hydrogen Program

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 H_2 binding Energy

Molecular Chemisorption at Unsaturated (Transition) Metal Binding Sites
(part of the framework, or extraframework)
⇒ **binding energies can easily reach >> 20 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

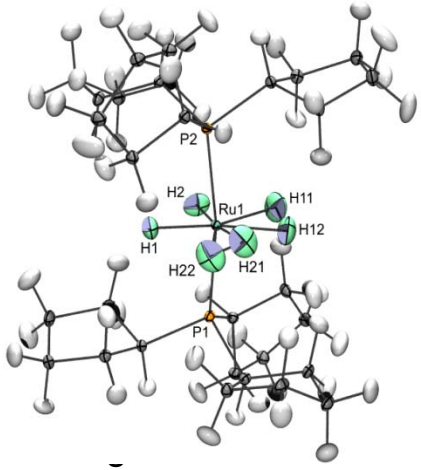
Approach

(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

*$RuH_2(H_2)_2[P(c\text{-pentyl})_3]_2$



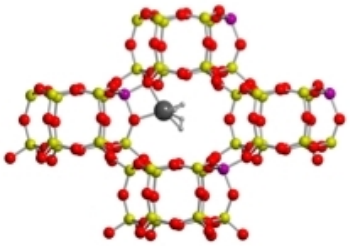
1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes)

create porous material with large numbers of unsaturated and accessible meta 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

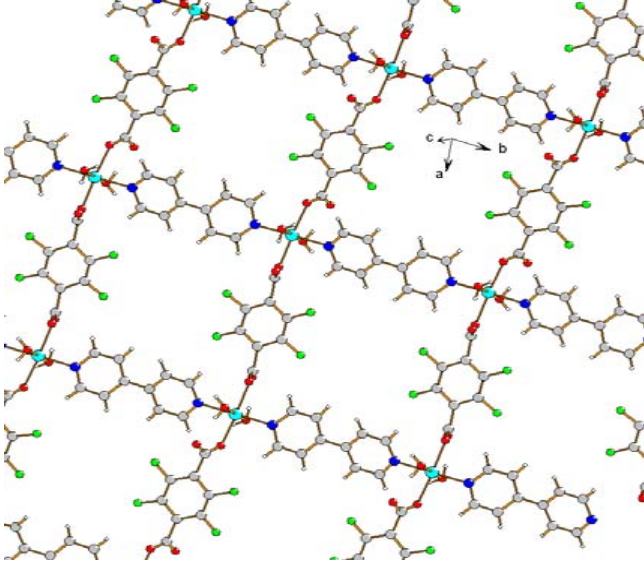
OR

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

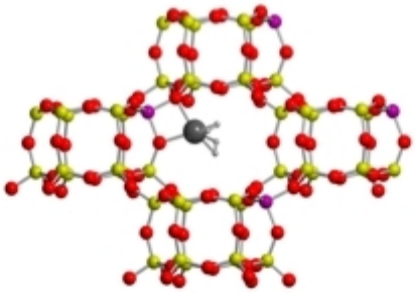
1. Adsorption isotherms, porosity, TPD, etc.

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/ANLwas **SHUT DOWN - must use mainly European Neutron Sources in the near term)**

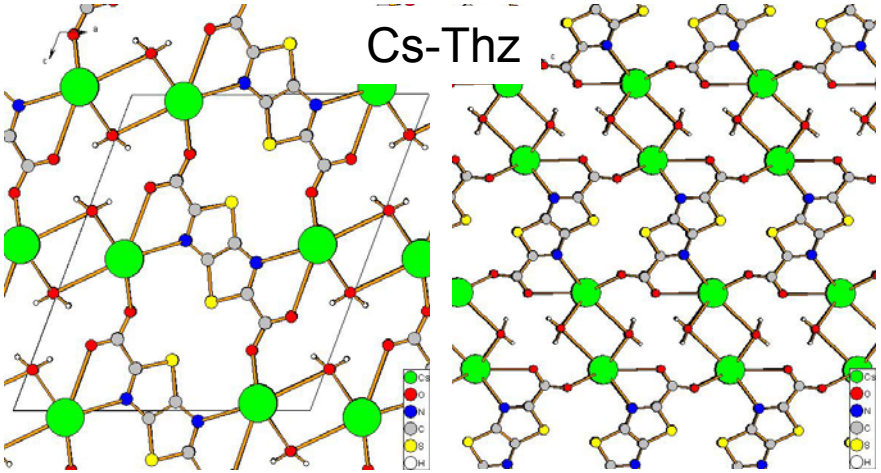


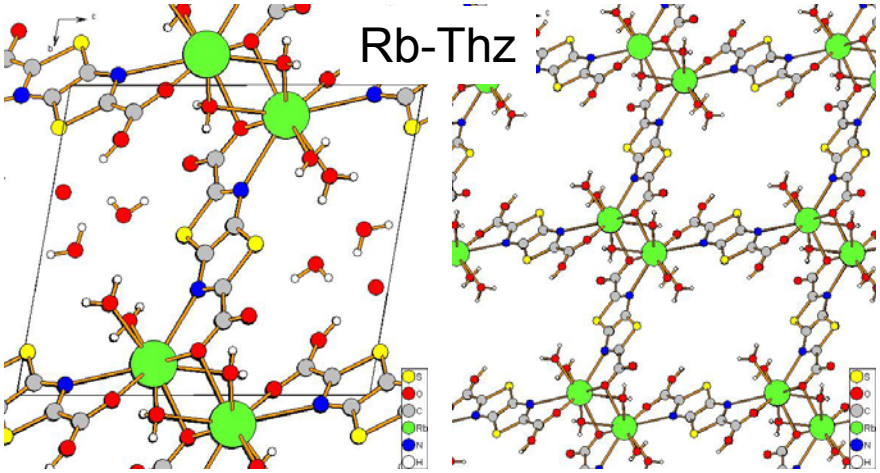
Technical Accomplishments
Progress/Results

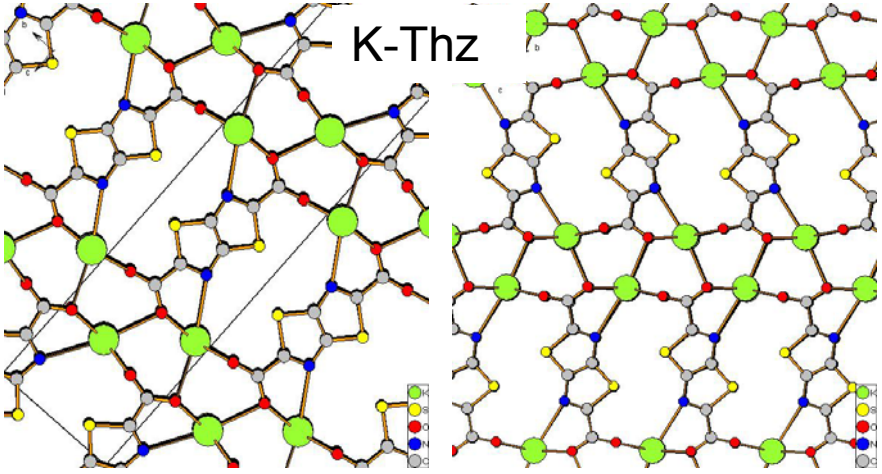
- Experimental observation of the existence of MOLECULAR chemisorption of hydrogen in several porous materials, including possibly the presence of multiple dihydrogen ligands on one metal site
- Synthesized and characterized structures of a series of hybrid materials using alkaline earths and alkali 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 $LiB(C_3N_2H_3)_4$ 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

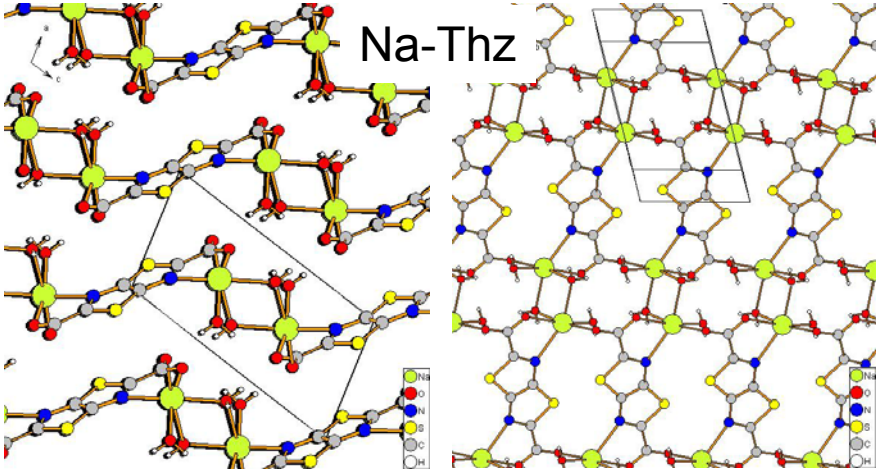
Accomplishment: Synthesis of Hybrid Materials with Alkali Metal Centers and a Highly Functionalized Organic Link:

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).



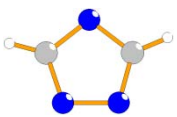




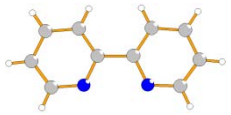


Accomplishment: development of novel, partially fluorinated hybrids

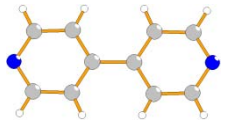
- our earlier attempts to make porous perfluorinated hybrids* were unsuccessful
- attempt make partially fluorinated hybrides with open metal sites
- explore this "ligand-metal space":



1,2,4-triazole

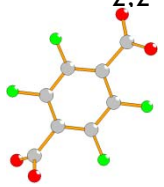


2,2'-bipyridine

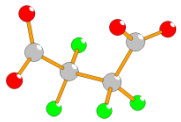


4,4'-bipyridine

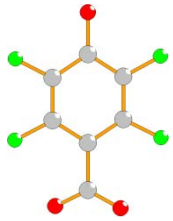
F_4-isophthalate



F_4-terephthalate

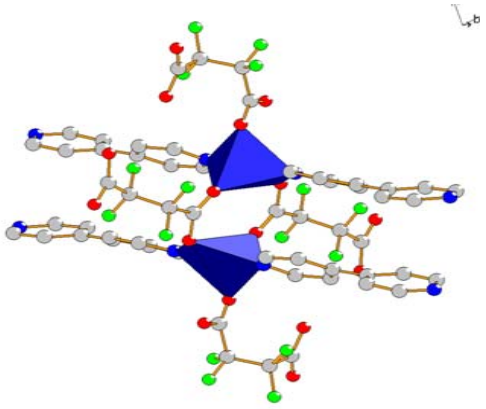


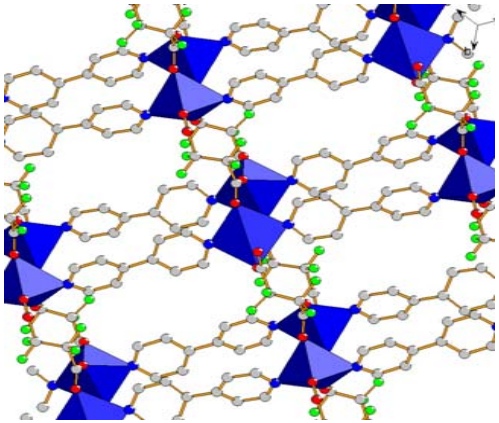
F_4-succinate



F_4-hydroxybenzoate

Example: Cu(F_4-succinate)(4,4'-bpy)





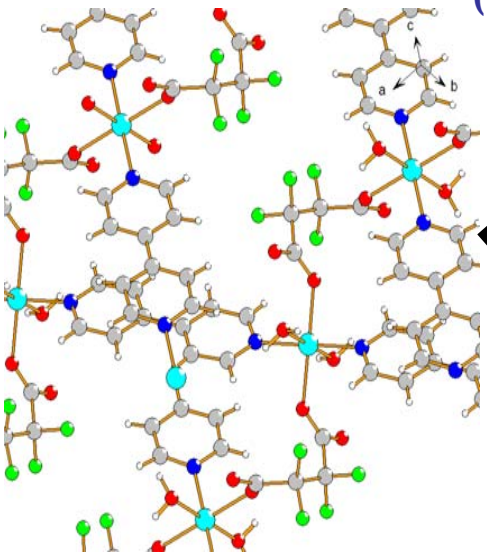
2-D layered structure

Dimer of Cu^{2+} trigonal bipyramids connects four F_4-succinate ligands

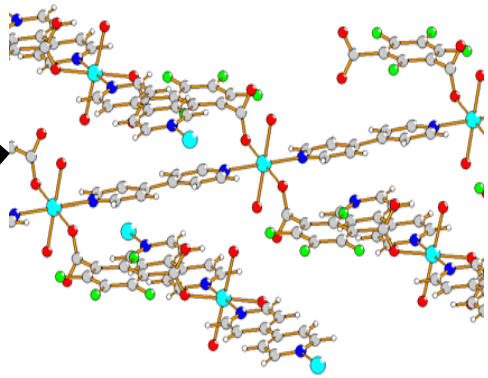
* Z. Hulvey, D. S. Wragg, Z. Lin, R. E. Morris and A. K. Cheetham Dalton Trans. 1131-1135 (2009)

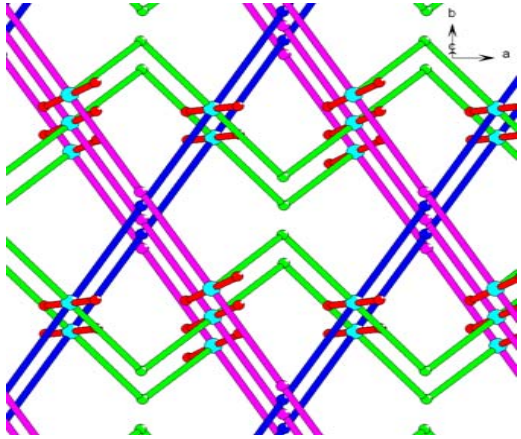
Acccomplishment: partially fluorinated structures with 4,4'-bpy

$Co(F_4\text{-succinate})(4,4'\text{-bpy})(H_2O)_2$
$(Co/Zn)(F_4\text{-isophthalate})(4,4'\text{-bpy})(H_2O)$



Structures have same basic connectivity



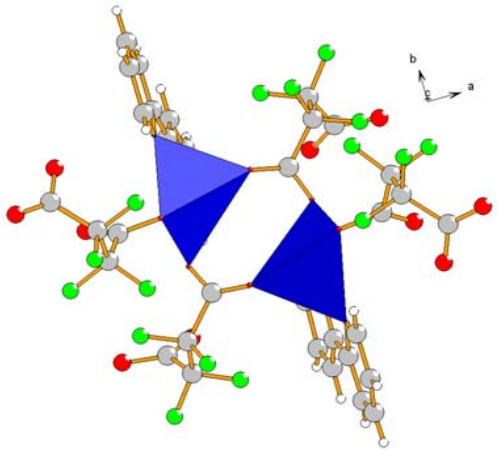


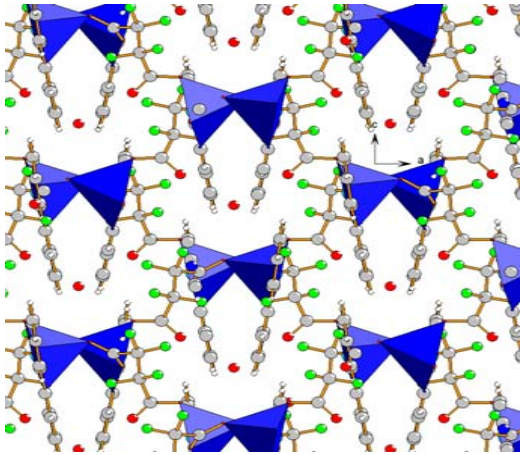
Pink/blue = 4,4'-bpy
Green = F_4-succinate or F_4-isophthalate
Aqua = Metal
Red = Water

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

Acccomplishment: partially fluorinated structures with 2,2'-bpy

$Cu(F_4\text{-succinate})(2,2'\text{-bpy}) \bullet 0.5\ H_2O$





Polar 3-D structure

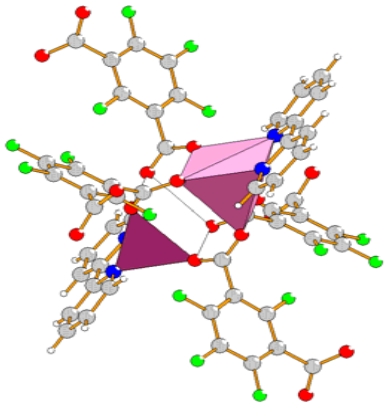
Dimer of Cu^{2+} square pyramids connects to four F_4-succinate ligands

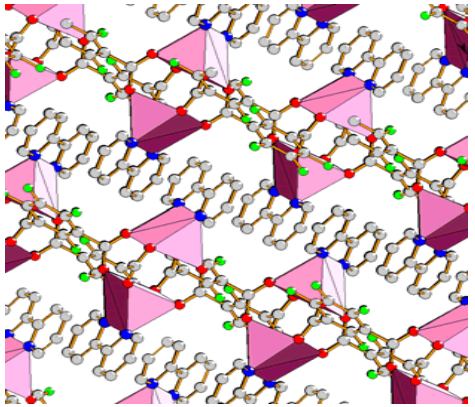
Potential for porosity, problem with purity

$Mn(F_4\text{-isophthalate})(2,2'\text{-bpy}) \bullet 0.5\ H_2O$

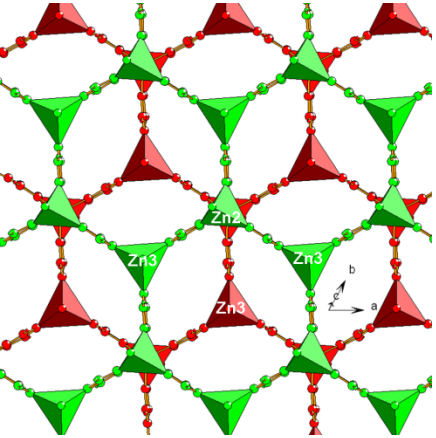
2-D layered structure

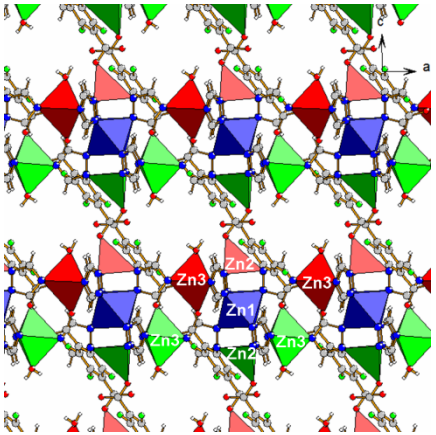
Dimer of Mn^{2+} trigonal prisms connects through four F_4-isophthalate ligands





Accomplishment '08: $Zn_{2.5}(1,2,4\text{-triazole})_3(\text{tetrafluoroterephthalate})(H_2O) \cdot 2H_2O$





Zn-triazolate

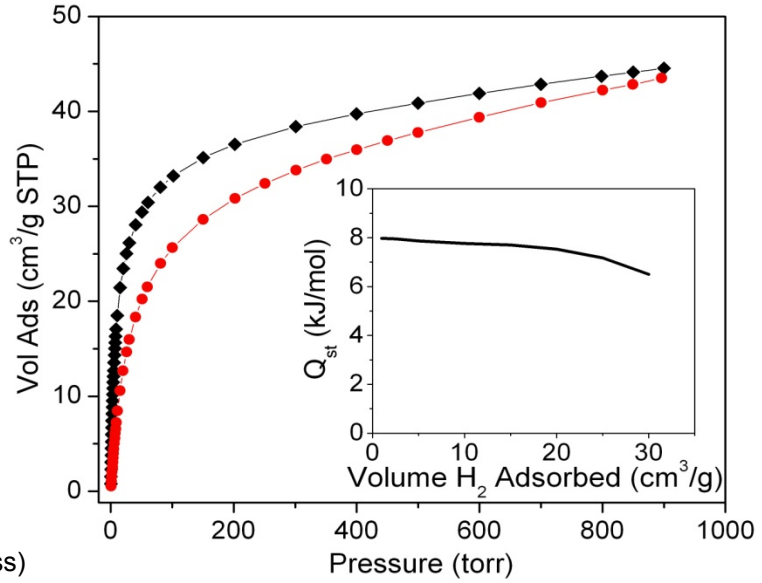
layers composed of two hexagonal arrays (left)

Layers connected by F_4-terephthalate to give porous 3-D structure

Desolvated structure contains 4 Å × 7 Å channel; adsorbs 0.4 wt% H_2 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

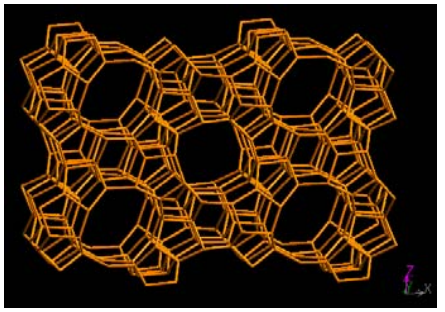


Z. Hulvey, E. H. L.Falcao, J. Eckert and A. K. Cheetham J. Mater. Chem. 2009 (in press)

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

New computational studies of 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 H_2 can bind at Cu site



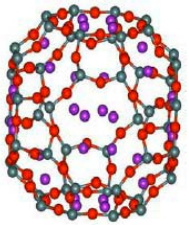
Follow-up on our previous observations:

-Room temperature H_2 isotherms in Cu-ZSM-5
(P. A. Gregoriev, A. Albinati and J. Eckert, Chemical Physics Letters **449**, 182, 2007).

-Hydrogen in Cu-ZSM-5
(P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert , J. Am. Chem. Soc. **129**, 8086, 2007)

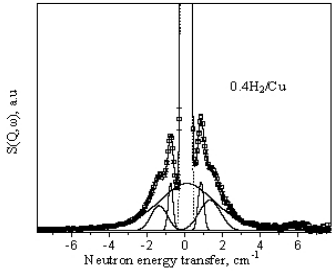
- THE FIRST observation: Hydrogen adsorbed in "over-exchanged" Fe-ZSM-5
(B. L. Mojet, J. Eckert, R. van Santen, A. Albinati and R. Lechner , J. Am. Chem. Soc. **123**, 8147 2001)

-Unsaturated Ni binding sites in the Nickel Phosphate VSB-5 and in Nickel-5-Sulfoisophthalate
(P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Ferey and A. K. Cheetham J. Am. Chem. Soc. **125**, 1309, 2003; P. M. Forster, J. Eckert, B. D. Heiken, J. B. Parise, J. W. Yoon, S. H. Jhung, J.-S. Chang, and A. K. Cheetham J. Am. Chem. Soc. **128**, 16846, 2006)



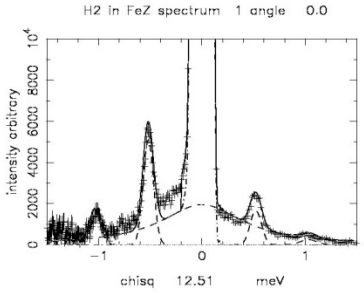
Cu-ZSM-5

H_2 loading



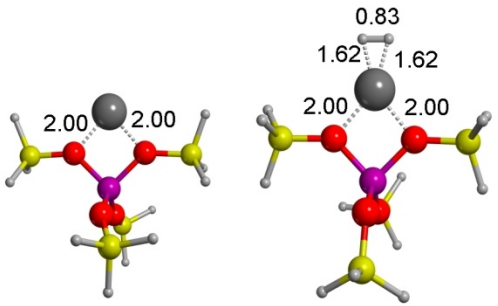
"Cu(η^2-H_2)" Complex

H_2 rotational tunneling Spectra(INS)

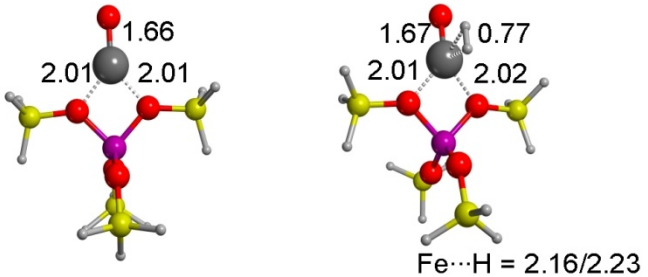


Note: Tunnel splitting in Fe-ZSM-5 >> Cu-ZSM-5 ⇒ Binding energy in Fe=-ZSM-5 lower

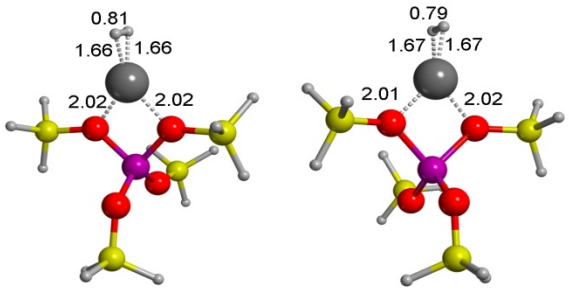
Accomplishment: Cluster models for H_2 binding at Fe and Cu sites in ZSM-5



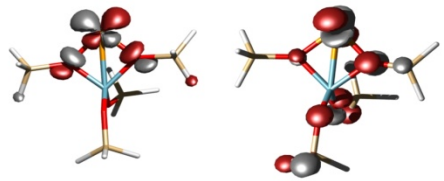
Cu5T/BL H_2-Cu5T/BL



$FeO5T_{BL}$ H_2-$FeO5T_{BL}$

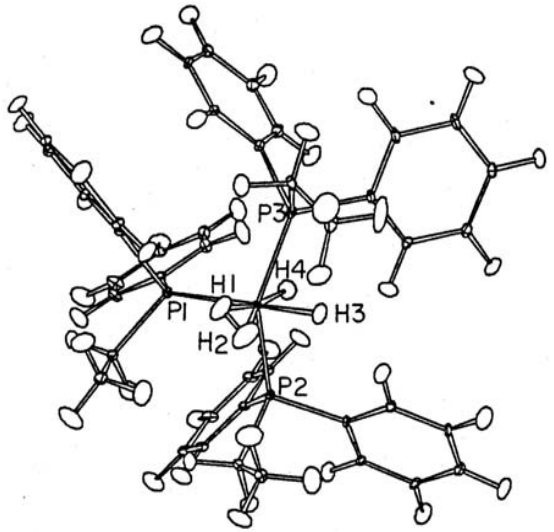


$(TS_{rot}\text{-}H_2\text{-}Cu5T)_{BL}$ $(TS_{rot}\text{-}H_2\text{-}Cu5T)_{BP}$



Adsorption complex Transition state

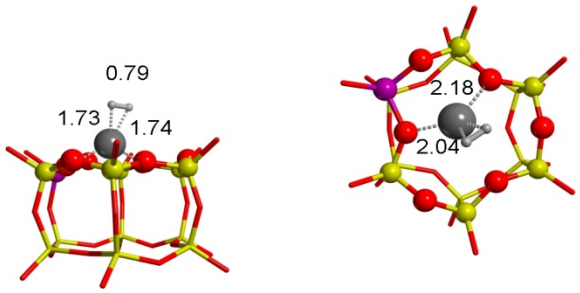
Comparison with Fe-dihydrogen complex
(single crystal neutron diffraction)



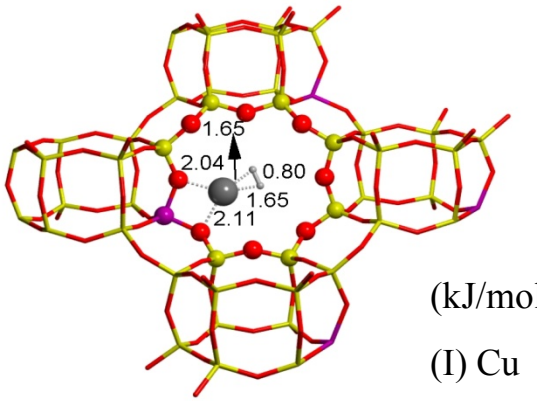
Fe-H= 1.57,1.61 Å
H-H = 0.82 Å

Xavier Solans-Montford and Mariona Soodupe Roure, Universitat Autónoma de Barcelona, Spain

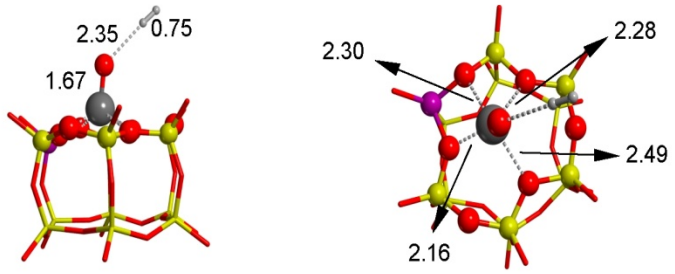
Accomplishment: Periodic models for H_2 binding at Fe and Cu sites in ZSM-5



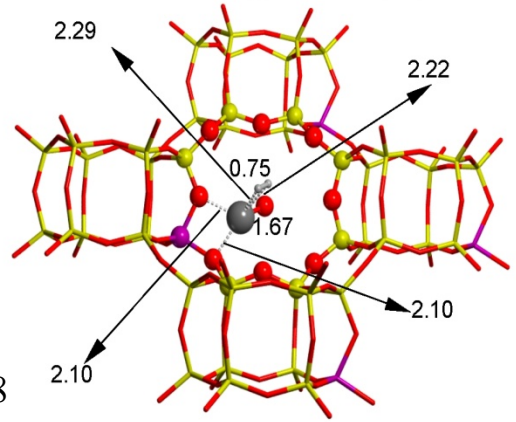
H_2-CuCHA(I)



H_2-CuCHA(IV)



H_2-FeO-CHA(I)FeO-CHA(IV)



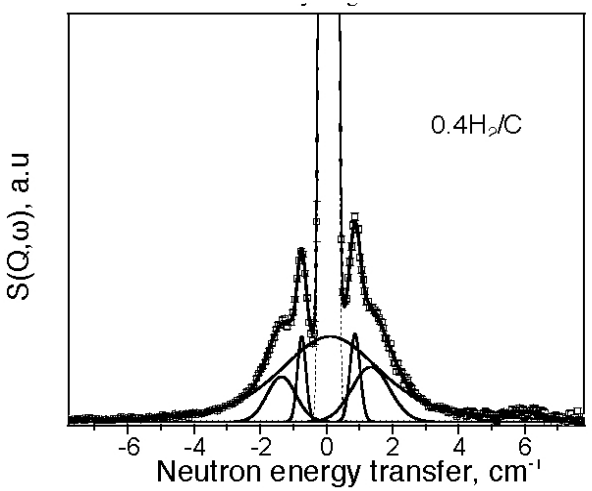
H_2-FeO-CHA(IV)

(kJ/mol)	E_{ads}	E_{INT}	D
(I) Cu	-15.0	-7.2	-7.8
(I) Fe	- 8.7	-0.7	- 8.0
(IV) Cu	-69.9	-58.2	-11.7
(IV) Fe	-13.0	-2.3	-10.7

CRYSTAL 03, DFT, with dispersion added according to Grimme

Xavier Solans-Montford and Mariona Soodupe Roure, Universitat Autónoma de Barcelona, Spain

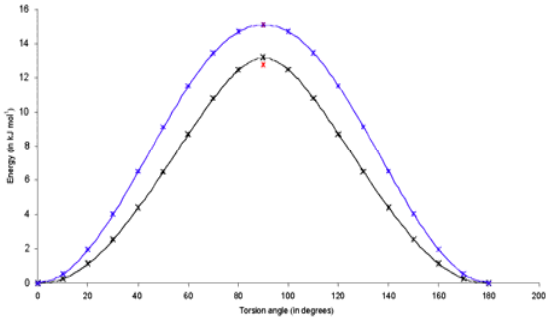
Accomplishment: Rotational Barriers for H_2 in in Fe- and Cu-ZSM-5 - Comparison of Calculations with Experiment



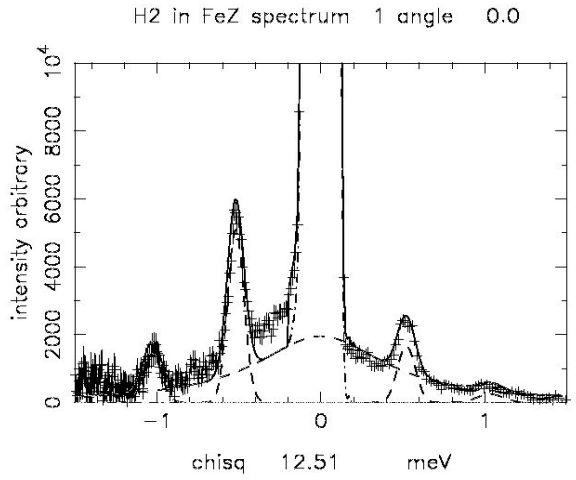
INS results

ω_t = 1 cm^{-1}
V_2 ~ 9 kJ/mol

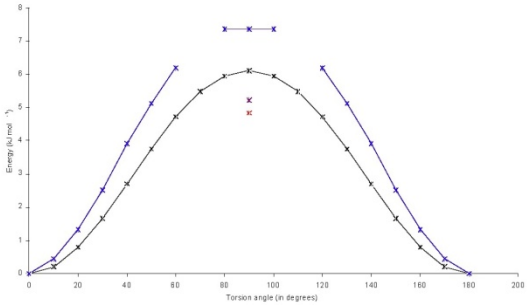
Calculation



V_2 ~ 13 kJ/mol



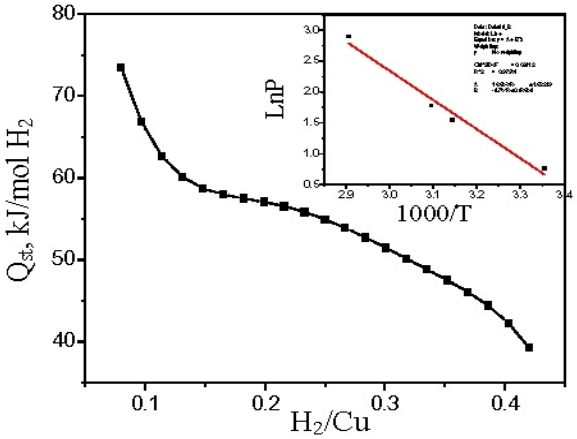
ω_t = 4 cm^{-1}
V_2 ~ 4 kJ/mol

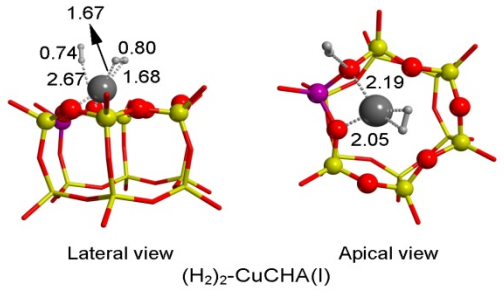


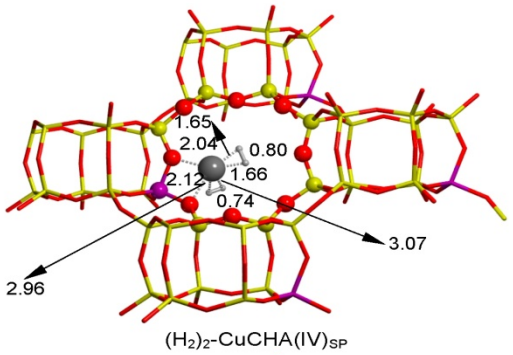
V_2 ~ 6.5 kJ/mol

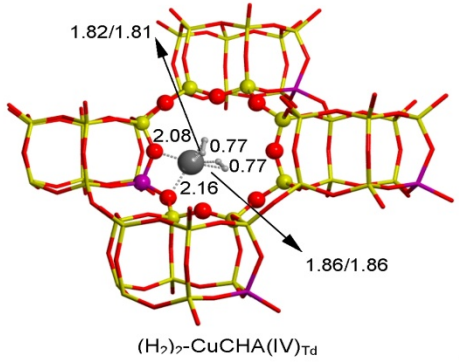
Accomplishment: Investigation of the Origin of the Loading dependence of Q_{st} in Cu-ZSM-5

Population of different sites?
Binding of multiple H_2 ligands?



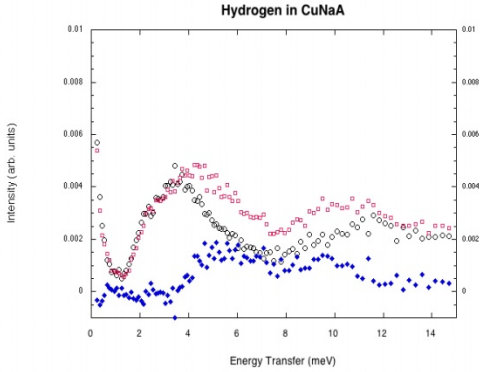


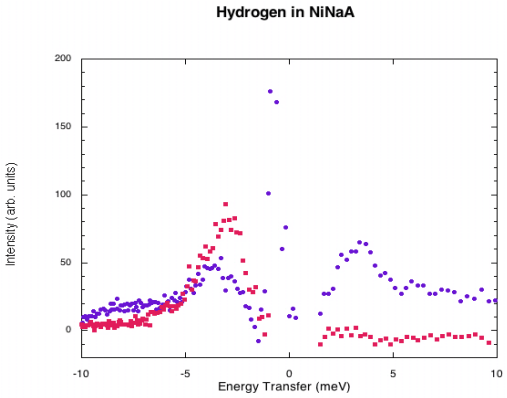




Second H_2 binds only with dispersive forces, ~ 9 kJ/mol

Accomplishment: INS studies of H_2 adsorption at "open" metal sites - in-framework vs. extraframework(zeolite) metal sites



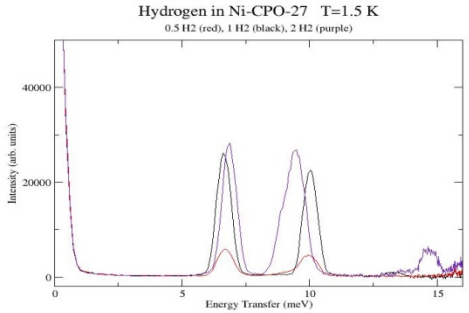


"0-1" rotational transition* for H_2 at

Cu in		Ni in	
Cu-ZSM-5	~0.15 meV	VSB-5	~ 1.5 meV
CuNaA	~ 3 meV	NiNaA	~ 2.9 meV
Cu-ATC (MOF-11)	~ 8 meV	Ni-SIPA	~ 4, 5.5 meV
Cu-BTC (HKUST-1)	~ 9 meV	Ni-CPO-27	~ 6.6 meV

Q_{st} values
HKUST-1 : 6.8 to < 6 kJ/mol
Cu-ZSM-5: 74 to < 40 kJ/mol (on Cu)

Why the big differences?
⇒location, location !! (M-H_2 distance):
2.39□Å in HKUST-1*, ~ 1.7Å for coordinated H_2



* Smaller value = larger barrier

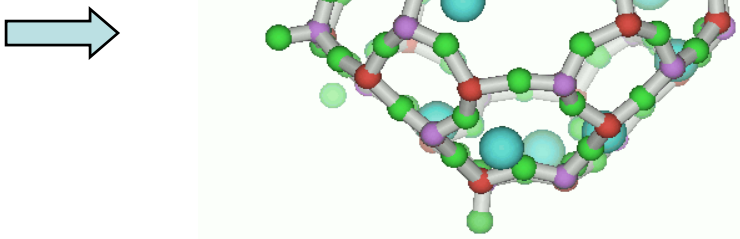
*V. K. Peterson, Y.Liu, C. M. Brown and C. J. Kepert, JACS 2006, 128, 15578

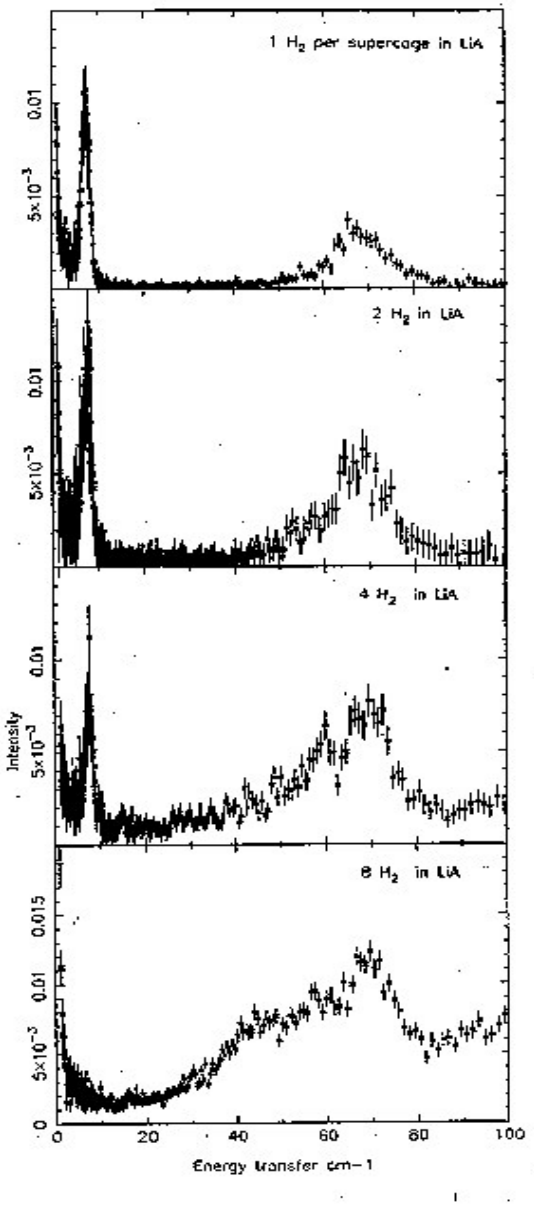
Accomplishment: INS studies of Li^+ in zeolites

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):





(IPNS)

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

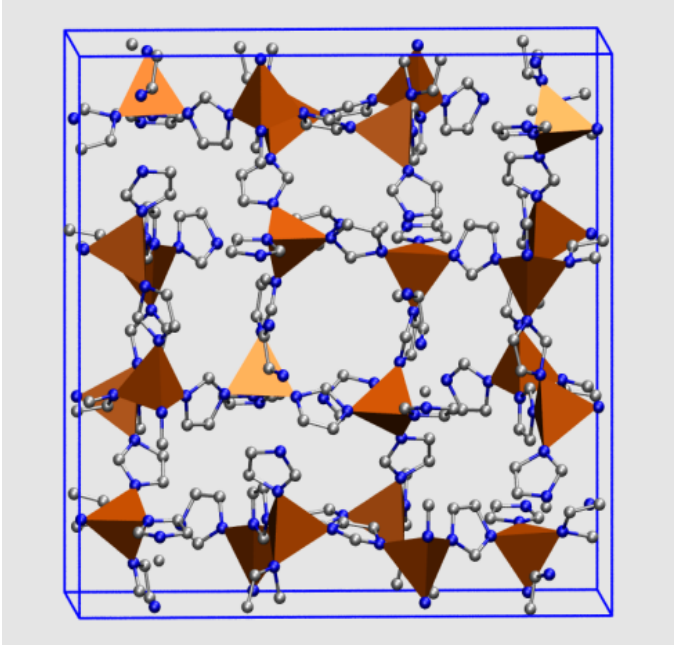
One or two EXPOSED cations (sites II) make for much stronger interaction: H_2 rot. transition at ~ 1 meV

J. Eckert , F. R. Trouw, B. L. Mojet, P. M. Forster, R. Lobo (J. Nanosci. Nanotechnol, 2009, in press)

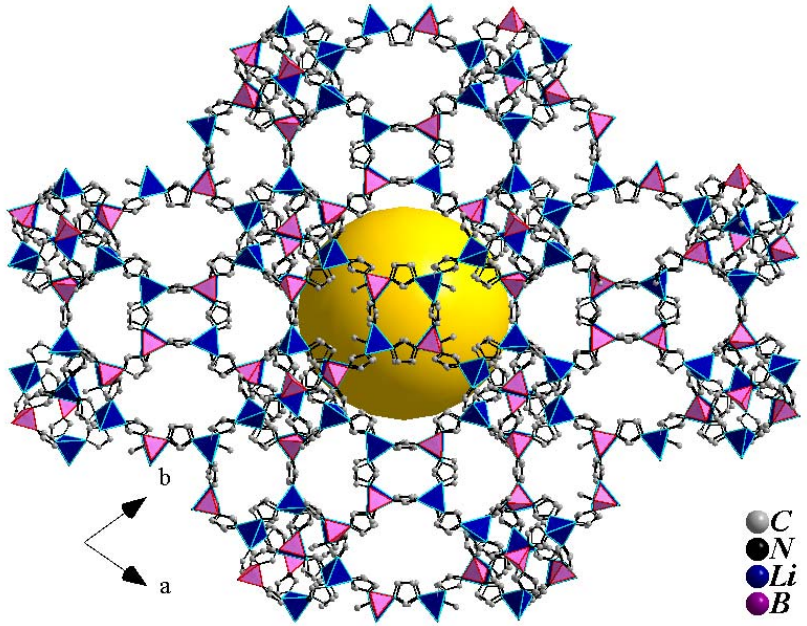
Accomplishment: Synthesis of Ultra Lightweight ZIFs

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

We have synthesized $LiB(C_3N_2H_3)_4$ 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)



LiB-ZIF with zni structure

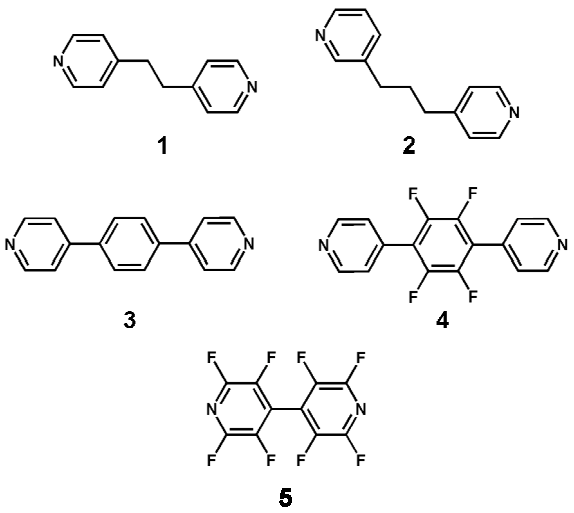


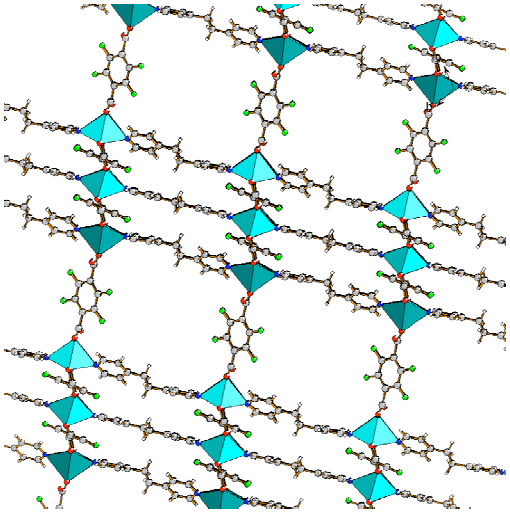
Computation: LiB-ZIF with LTA structure (+10 kJ/mol)

Reisner, Thirumurugan, Foster and Cheetham, Unpublished

Future Work: Phase 2

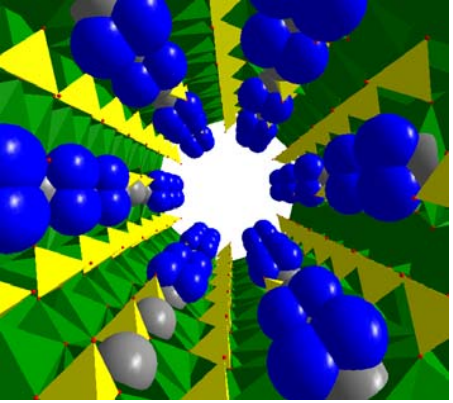
- Improvements in Ni-SIPA* to raise binding energies from the current 10-11 kJ/mol
  - use metals other than Ni; will effect pore size as well
  - substitute Li, K, or Rb for Na
- Create highly undercoordinated metal binding sites in MOF's by insertion
  - use approaches similar to that in ZSM-5 in high-T 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





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

Initial result: zinc, **1**, and tetrafluoroterephthalate



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