DOE Hydrogen Program

Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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University of California Santa Barbara

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Project ID: ST 26

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Overview

Timeline

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

Barriers

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

Budget

- Total project funding
  - DOE share: $1,199,073
  - Contractor share: $299,674
- Funding received in FY07
  $ 400,000
- Funding expected in FY08
  $ 287,000

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)
- L. L. Daemen (LANL)
- Paul 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

(can reach > 20 kJ/mol)

Bind Multiple Dihydrogen Ligands

Density too high?

Lighter Metals: alkali, alkaline earth hybrids

Not enough such sites?

Framework Modifications:
fluorinated linkers
Anionic frameworks (Eddaoudi, USF)

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 e.g. carbons, or most MOF's, using this approach:

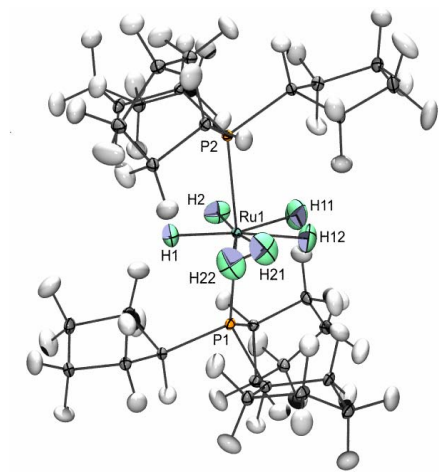
(a) Materials with unsaturated metal binding sites

combined with

(b) Framework modifications

(2) Then synthesize analogs with larger surface areas

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



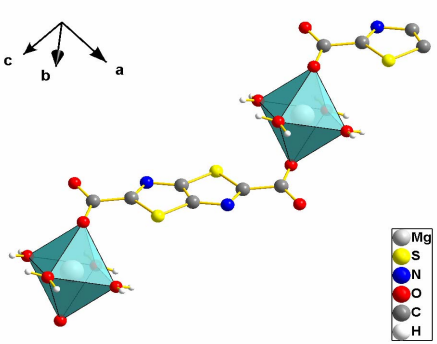
1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes >)

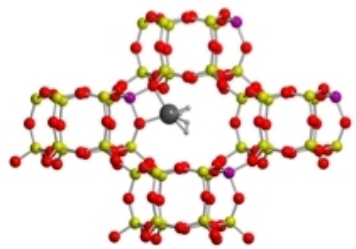
create porous material with large numbers of unsaturated metal binding sites, and/or other metal sites (e.g. extraframework cations, post-synthesis insertion)

for transition metals: increase H_2 capacity by binding multiple dihydrogen ligands to a metal site -

OR

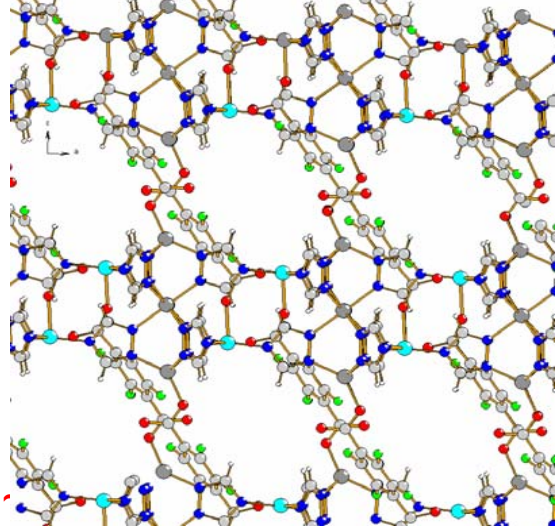
hybrid materials with lighter metals instead of transition metals





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

Approach



2. Use fluorinated organic linkers:
increase H_2 binding by ~ 50%

3. charged frameworks increase H_2 binding energy by at least
(Collaboration* with M. Eddaoudi, USF)

* BES

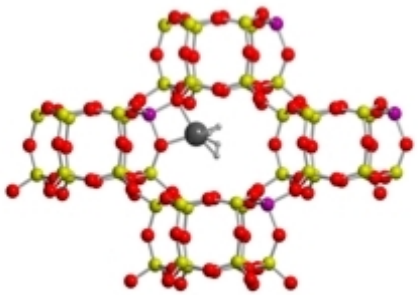
4. Characterize Binding of Hydrogen by Bulk Measurements and Inelastic Neutron Scattering

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 at IPNS/ANL- **SHUT DOWN !! - must use European Neutron Sources in the near term)**

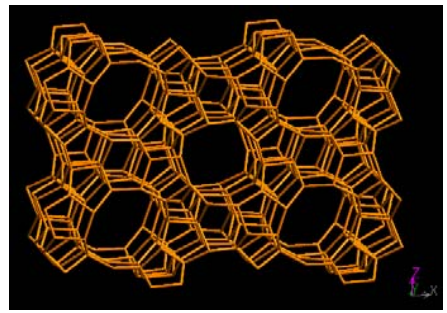


Technical Accomplishments Progress/Results

- 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
- Demonstrated increase in H_2 capacity and binding energies with metal doping in sililicate structures
- Synthesized and characterized structures of a series of hybrid materials using transition metals, alkaline earths and alkali metals with a highly functionalized organic link:
- Demonstrate substantial increase in H_2 binding energy for charged frameworks relative to those that are neutral: e.g. extra framework cations in zeolites vs. neutral analogs
- Synthesized and characterized porous hybrids with mixed fluorinated and normal organic links, AND open metal sites

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

-Room temperature H_2 isotherms in Cu-ZSM-5: Q_{st} for MOLECULAR H_2 38 - 70 kJ/mol.
-(P. A. Gregoriev, A. Albinati and J. Eckert (Chemical Physics Letters **449**, 182, 2007).

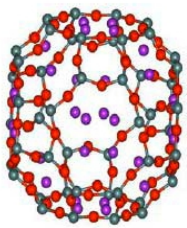


Follow-up on our previous observations:

-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)

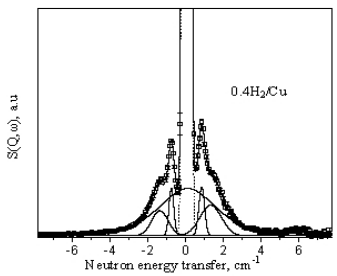
-- THE FIRST observation: Hydrogen adsorbed in "over-exchanged" Fe-ZSM-5
(B. L. Mojet, J. Eckert, R. van Santen, A. Albinati and R. Lechner , J. Am. Chem. Soc. **123**, 8147 2001)

-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)



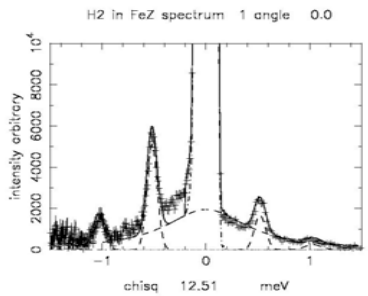
Cu-ZSM-5

H_2 loading



"Cu(η^2-H_2)" Complex

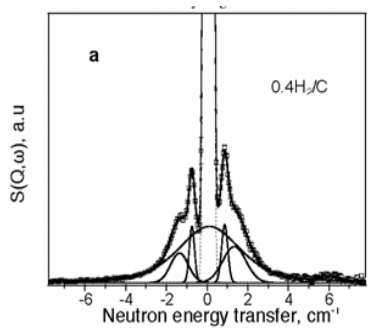
H_2 rotational tunneling Spectra(INS)

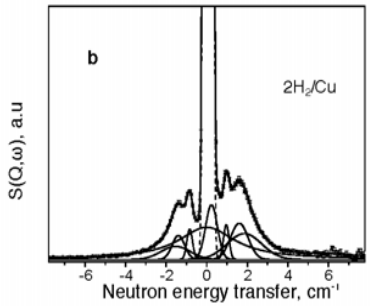


Note: Tunnel splitting in Fe-ZSM-5 >> Cu-ZSM-5 ⇒ Binding energy in Fe=-ZSM-5 lower, close to what is needed ?

Strong Molecular Chemisorption* of H_2 on Cu in ZSM-5

P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert (JACS **2007**, 129, 8086)
Instrument: IN5 at ILL(Grenoble, France)





Rotational tunneling spectra (INS) at 5K: at least two well-defined sites, plus a distribution of binding sites.

Interacting molecules on the same site ?

Note: FIVE times H_2 loading gives only ~10% in intensity
Where did the extra H_2 go?
⇒ other parts of the zeolite surface (below) - weakly bound

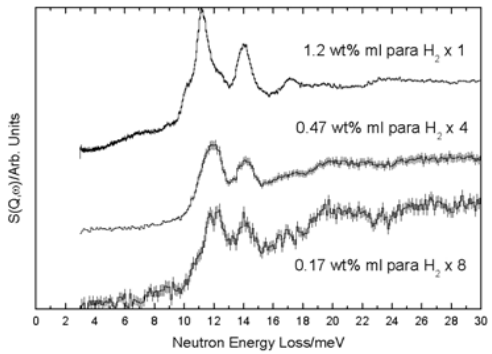


Figure 3. The rotational spectra of para-hydrogen in CuZSM5 at different H_2 loadings.

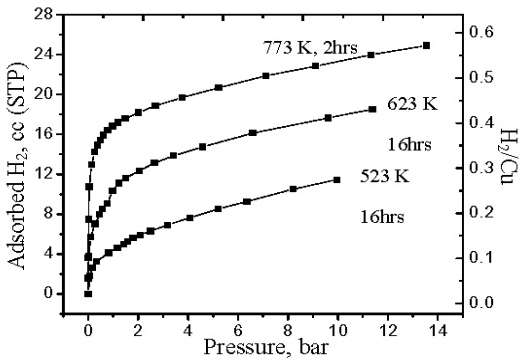
Ramirez-Cuesta, A. J.; Mitchell, P. C. H., Cat. Today **2007**, 120, 368.

* Previously observed by IR only (ν(HH); Kazansky et al.; e.g. Cat. Today **2005**, 110, 281)

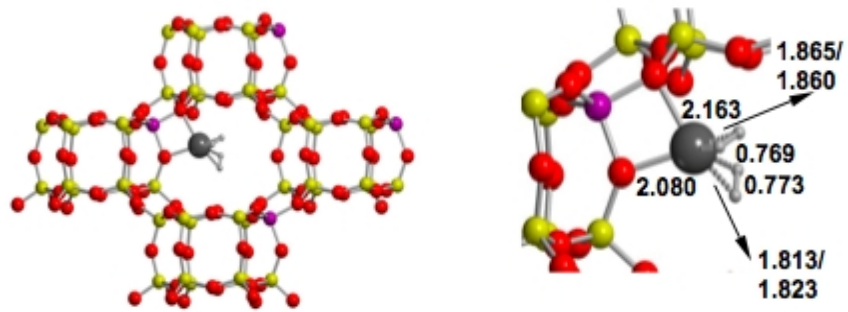
Molecular Hydrogen Adsorption Isotherm - H_2 in Cu-ZSM-5 above RT, very modest pressures:

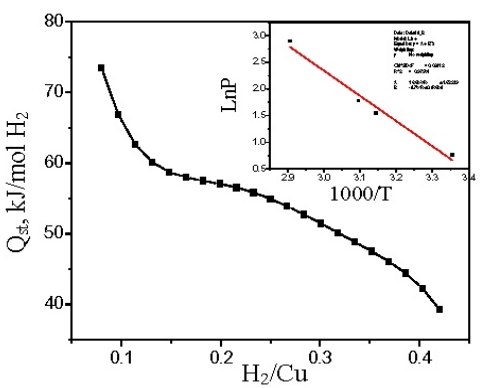
P. A. Gregoriev, A. Albinati and J. Eckert (Chemical Physics Letters **449**, 182, 2007).

Isosteric Heat of adsorption: H_2 on Cu ~38 - 74 kJ/mol !!!



Measurements at 298, 318, 323 and 344K





Calculation (periodic DFT/chabazite "model"):
Binding energy: -70 kJ/mol (1 H_2),
~ 8 kJ/mol less for 2 H_2

INS spectrum, Q_{st} support the possibility that two dihydrogen molecules bind to one Cu site

Approaches to the Synthesis of "Naked Metal Ions" and Hydrogen-Rich Metal Complexes for Hydrogen Storage

Synthesize highly unsaturated first-row metal species with multiple H_2 ligands via metal akyl, aryl,or hydride complexes

$$MR_2 + 2H^+ \xrightarrow[H_2]{\text{ionic liquid}} [M(H_2)_n]^{2+} + 2RH \qquad M = Fe, Mn, Co, Ni$$

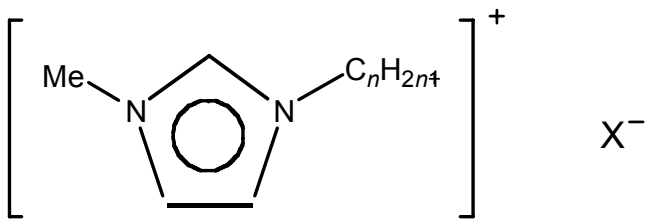
$$[FeH_6]^{4-} + H^+ \longrightarrow [FeH_5(H_2)]^{3-} \qquad [FeH_2(H_2)_4] \text{ on further protonation?}$$

[Linn]

acid with low-coordinating anion

If unstable, embed H_2-rich species into nanoporous media (zeolites, MOF)

- **First results:**
  - **Co polyhydride anion (small crystals)**
  - **Fe polyhydride anion (unstable)**
    (interference from $MgBr_2$ cations?)



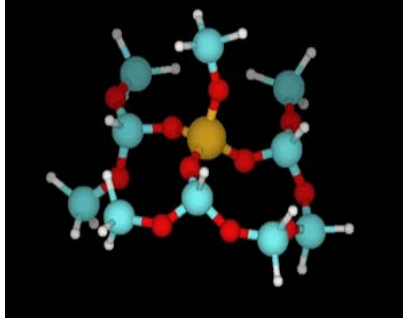
I $n = 4$, X = $[PF_6]$; [bmim][PF_6]
II $n = 4$, X = $[(CF_3SO_2)_2N]$; [bmim][Tf_2N]
III $n = 2$, X = $[(CF_3SO_2)_2N]$; [emim][Tf_2N]

Ionic liquids

We have already demonstrated Dihydrogen Binding to Fe and Cu clusters in ZSM-5
Molecular complexes can also be grafted to nanoporous materials surfaces

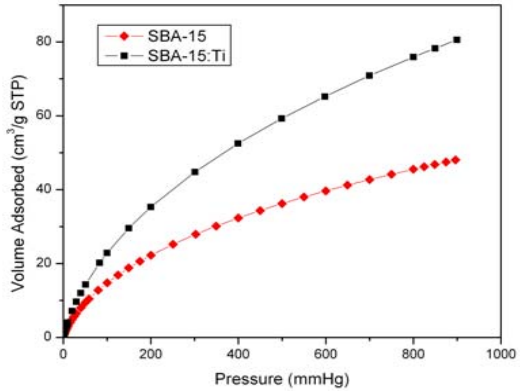
Accomplishment: Enhanced H_2 Capacity and Binding of SBA-15 by Ti doping

: chemisorption at elevated pressures?

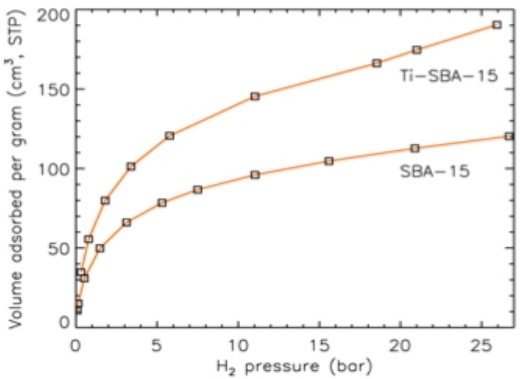


Cluster model for Ti in TS-1

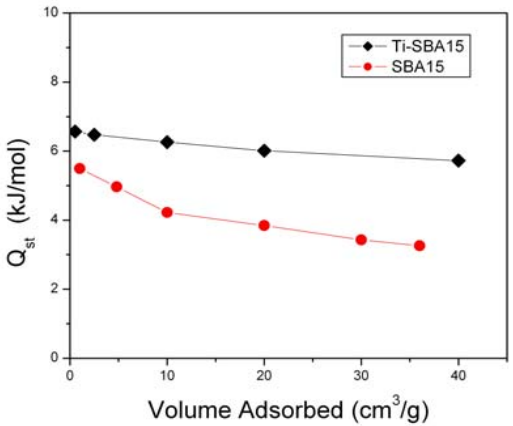
low pressure



high pressure

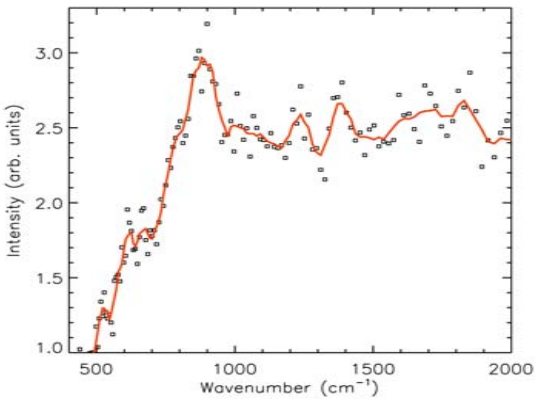


Note divergence in slopes above ~ 10 bar



~ 20 - 50% increase in Q_{st}

INS Spectrum(FDS, Lujan Center, LANL)



Vibrational spectrum:

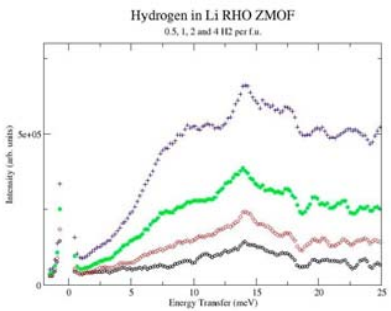
some chemisorbed H ?

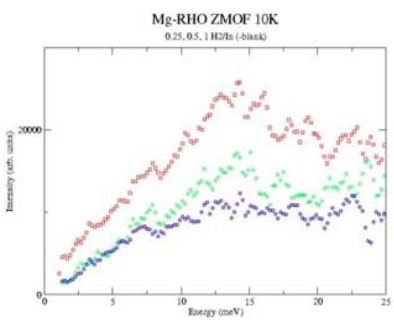
Difference spectrum
{H_2/Ti-SBA-15}-{H_2/SBA-15}

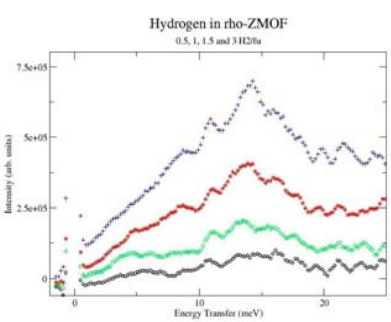
Charged frameworks and ionic species improve H_2 binding significantly

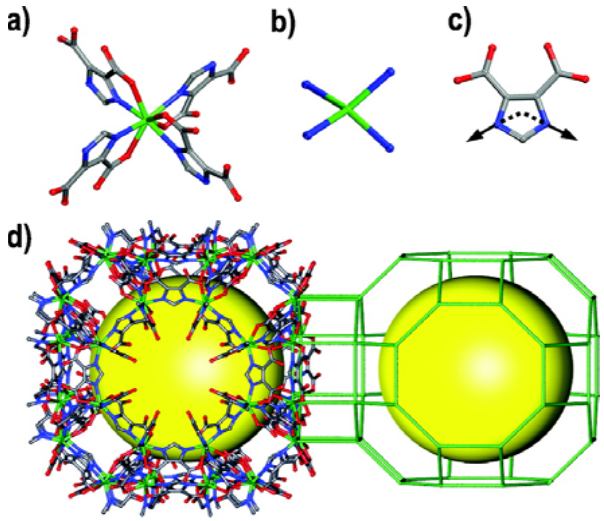
Hydrogen in Anionic Frameworks

(Collaboration with M. Eddaoudi)

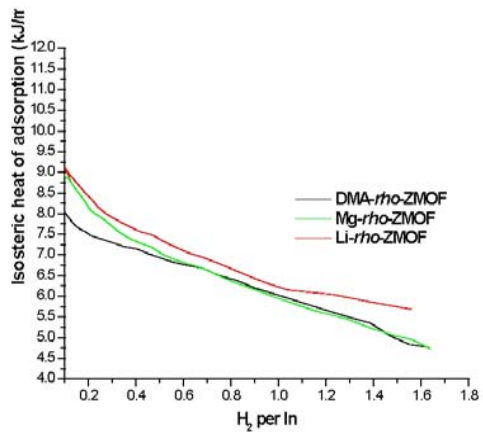






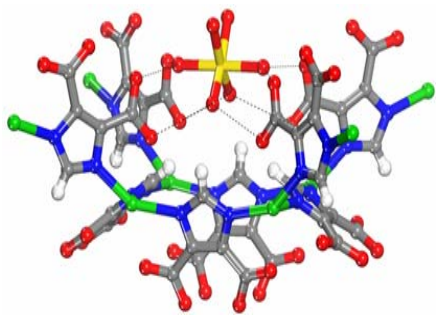


ZMOF's - anionic frameworks with charge compensating cations - built with imidazole dicarboxylic acid linkers*



Isosteric heat of adsorption
- nearly twice that in MOF-5
- only weakly dependent on the nature of the cation
- cation not accessible - present as aquo complex

⇒Electrostatics !!

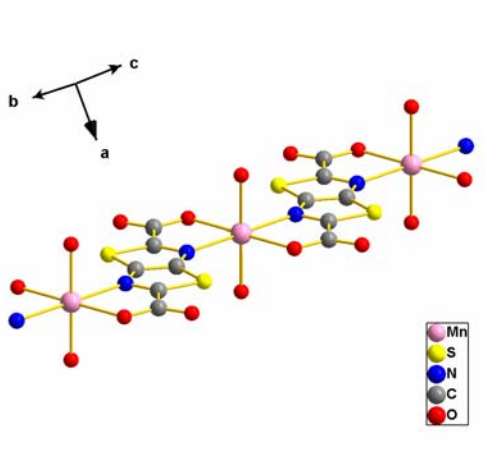


Binding sites not as well defined as in (e.g.) MOF-5

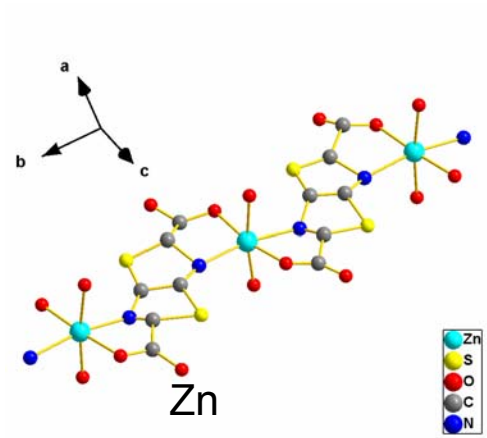
Center of gravity of spectrum shifted to significantly lower energies

*Y. Liu, V. C. Kravtsov, R. Larsen and M. Eddaoudi, Chem. Comm. 2006, 1488

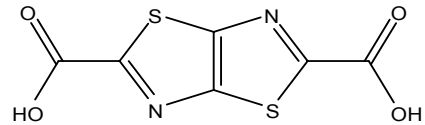
Accomplishment: Synthesis of Hybrid Materials with Metal Centers and a Highly Functionalized Organic Link: (1) Transition Metals



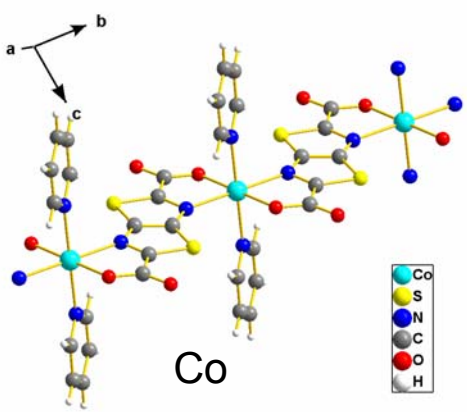
Mn



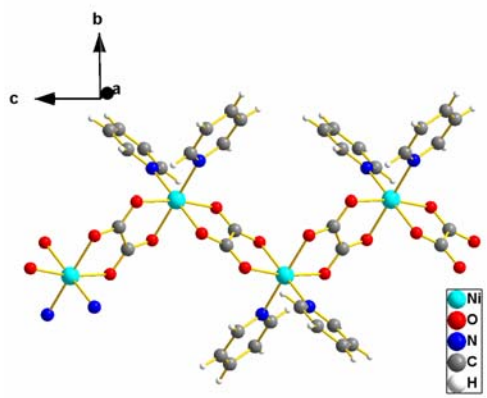
Zn



[5,4-d]thiazoledicarboxylic 2,5-Thiazolo acid

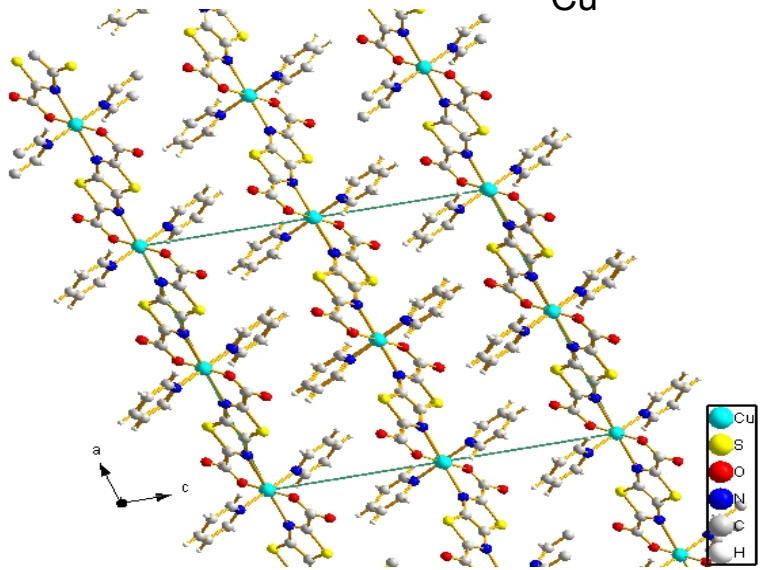


Co



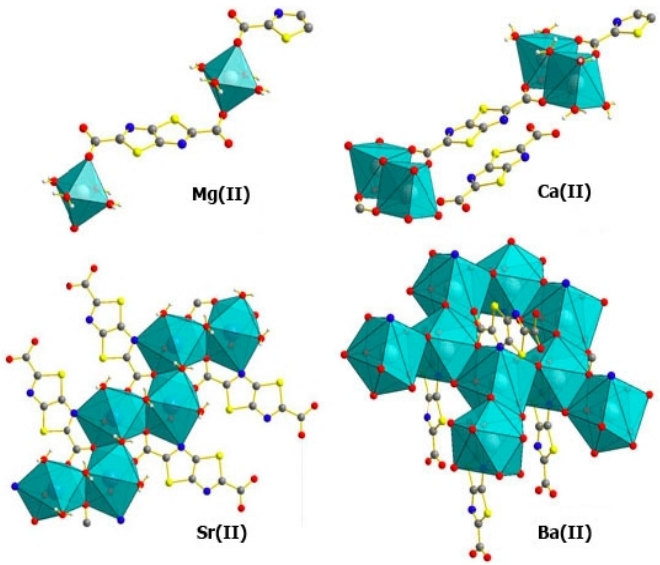
Ni

Cu

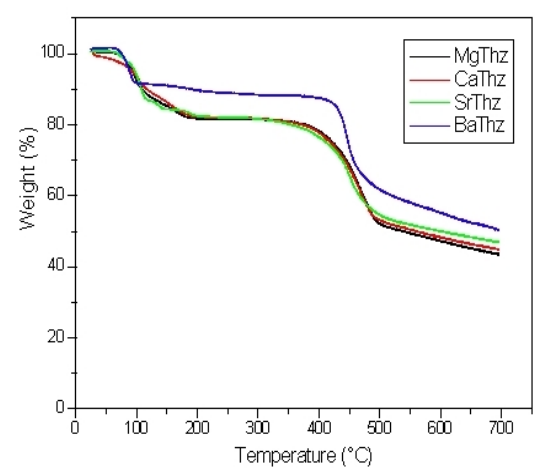


- Mn and Zn: water molecules on axial positions (solvent system: water/pyridine, same as used for all other reactions)
- MnThz: MW conditions (no crystals obtained from solvothermal).
- Nickel: Thz decomposes to oxalate.

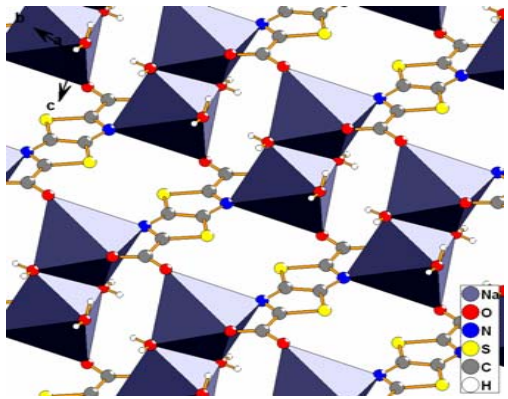
Accomplishment: Synthesis of Hybrid Materials with Metal Centers and a Highly Functionalized Organic Link: (2) Alkaline Earths

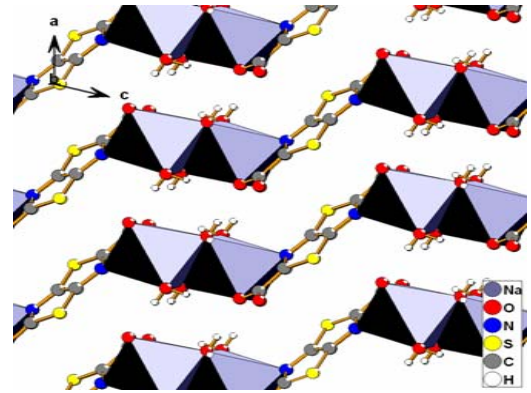


Metal Cation	Overall Dimension	Coordination	Edge-Sharing
Mg(II)	1	6	0
Ca(II)	1	7	1
Sr(II)	1	8	2
Ba(II)	2	10	3

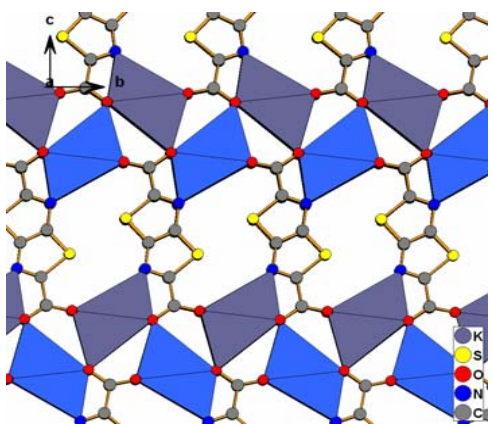


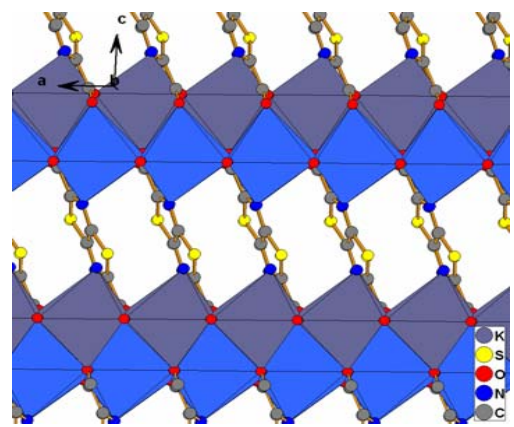
Accomplishment: Synthesis of Hybrid Materials with Metal Centers and a Highly Functionalized Organic Link: (3) Alkali Metals





$Na_2(Thz)(H_2O)_4$

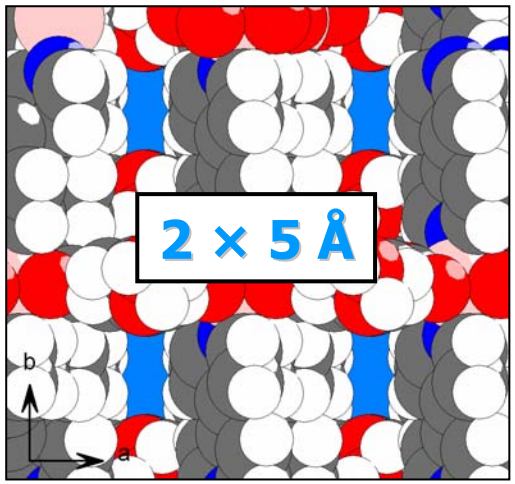


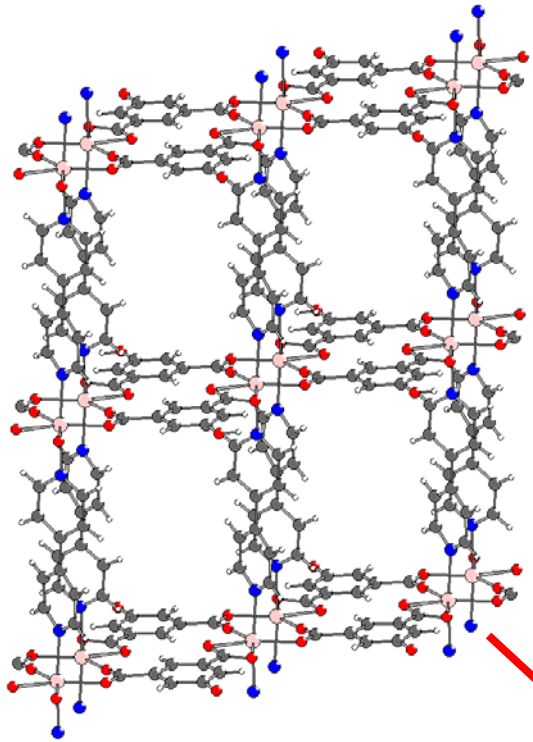


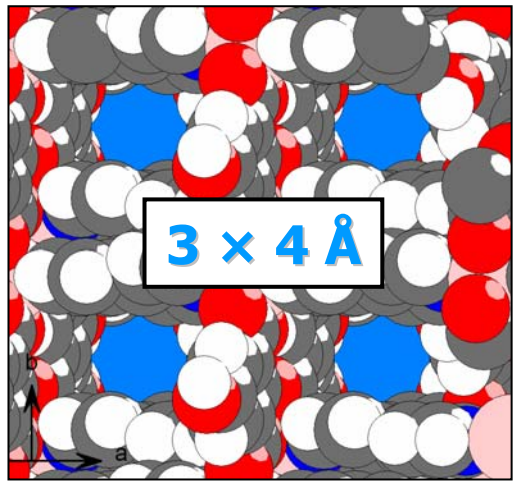
$K_2(Thz)$

-Structure evolves from 2D with Na to 3D with K. Also, K is anhydrous.

Transition Metal Bipyridyl/Hydroxyisophthalates



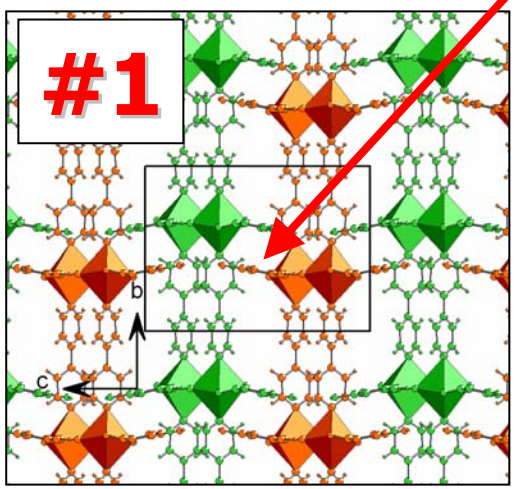




rotate

rotate

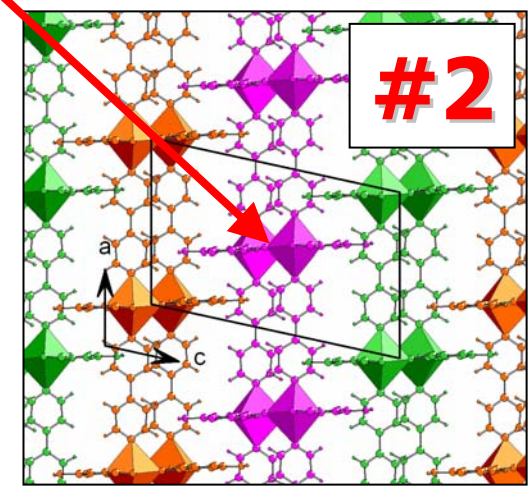
Mn(bipyridyl)(5-HIP) hydrates, #1 and #2



Two stackings of gridlike motif

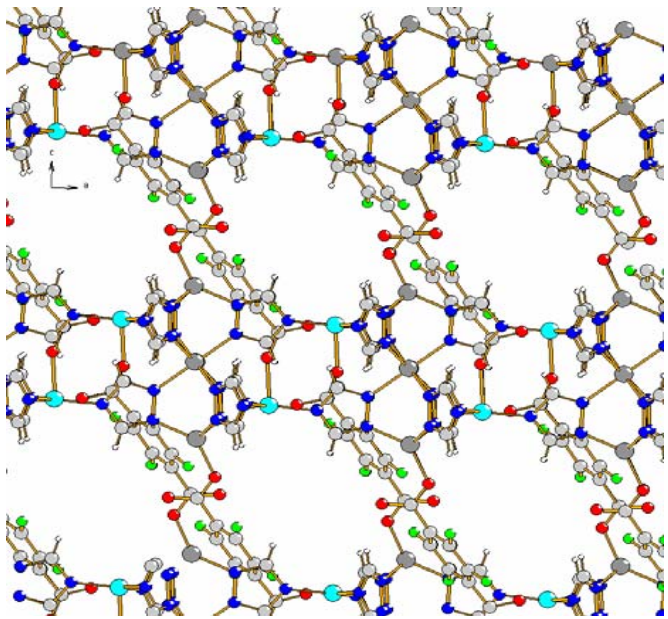
Guest species all uncoordinated

Two different channel shapes



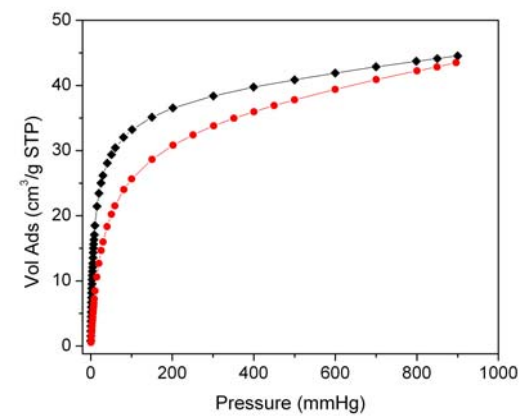
Accomplishment: development of porous, partially fluorinated hybrids with open metal sites:

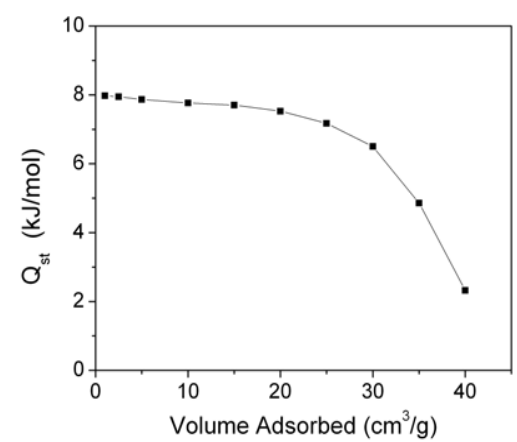
$Zn_{2.5}$(1,2,4-triazole)$_3$(tetrafluoroterephthalate)(H_2O) . $2H_2O$



Zn takes up 3 different coordination geometries

H_2 isotherms, 77 and 87K





INS results delayed because of shutdown of IPNS (ANL) !!

Use of F instead of H on the organic linker **improves H_2 binding energies by ~ 50%**

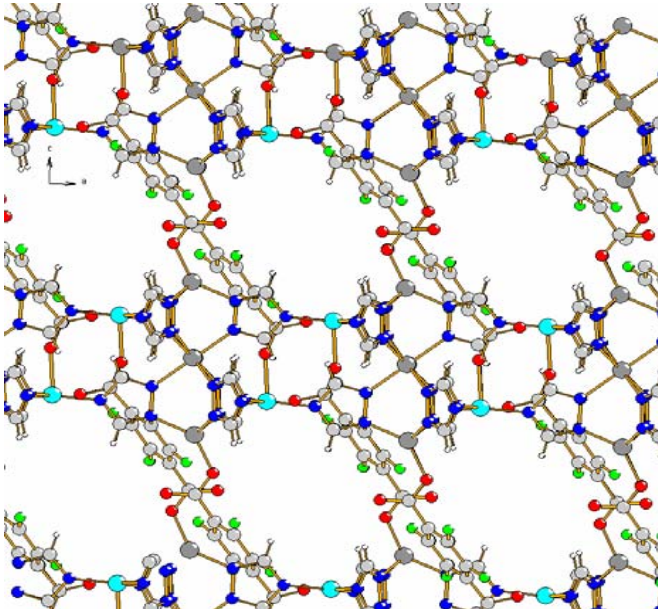
Future Work

- Develop compounds with unsaturated (and highly accessible) metal binding sites.
  - Synthesize analogs with larger surface areas (FY08-09)

- Bind Multiple Dihydrogen Ligands
  - Theoretical Analysis of INS results on Fe-ZSM-5 (FY08): lower binding energy than in Cu-ZSM-5 ? (FY08)
  - Hydrogen sorption experiments

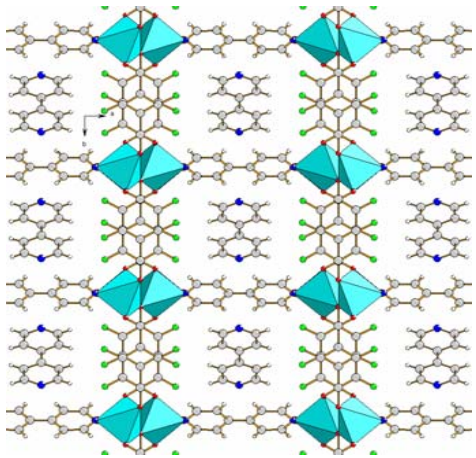
- Alkali, alkaline earth metal hybrids with [5,4-d]thiazoledicarboxylic 2,5-Thiazolo acid link
  - Achieve porosity, characterize H_2 binding
  - Go/no-go decision 12/31/2008

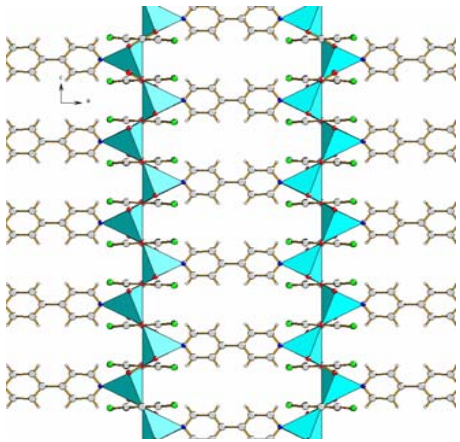
- Fluorinated linkers in hybrid materials
  - Synthesize materials with open metal sites other than Zn
  - improve H_2 binding above 10 kJ/mol
  - achieve greater porosity (FY08-FY09)



Accomplishment: development of partially fluorinated hybrid with infinite inorganic connectivity in one dimension:

Zn(bipy)(tetrafluorohydroxybenzoate) . bipy



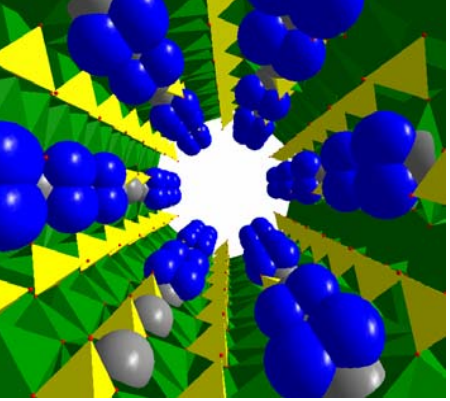


Note: F's point into the cacity

$\Rightarrow$ large number of similar binding sites (IF the bipy can be removed)

Future Work: further development of fluorinated hybrids

- different ("better" than Zn) or mixed metals in
- increase porosity
- introduce more open metal sites



Summary

- Demonstrated the Presence of Molecular Chemisorption of Hydrogen in a number of porous materials ⇒ higher binding energies than physisorption
  - well over 10 kJ/mol for the entire material (Ni-SIPA; Cu-ZSM-5)
- Synthesized porous material with fluorinated organic AND open metal sites
- 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 also be directly accessible by H2;
  :main problem with MOST such materials reported to date;
  also: oxidation state
- Transition metal sites in porous materials ⇒ weight penalty addressed by
  - Use of lightweight frameworks
  - Binding multiple dihydrogen ligands - requires very open metal site
  - Framework modifications: ~50% gains ⇒ F for H on linkers; charged frameworks
- Combination of the above should make it possible to reach ~ 20 kJ/mol or better
- Practical materials of this type need increased surface area