

# Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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Project ID: ST 26

# 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 FY07  
\$ 400,000
- Funding expected in FY08  
\$ 287,000

## 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)
- L. L. Daemen (LANL)
- Paul Forster (UNLV)

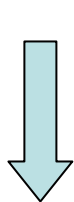
# Overall Objective

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

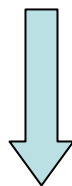
# Path to Sorption-based Material with greater H<sub>2</sub> binding Energy

**Molecular** Chemisorption at Unsaturated (Transition) Metal Binding Sites  
(can reach > 20 kJ/mol)



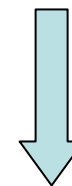
Density too high?

Bind Multiple  
Dihydrogen Ligands

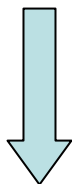


Not enough such sites?

Lighter Metals:  
alkali, alkaline  
earth hybrids



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<sub>2</sub>** **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

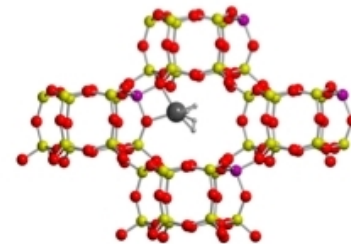
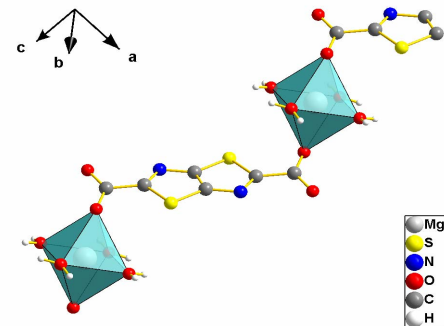
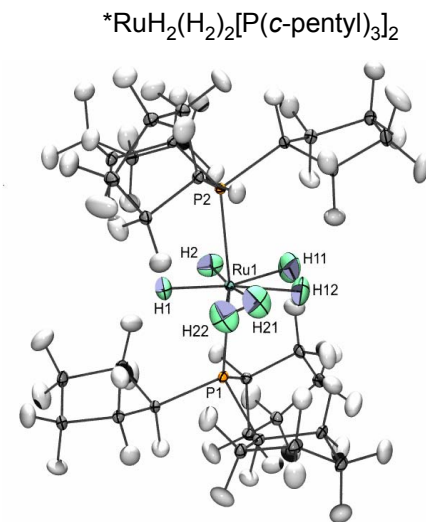
1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes >)

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

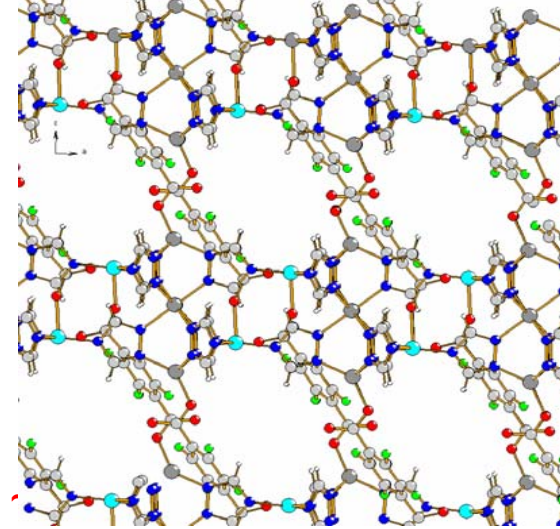
for transition metals: increase H<sub>2</sub> capacity by binding multiple dihydrogen ligands to a metal site -

**OR**

hybrid materials with lighter metals instead of transition metals



# Approach



2. Use **fluorinated organic** linkers:  
increase H<sub>2</sub> binding by ~ **50%**

3. **charged** frameworks increase H<sub>2</sub> binding energy by at least  
(Collaboration\* with M. Eddaoudi, USF)

\* BES

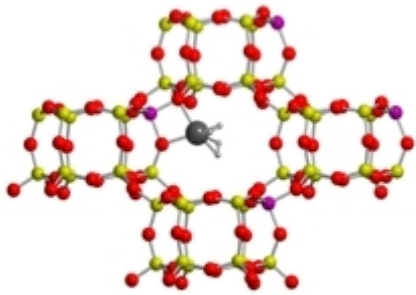
4. Characterize Binding of Hydrogen by Bulk Measurements and  
Inelastic Neutron Scattering

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<sub>2</sub> 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<sub>2</sub> capacity and binding energies with metal doping in silicate 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<sub>2</sub> 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

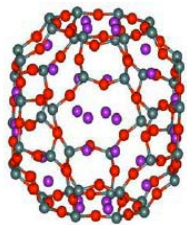
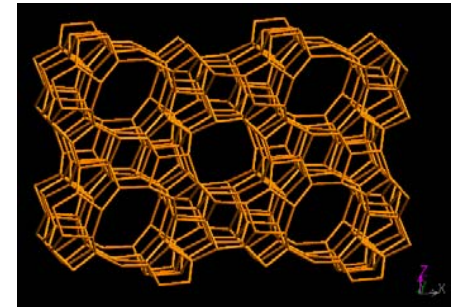
-(P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert J. Am. Chem. Soc. **129**, 8086, 2007)

-- **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)

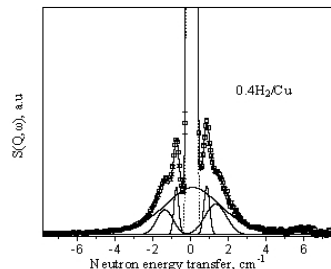
-Unsaturated Ni binding sites in the Nickel Phosphate VSB-5 and in Nickel-5-Sulfoisophthalate

(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. Jung, J.-S. Chang, and A. K. Cheetham J. Am. Chem. Soc. **128**, 16846, 2006)



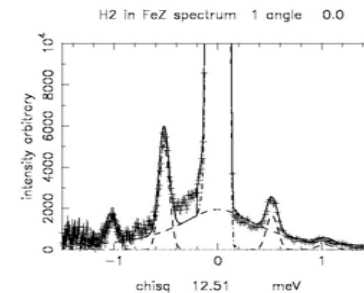
Cu-ZSM-5

H<sub>2</sub> loading



“Cu( $\eta^2$ -H<sub>2</sub>)” Complex

H<sub>2</sub> rotational tunneling Spectra(INS)



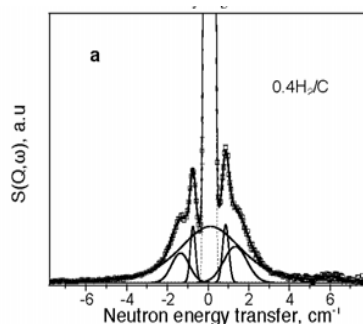
**Note:** Tunnel splitting in Fe-ZSM-5  $\gg$  Cu-ZSM-5  $\Rightarrow$  Binding energy in Fe-ZSM-5 lower, close to what is needed ?



# Strong **Molecular** Chemisorption\* of H<sub>2</sub> 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<sub>2</sub> loading gives only ~10% in intensity

Where did the extra H<sub>2</sub> go?

⇒ other parts of the zeolite surface (below) - weakly bound

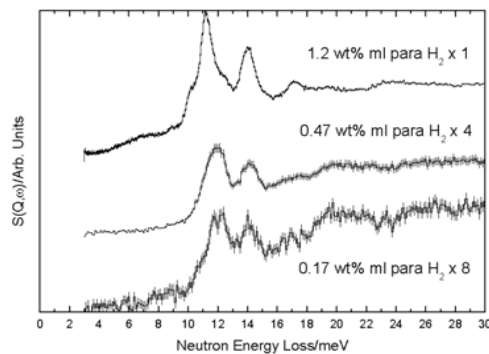
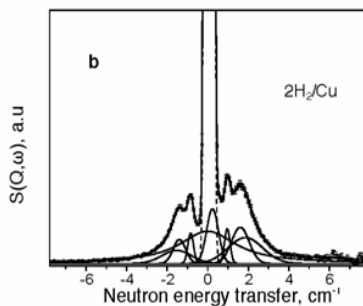


Figure 3. The rotational spectra of para-hydrogen in CuZSM5 at different H<sub>2</sub> loadings.

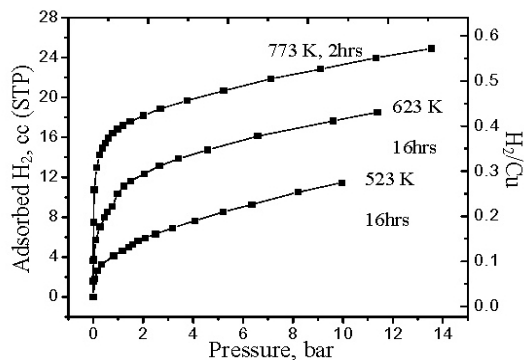
Ramirez-Cuesta, A. J.; Mitchell, P. C. H., *Cat. Today* **2007**, 120, 368.

\* Previously observed by IR only (  $\nu(\text{HH})$ ; Kazansky et al.; e.g. *Cat. Today* **2005**, 110, 281 )

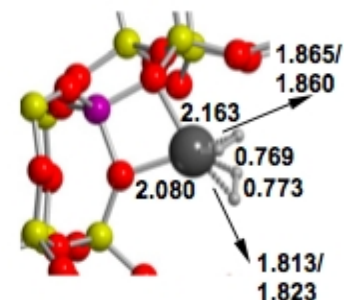
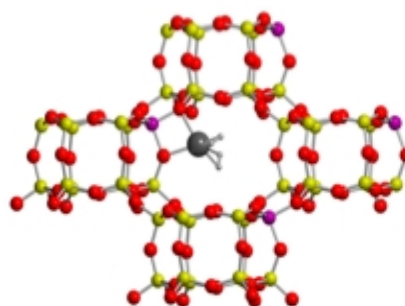
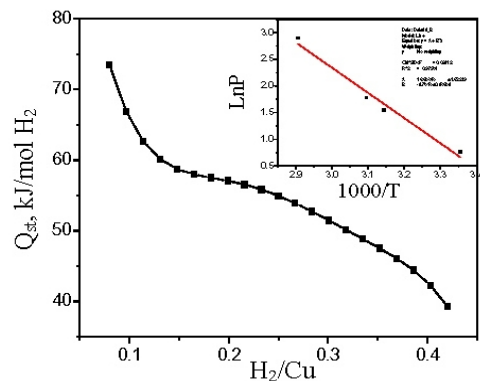
# Molecular Hydrogen Adsorption Isotherm - H<sub>2</sub> in Cu-ZSM-5 above RT, very modest pressures:

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

Isosteric Heat of adsorption: H<sub>2</sub> on Cu ~38 - 74 kJ/mol !!!



Measurements at 298, 318, 323 and 344K

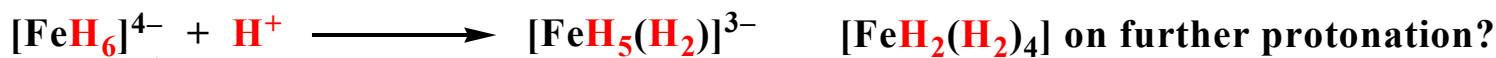
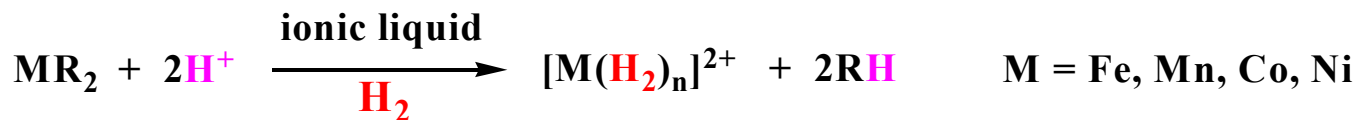


Calculation (periodic DFT/chabazite “model”):  
Binding energy: -70 kJ/mol (1 H<sub>2</sub>),  
~ 8 kJ/mol less for 2 H<sub>2</sub>

INS spectrum, Q<sub>st</sub> 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<sub>2</sub>** ligands via metal alkyl, aryl, or hydride complexes



[Linn]

acid with low-coordinating anion

If unstable, embed H<sub>2</sub>-rich species into nanoporous media (zeolites, MOF)

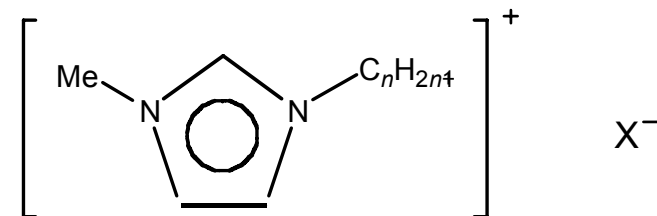
## •First results:

**Co polyhydride anion (small crystals)**

**Fe polyhydride anion (unstable)**

(interference from MgBr<sub>2</sub> cations?)

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

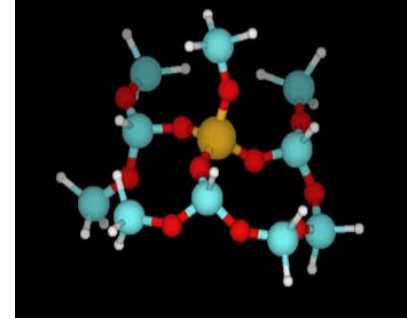


- I  $n = 4$ , X = [PF<sub>6</sub>]; [bmim][PF<sub>6</sub>]
- II  $n = 4$ , X = [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]; [bmim][Tf<sub>2</sub>N]
- III  $n = 2$ , X = [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]; [emim][Tf<sub>2</sub>N]

Ionic liquids

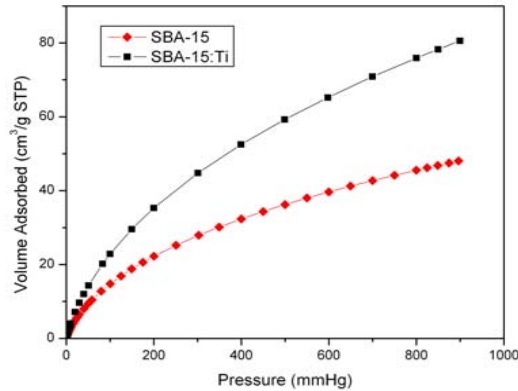
# Accomplishment: Enhanced H<sub>2</sub> Capacity and Binding of SBA-15 by Ti doping

: chemisorption at elevated pressures?

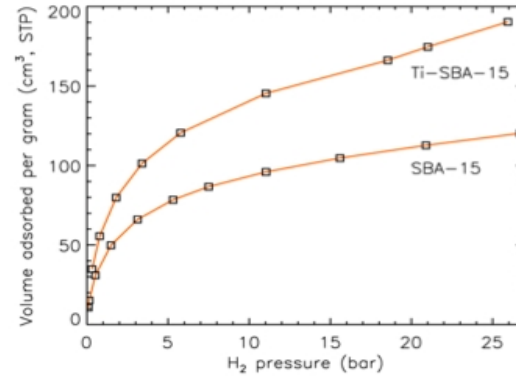


Cluster model for Ti in TS-1

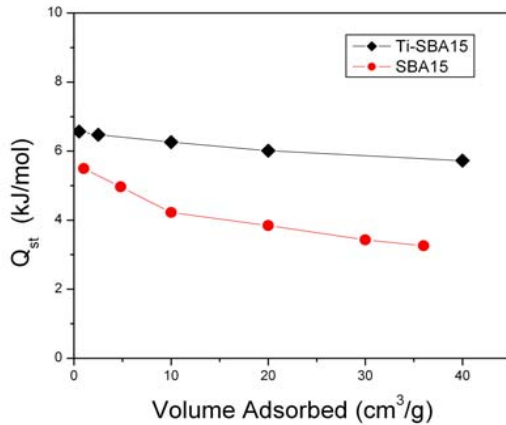
low pressure



high pressure

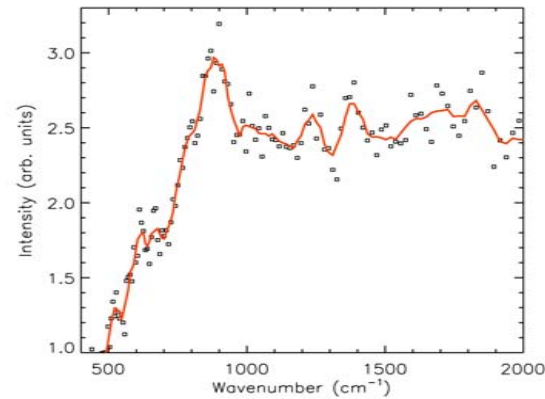


Note divergence in slopes above ~ 10 bar



~ 20 - 50% increase in Q<sub>st</sub>

INS Spectrum(FDS, Lujan Center, LANL)



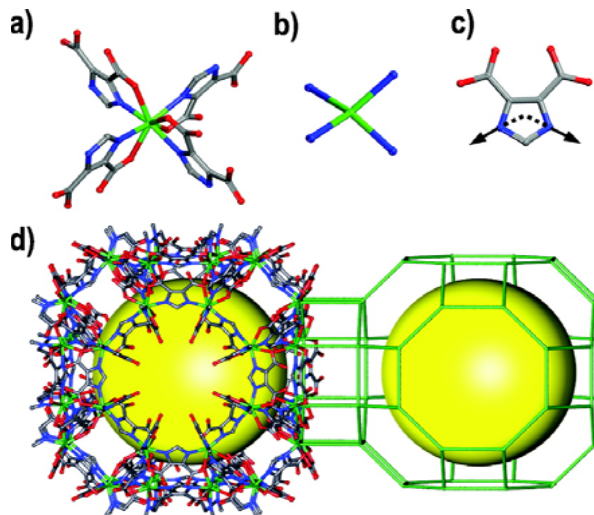
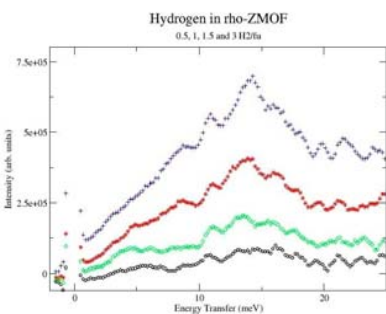
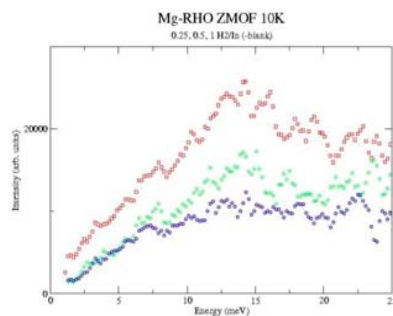
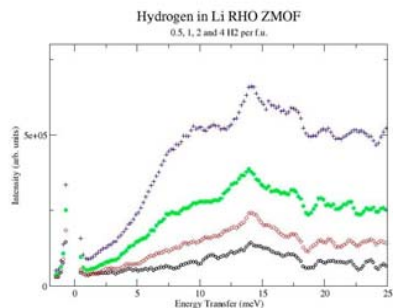
Vibrational spectrum:  
some chemisorbed H ?

Difference spectrum  
{H<sub>2</sub>/Ti-SBA-15}-{H<sub>2</sub>/SBA-15}

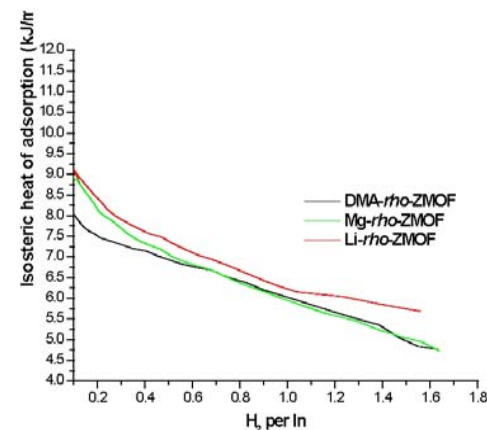
# Charged frameworks and ionic species improve H<sub>2</sub> binding significantly

## 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

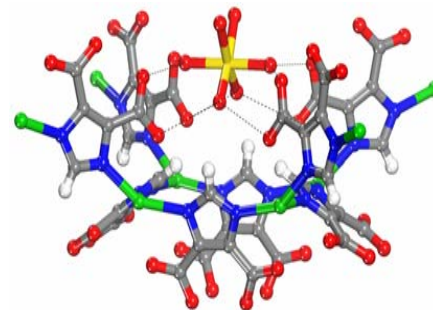
-only weakly dependent on

the nature of the cation

-cation not accessible - present as

aquo complex

⇒ **Electrostatics !!**

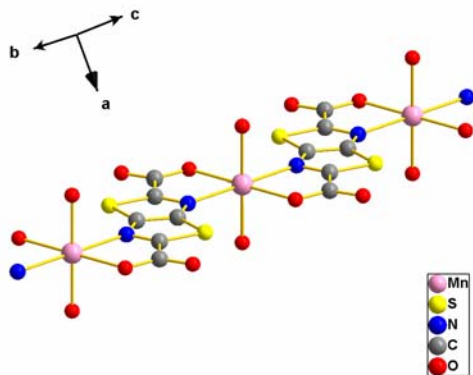


Binding sites not as well defined as in (e.g.) MOF-5

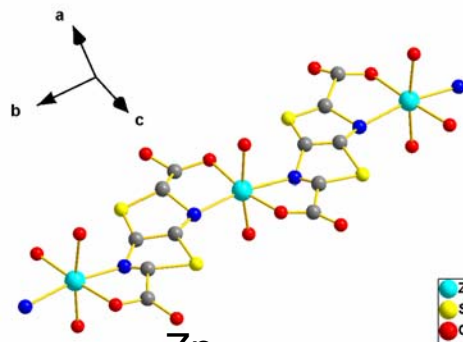
Center of gravity of spectrum shifted to significantly lower energies

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

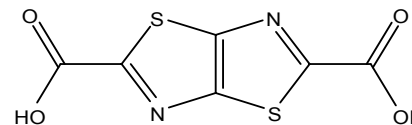
# Accomplishment: Synthesis of Hybrid Materials with Metal Centers and a Highly Functionalized Organic Link: (1) Transition Metals



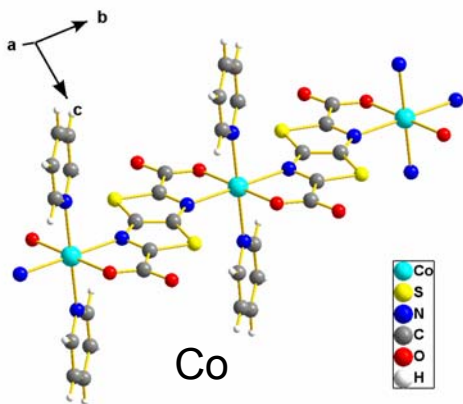
Mn



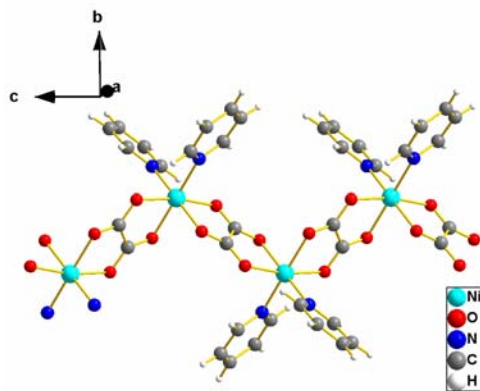
Zn



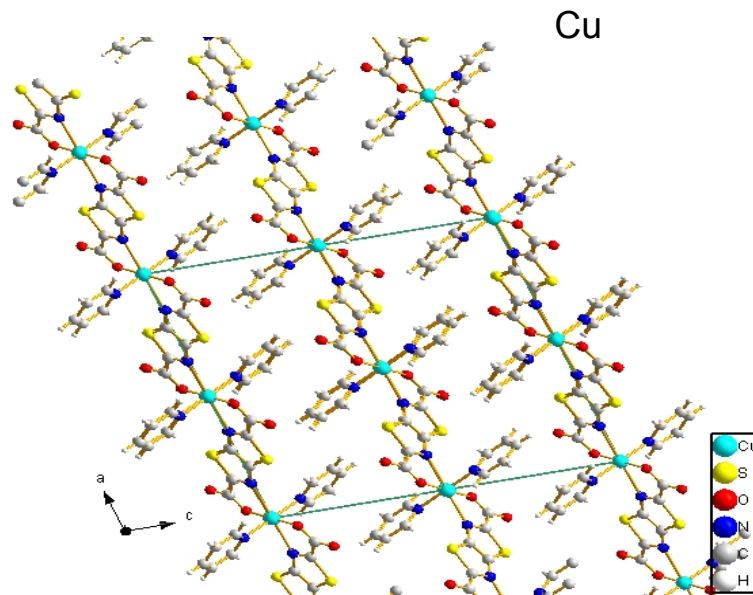
[5,4-d]thiazoledicarboxylic 2,5-Thiazolo acid



Co



Ni

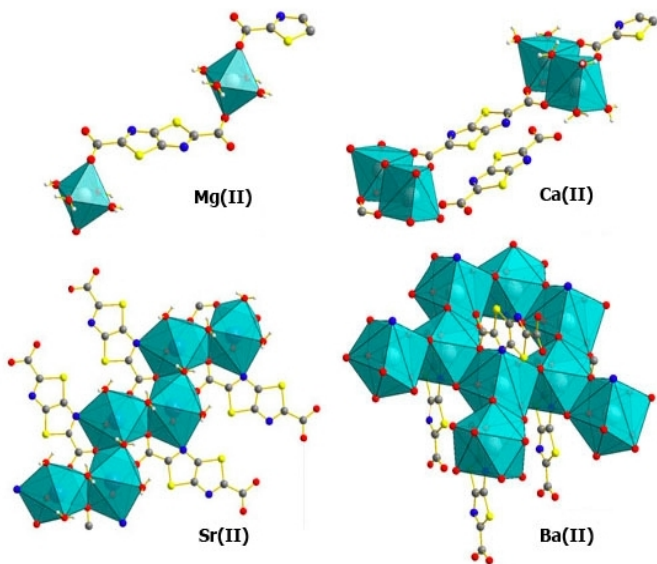


Cu

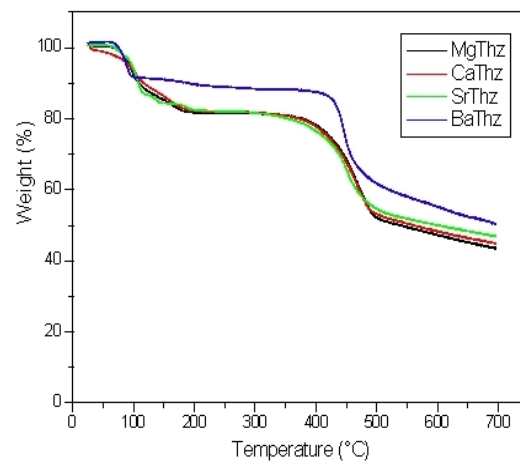
- Mn and Zn: water molecules on axial positions (solvent system: water/pyridine, same as used for all other reactions)
- MnThz: MW conditions (no crystals obtained from solvothermal).
- Nickel: Thz decomposes to oxalate.



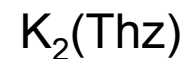
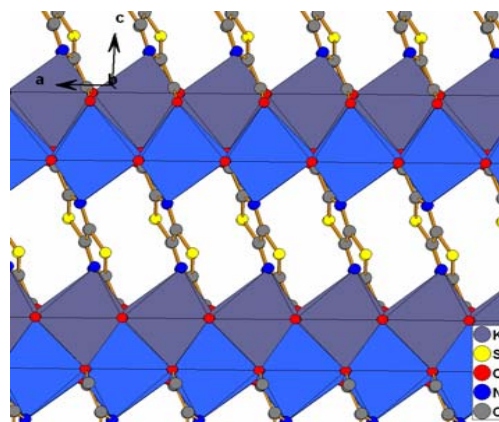
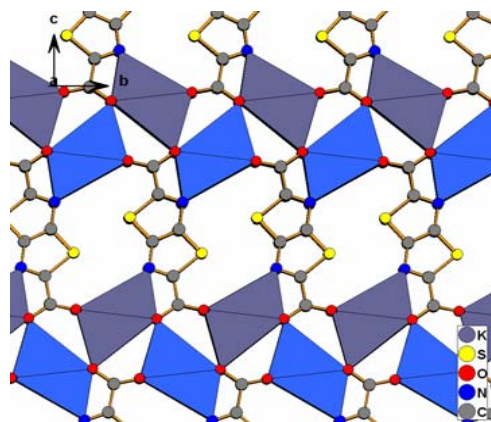
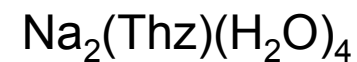
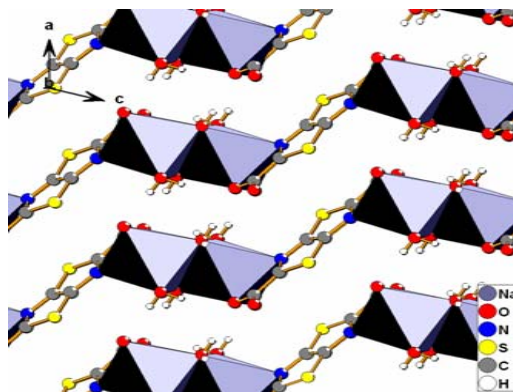
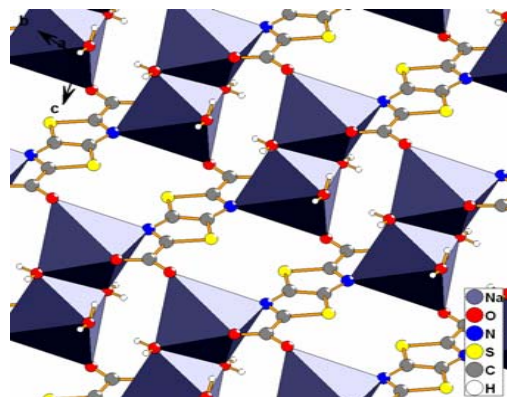
# Accomplishment: Synthesis of Hybrid Materials with Metal Centers and a Highly Functionalized Organic Link: (2) Alkaline Earths



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



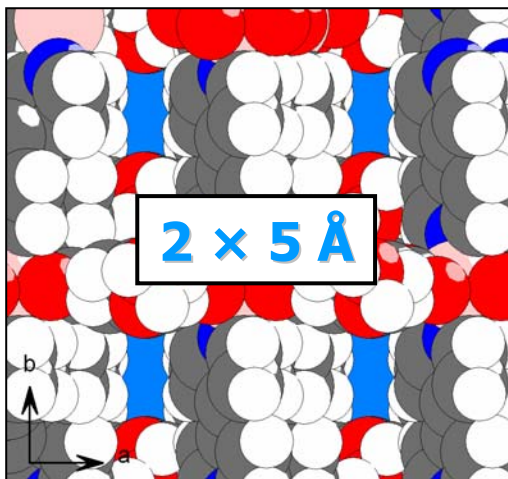
# Accomplishment: Synthesis of Hybrid Materials with Metal Centers and a Highly Functionalized Organic Link: (3) Alkali Metals



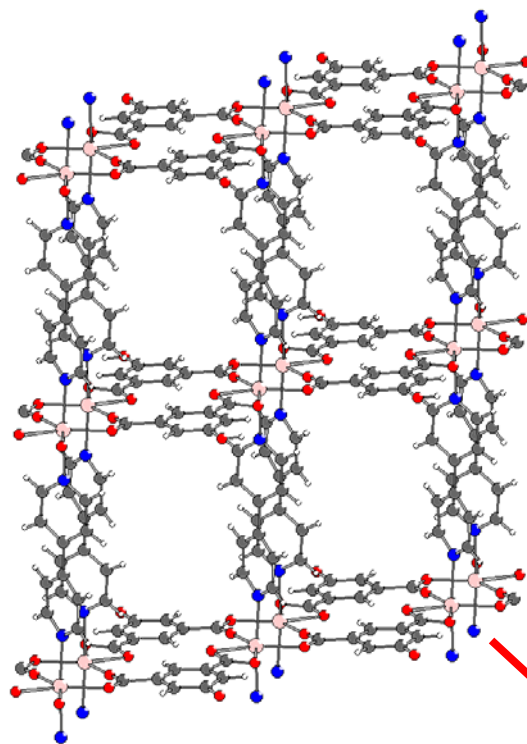
-Structure evolves from 2D with Na to 3D with K. Also, K is anhydrous.



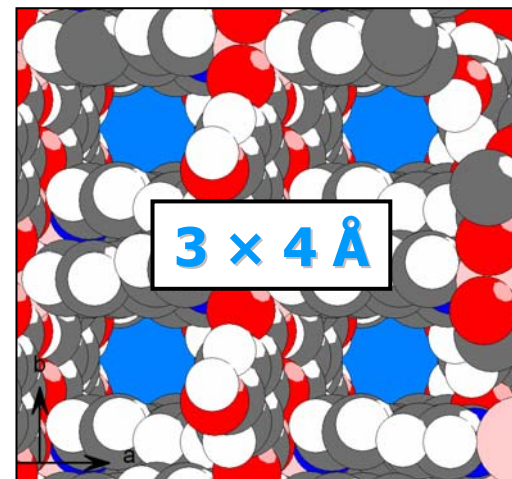
# Transition Metal Bipyridyl/Hydroxyisophthalates



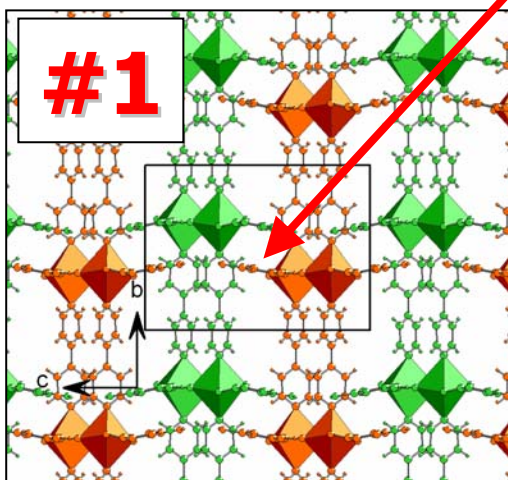
rotate



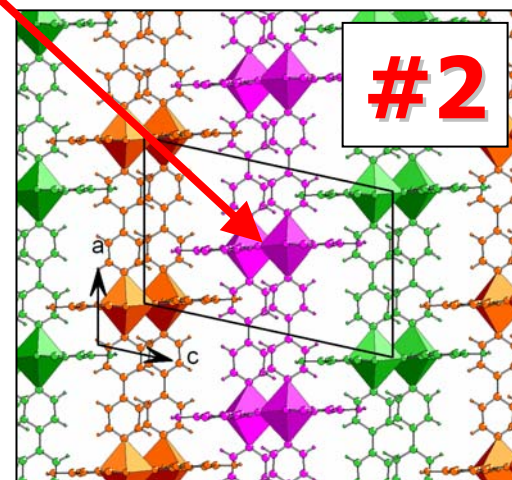
**Mn(bipyridyl)(5-HIP)  
hydrates, #1 and #2**



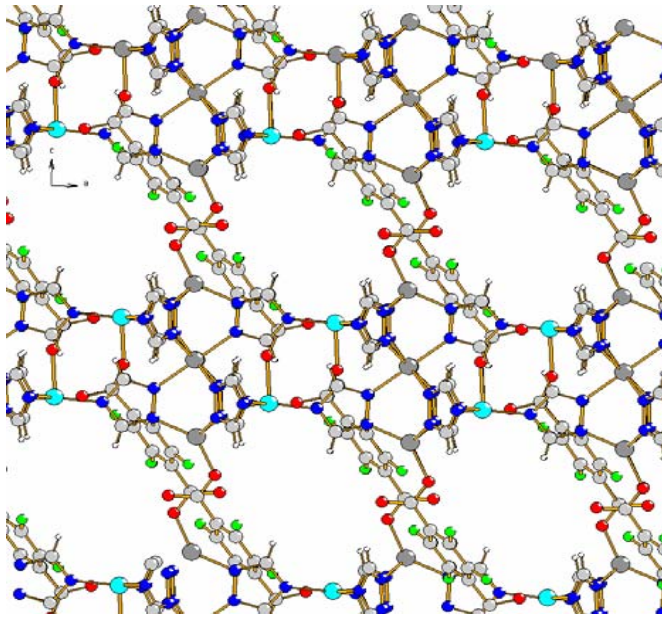
rotate



Two stackings of gridlike motif  
Guest species all uncoordinated  
Two different channel shapes

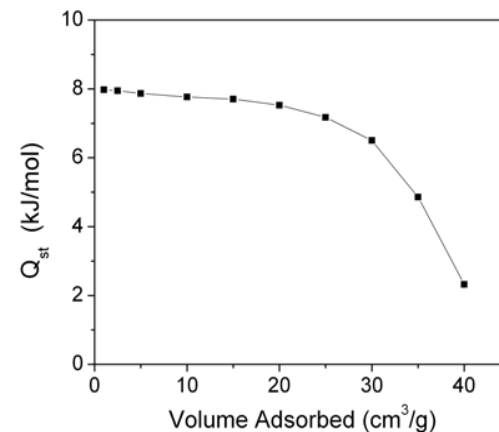
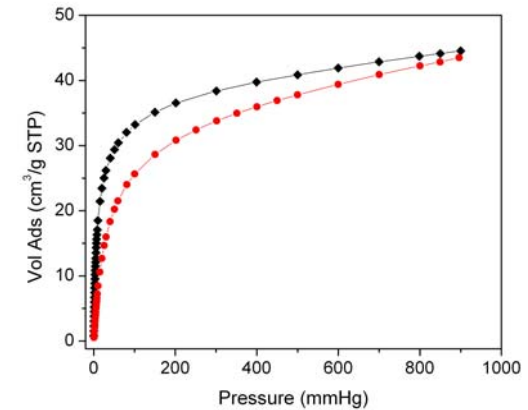


Accomplishment: development of porous, partially **fluorinated** hybrids  
with **open metal** sites:



Zn takes up 3 different coordination geometries

H<sub>2</sub> isotherms, 77 and 87K

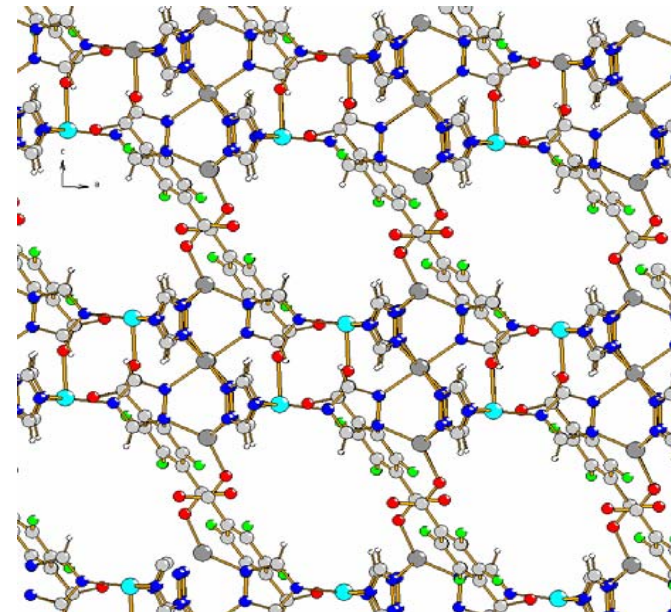


**INS results delayed because of shutdown of IPNS (ANL) !!**

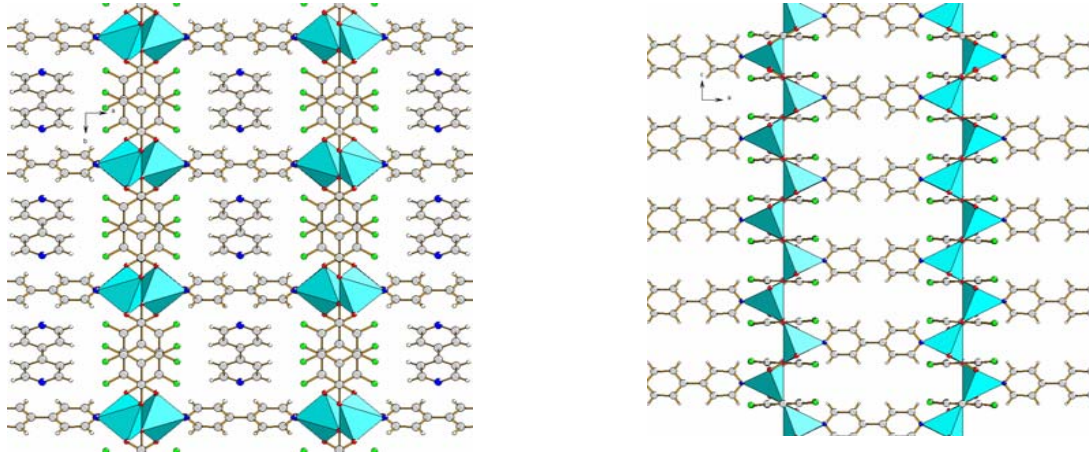
Use of F instead of H on the organic linker **improves H<sub>2</sub> binding energies by ~ 50%**

# 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<sub>2</sub> binding
  - Go/no-go decision 12/31/2008
- Fluorinated linkers in hybrid materials
  - Synthesize materials with open metal sites other than Zn
  - improve H<sub>2</sub> binding above 10 kJ/mol
  - achieve greater porosity (FY08-FY09)



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



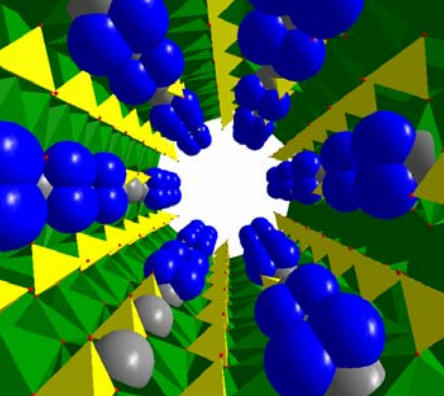
Note: F's point into the cavity

⇒ 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  $\Rightarrow$  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<sub>2</sub> hindered rotor: most sensitive technique for the study of H<sub>2</sub>/host interactions at specific binding sites
- Open metal sites must also be directly accessible by H<sub>2</sub>;  
:main problem with MOST such materials reported to date;  
also: oxidation state
- Transition metal sites in porous materials  $\Rightarrow$  weight penalty addressed by
  - Use of lightweight frameworks
  - Binding multiple dihydrogen ligands - requires very open metal site
  - Framework modifications: ~50% gains  $\Rightarrow$  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