

Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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Project ID: ST 11

Overview

Timeline

- Project start date: 4/1/2005
- Project end date: 3/31/2009

Budget

- Total project funding
 - DOE share: \$1,199,073
 - Contractor share: \$299,674
- Funding* received in FY06
\$ 200,000
- Funding* expected for FY07
\$ 380,000

* including LANL portion

Barriers

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

Partners

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

Collaborators

- J.-S. Chang (KRICT)
- A. Albinati (U. di Milano, Italy)
- M. Eddaoudi (USF)
- A. Bug (Swarthmore College)
- N. J. Henson (LANL)

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)

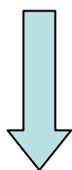
- **Goal is to reach binding energies of 15 - 25 kJ/mol**

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 H₂ binding Energy

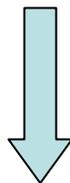
Unsaturated (Transition) Metal Binding Sites

(can reach > 20 kJ/mol)



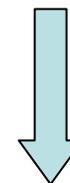
Density too high?

Bind Multiple
Dihydrogen Ligands
(Kubas, LANL)

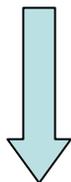


Not enough such sites?

Lighter Metals:
Mg Hybrids



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



Add "Chemistry": Reversible H₂ addition to C=C Bonds on Linkers

Approach

(1) Focus **first** on **synthesis** of materials, which bind **molecular H₂ 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

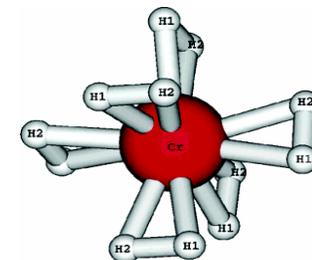
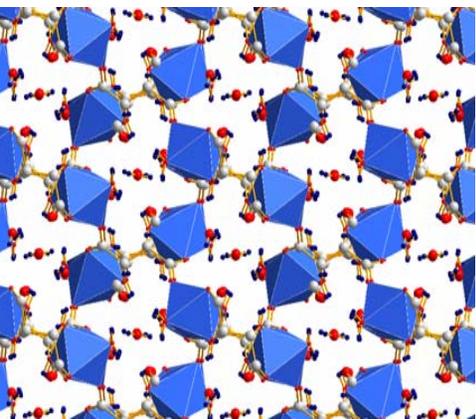
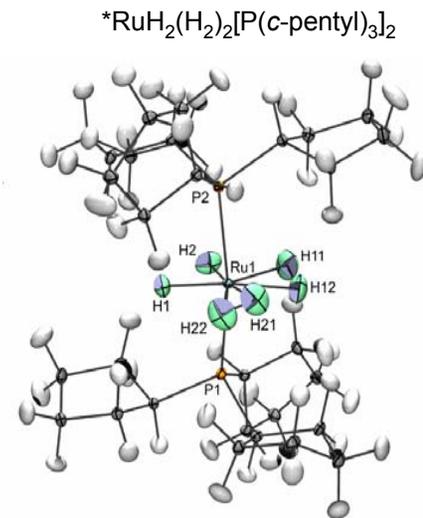
1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes >)

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

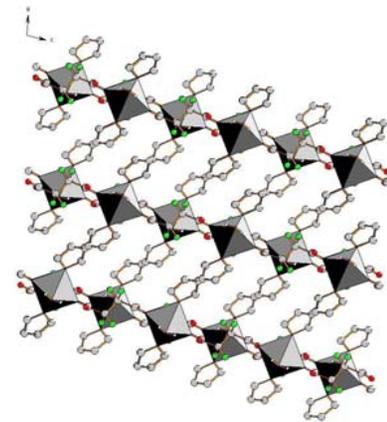
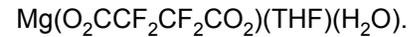
for transition metals: increase H₂ capacity by binding multiple dihydrogen ligands to a metal site -

OR

hybrid materials with lighter metals (eg. Mg) instead of transition metals



Approach



2. Use **fluorinated organic** linkers:

increase H_2 binding by **~ 50%** (calc.)

3. (Collaboration* with M. Eddaoudi, USF): **charged** frameworks increase H_2 binding energy appreciably (e.g. zeolites: **~ 50%** relative to carbons)

* Not funded by EERE/DOE

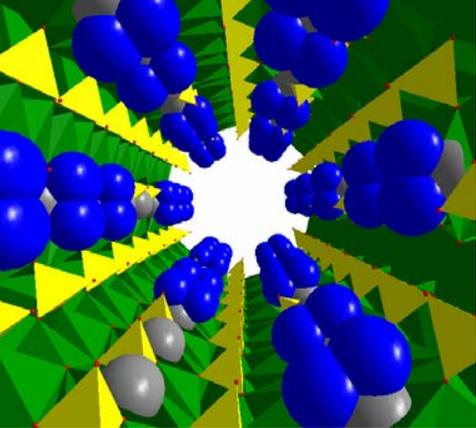
4. Characterize Binding of Hydrogen by Bulk Measurements and Inelastic Neutron Scattering

1. Adsorption isotherms, porosity, TPD, etc.

2. Structural studies: sorption sites,

3. Computational work (funded by BES)

3. **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 (QENS spectrometer at IPNS/ANL)



Technical Accomplishments Progress/Results

- Experimental observation of the existence of MOLECULAR chemisorption of hydrogen in several porous materials
- Synthesized and characterized H₂ binding in several promising new Mg based hybrid materials
- Synthesized new hybrids with unsaturated (Co-) binding site
- Demonstrate substantial increase in H₂ binding energy for charged frameworks relative to those that are neutral: e.g. extra framework cations in zeolites vs. neutral analogs
- Synthesized hybrids with fluorinated carboxylic acids in ionic liquids.

Accomplishments:

Demonstration of the Existence of **Molecular** Chemisorption of Hydrogen in Porous Materials

- **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 metal binding sites in the Nickel Phosphate VSB-5

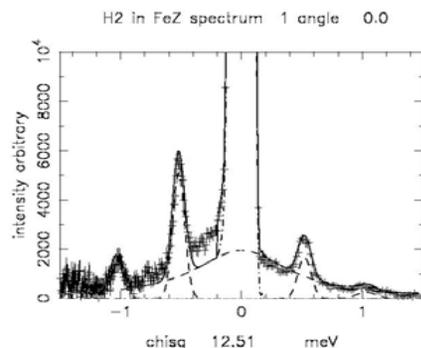
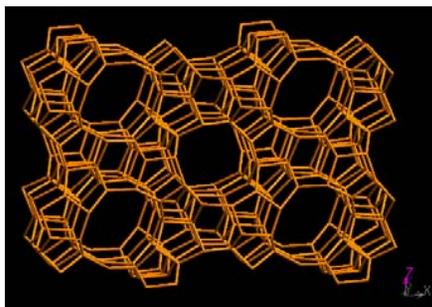
(P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Ferey and A. K. Cheetham J. Am. Chem. Soc. **125**, 1309, 2003)

- Unsaturated metal binding sites in the Nickel-5-Sulfoisophthalate

(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)

- Hydrogen in Cu-ZSM-5

P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert (submitted for publication)



H₂ rotational tunneling
Spectrum(INS) - analogy with
Fe-dihydrogen complex

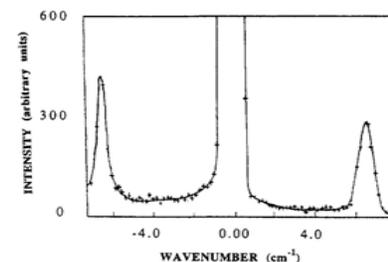
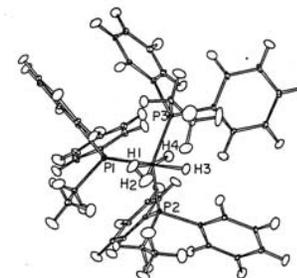
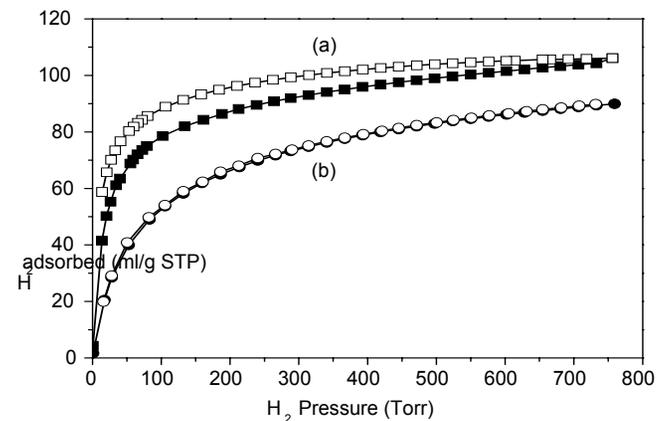
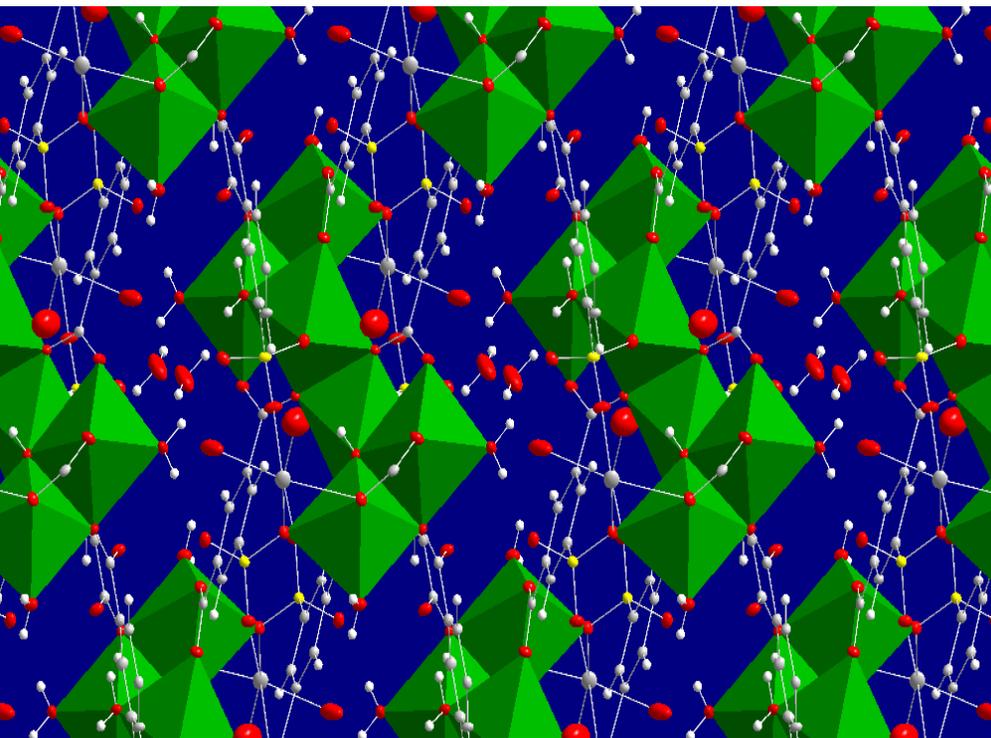
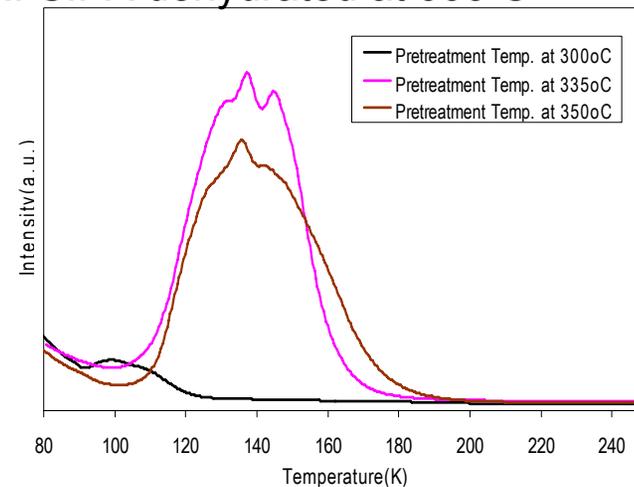


Figure 4. Rotational tunneling spectrum of the H₂ ligand in Fe(H₂)₂(H₂)(PEtPh₂)₂, obtained at 1.5 K on the INS spectrometer at the ILL.

A thermally stable **Nickel 5-Sulfoisophthalate** with remarkable H₂ sorption properties



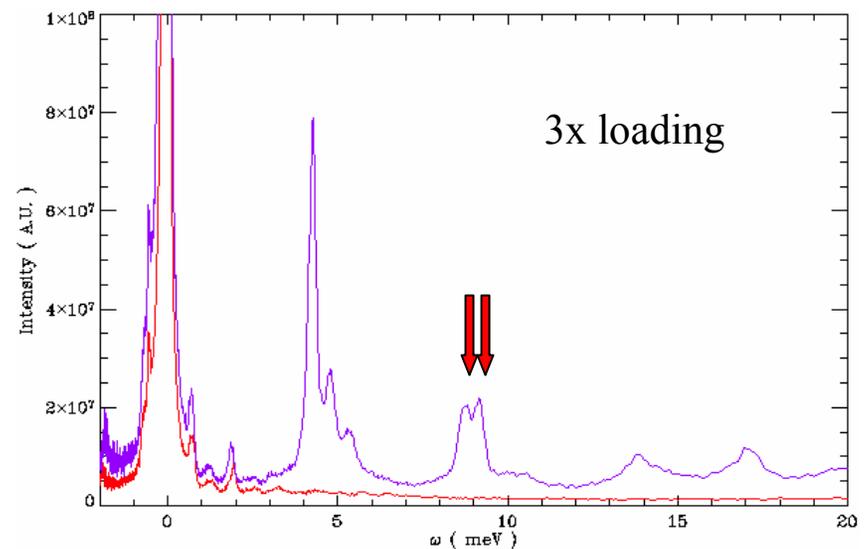
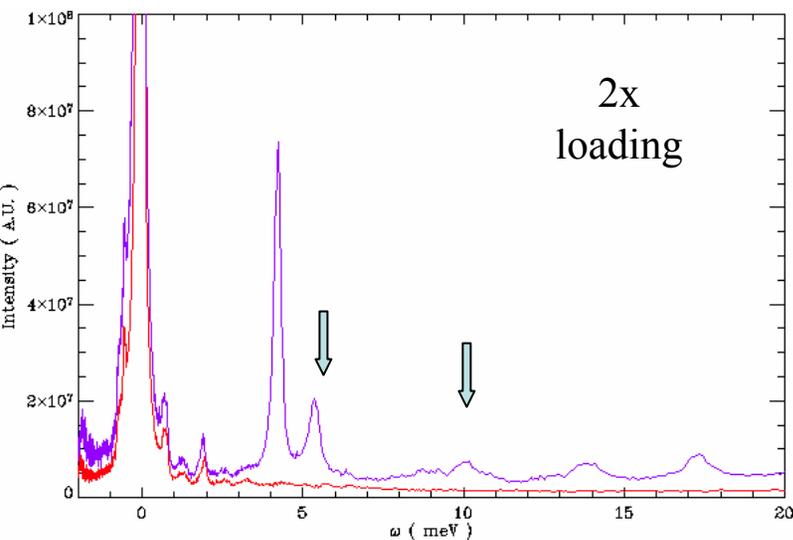
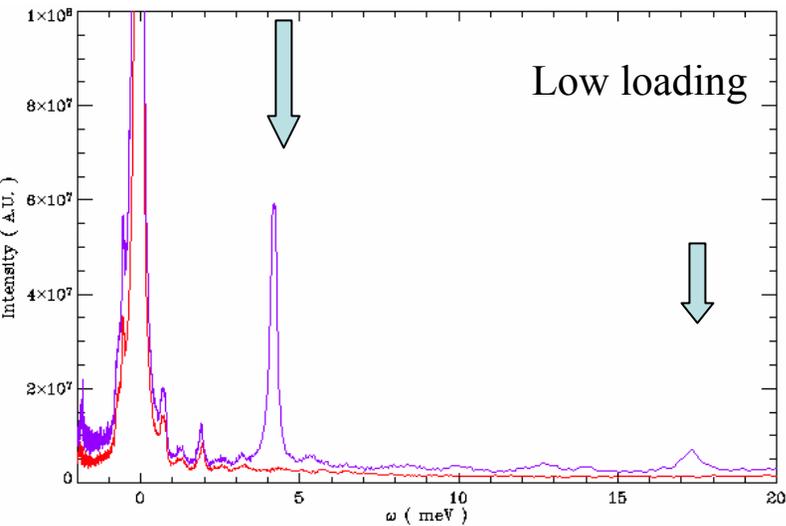
Ni-SIPA dehydrated at 335 C



D.S. Kim, P. M. Forster, R. L. Toquin, A. K. Cheetham, Chem. Comm. **2004**, 2148

Rotational tunneling spectra of H₂ in Nickel 5-Sulfoisophthalate

several well-defined binding sites with strong guest-host interaction
(\gg than carbons or MOF-5)
sites with **planar** rotation
chemisorbed H₂ at unsaturated Ni sites)
and **3-D** rotation **physisorbed H₂**

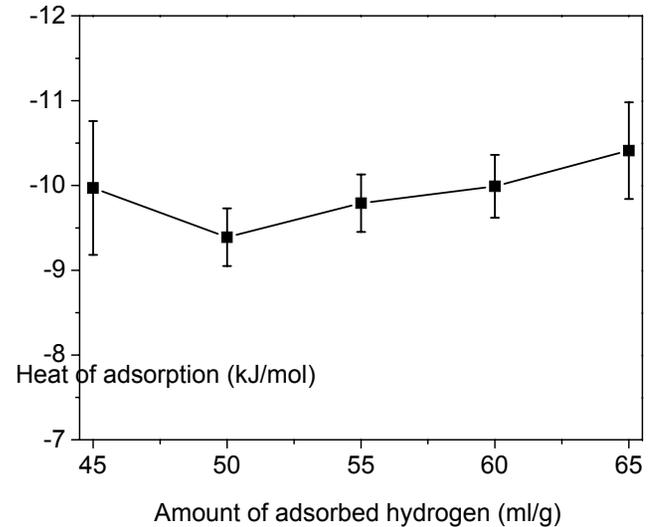


Nickel 5-Sulfoisophthalate Hydrogen Sorption Properties

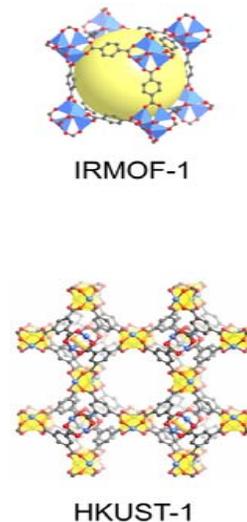
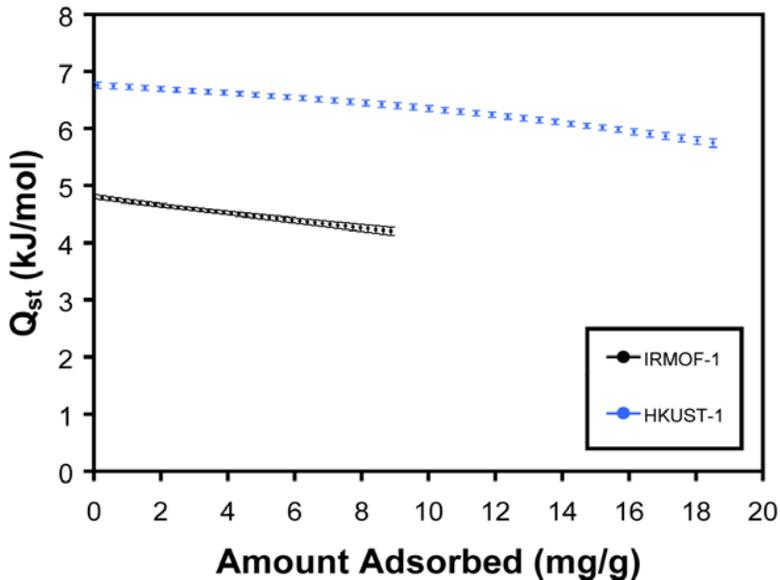
surface area: 743 m²/g
gravimetric capacity (77K) ~ 1 wt. %

>>need more Ni sites, multiple H₂ ligands

binding energy ~ twice that in MOF's



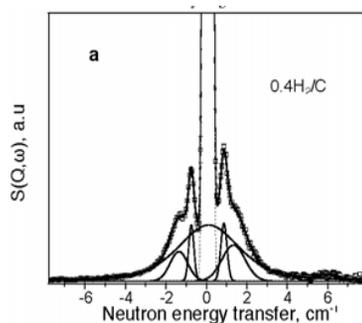
Isosteric heat of hydrogen adsorption estimated using the Clausius-Clapeyron equation and the H₂ adsorption isotherms at 77 K and 87 K (Note: average over ALL sites)



Comparison
with MOF-5 (IRMOF-1)
and
Cu-BTC (HKUST-1)

Strong Molecular Chemisorption* of H₂ on Cu in ZSM-5

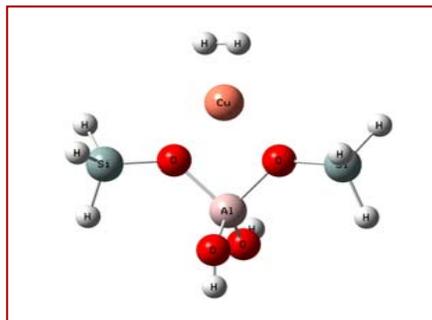
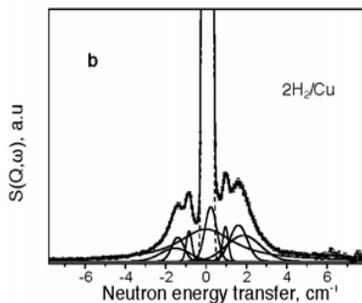
P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert (submitted to JACS); IN5 at ILL(Grenoble, France)



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

Note: FIVE times H₂ loading gives only ~10% in intensity
Where did the extra H₂ go?

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



Model for Cu⁺ in ZSM-5

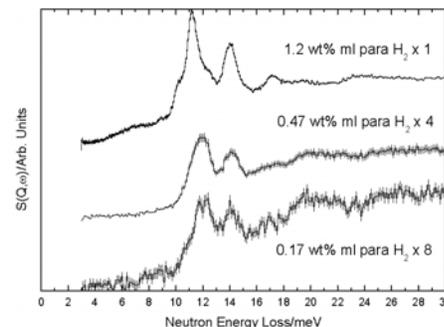


Figure 3. The rotational spectra of para-hydrogen in CuZSM5 at different H₂ loadings.

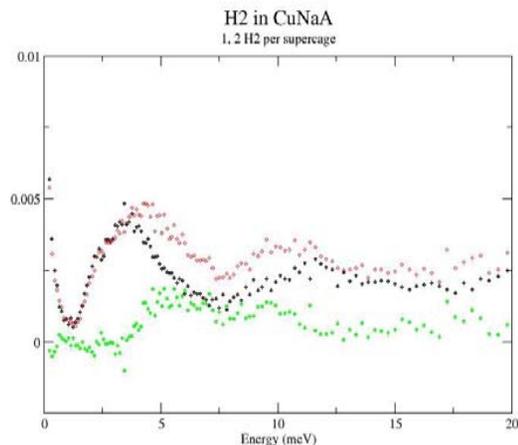
Calculated binding energy = 56 kJ/mol (!!!)

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)

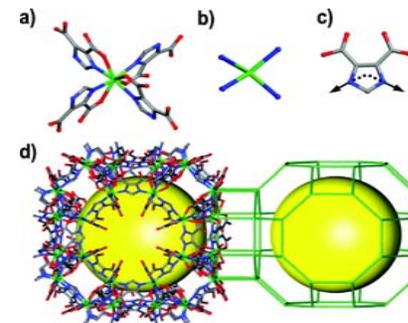
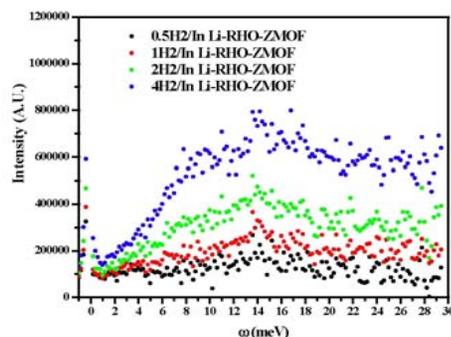
Charged frameworks and ionic species improve H₂ binding significantly

Hydrogen adsorption at Cu sites:
cationic vs. neutral



Hydrogen in Anionic Framework
(Collaboration with M. Eddaoudi)

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



“0-1” rotational transition* for H₂ at

Cu in Cu-ATC: ~ 8 meV

Cu²⁺ in zeolite A: ~ 3 meV

Cu⁺ in zeolite ZSM-5 ~0.15 meV

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

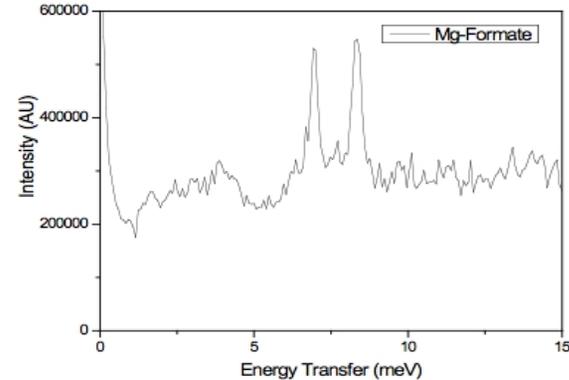
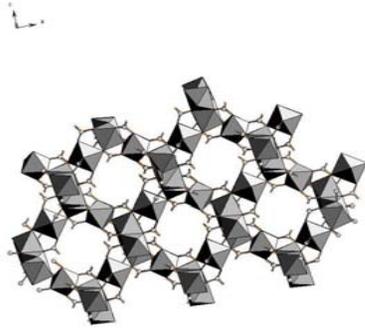
Center of gravity of spectrum shifted to significantly lower energies*

Note: Heats of adsorption in zeolites ~ 50% greater than on carbons

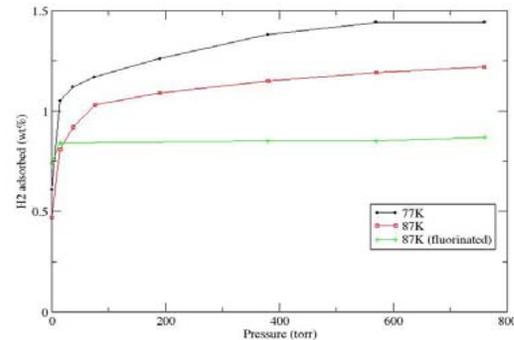
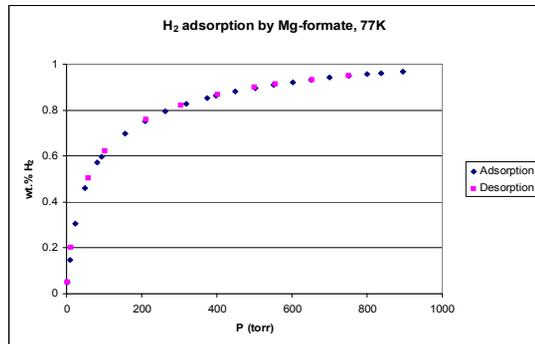
* Smaller value > larger barrier

Synthesis of Mg based Hybrids

Example of a Mg-based hybrid material: Magnesium Formate*



INS spectrum: two distinct binding sites, both **appreciably stronger** than for H_2 on the surface of MgO (rot. trans. at ~ 11 meV; J. Z. Larese)

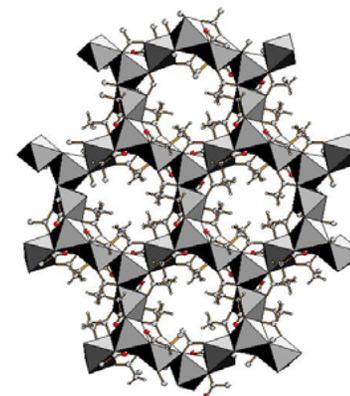
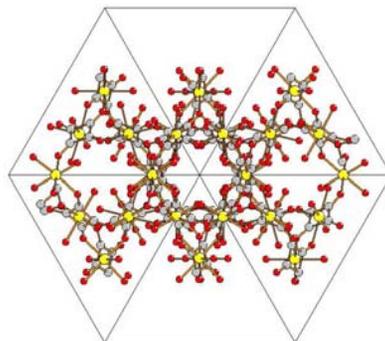
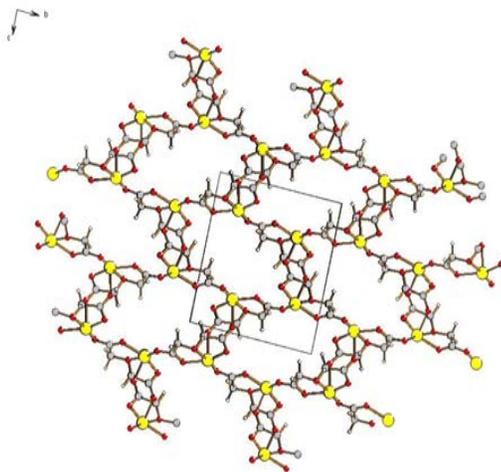


Experimental* and calculated (GCMC/DIZZY: E. Sullivan) H_2 Isotherms

Note: 1 wt% loading requires filling pores > small surface area

*Rood, J. A.; Noll, B. C.; Henderson, K. W.; Inorg. Chem. 2006, 45, 5521; J. Long (personal communication)

Synthesis of New, Porous, Mg-based Hybrid Materials



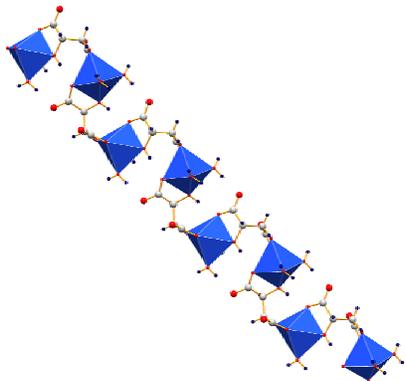
Magnesium Diglycolate: $\text{Mg}(\text{H}_2\text{O})(\text{C}_4\text{H}_4\text{O}_5) \cdot \text{H}_2\text{O}$
Shown **without water** guests: **vacant Mg binding site**
Has $\sim 9\text{\AA}$ wide channels

Magnesium Squarate
 $\text{Mg}(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)$

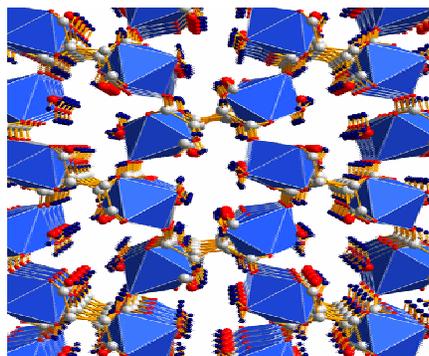
Magnesium Glutarate
 $\text{Mg}(\text{C}_5\text{H}_6\text{O}_4)$

BUT: these structures not stable to removal of guests

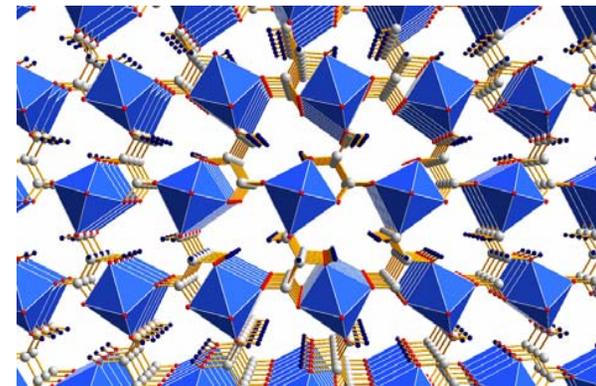
Synthesis of New, Porous, Mg-based Hybrid Materials Magnesium Tartrate



(1D chains, 2 waters coordinated to each Mg atom)

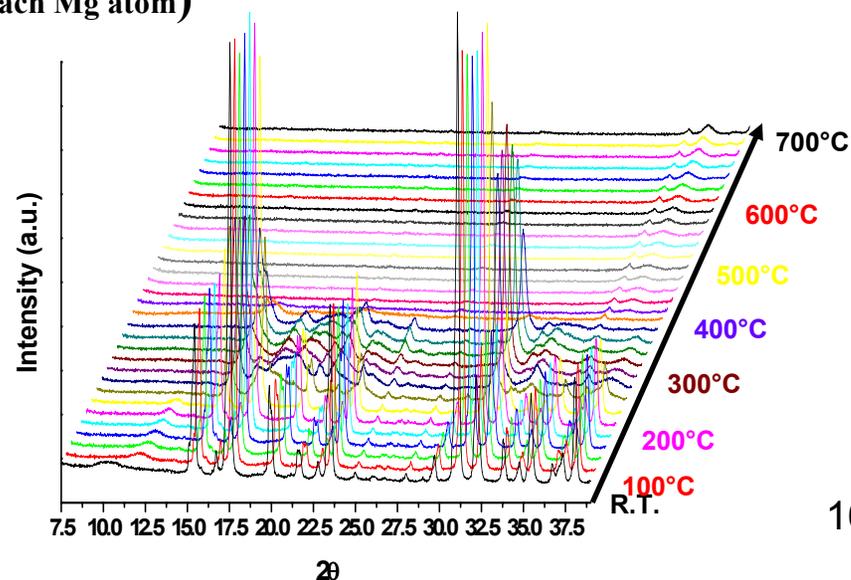


(2D layered structure, pore is 6 membered rings, 1 water coordinated to each Mg atom)



3D framework, 3 membered rings

Porous, stable to water removal, $T \sim 300^\circ\text{C}$



Accomplishment: initial development of fluorinated hybrids

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

Different solvents are required for fluorinated organics: use ionic liquids*

A. Synthesis

1:1 molar mixture of **ethylmethylimidazolium (emim) bromide** and **emim-triflimide**

Triflimide: strongly hydrophobic; solubilizes fluoro-organics, but noncoordinating

Bromide: strongly hydrophilic; easily solubilizes the metal.

> formation of this phase is concentration dependent

B. Structure

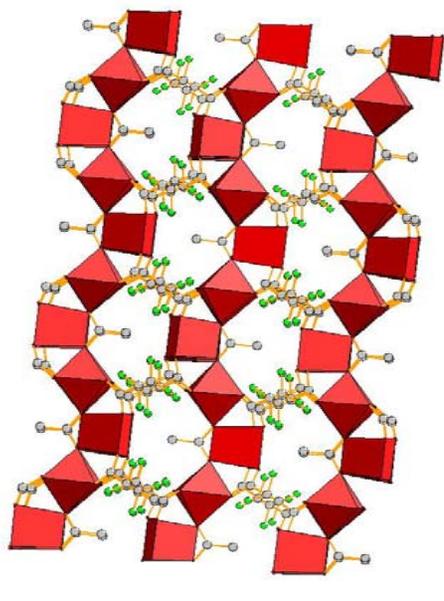
- chain of alternating, corner-sharing octahedral trigonal prismatic CoO_6 units

-acetate ions (bridge trigonal prism) kinking the chain

-tetrafluorosuccinate anions linking the chains.

* Collaboration with Russell Morris (St. Andrews)

* **Calculated for Mg Formate**



Future Work

- Develop compounds with unsaturated (and accessible) metal binding sites.
 - High Pressure adsorption studies (J.-S. Chang, KRICT)
 - Synthesize analogs with larger surface areas (FY08)
- Bind Multiple Dihydrogen ligands (G. J. Kubas, LANL)
 - Protonate bare metal ions in noncoordinating solvents (FY07)
 - Bind resulting clusters in porous materials (FY08 on)
- Magnesium based hybrids with larger surface areas (FY07-08)
- Fluorinated linkers in hybrid materials
 - Optimize synthesis in ionic liquids (FY07)
 - Achieve porosity: Synthesize materials with removable guests (FY08)
- (Reversible) Hydrogen addition to C=C double bonds (FY08)
 - Attempt solid state analog of Air Products approach (in liquid) to boost hydrogen capacity
 - Synthesize new framework materials containing functional groups that are prone to undergo hydrogenation.
 - Quinone-containing moieties are of particular interest >
 - We plan to synthesize hybrid frameworks utilizing organic ligands such as p-benzoquinonedicarboxylic acid, anthraquinonedicarboxylic acids, tetrahydroxy-p-benzoquinone, anthraquinonedisulfonic acid.

Future Work - Continue search for hybrids with effective open metal binding sites

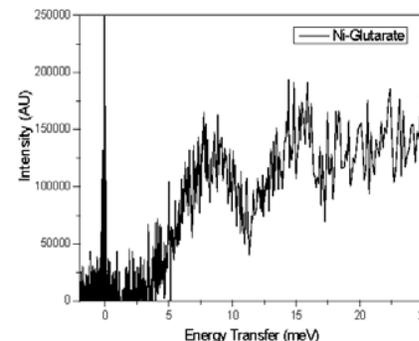
- Recent compounds prepared (E. Falcao)
- Some linkers are chosen to offer the possibility of H₂ addition to C=C bonds

Table 1. Textural characterization of selected frameworks

Compound	BET Surface Area ^d (m ² /g)	Density ^f (g/cm ³)
Ni-2,6NDC ^a	230	2.18
Ni-glutarate	200-300	1.84
Mg-formate	40	1.65
Co-2,6NDC ^a	10	1.61
Ni-1,2PhDA ^b	20	1.89
Ni-TOHQ ^c	30	nd ^g
Mg-TOHQ ^c	25	1.85
Mg-tartrate	60 ^e	1.74

^a NDC: naphthalenedicarboxylate; ^b PhDA: phenylenediacetate; ^c TOHQ: tetrahydroxvquinone; ^d determined with a Micromeritics Tristar equipment; ^e determined with a Micromeritics AccuPyc equipment; ^f nd: not determined.

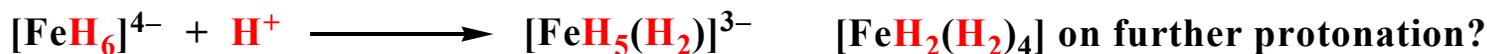
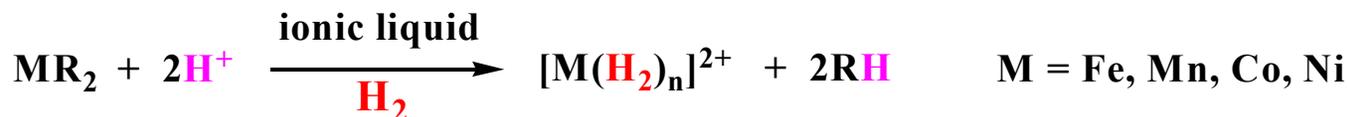
- Characterize H₂ binding*
- If favorable, synthesize analogs with larger surface area



*INS spectrum of H₂ in Ni-glutarate; no open metal sites, but fairly strong binding

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 H₂** ligands via metal alkyl, aryl, or hydride complexes



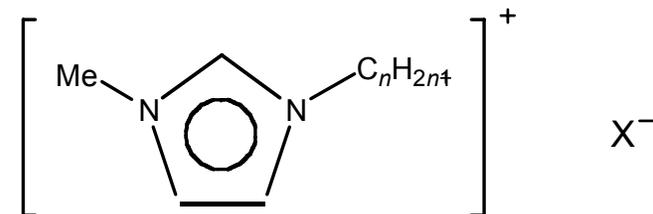
[Linn]

acid with low-coordinating anion

If unstable, embed H₂-rich species into nanoporous media (zeolites, MOF)

We have already demonstrated Dihydrogen Binding to Fe and Cu clusters in ZSM-5

Molecular complexes can also be grafted to nanoporous materials surfaces



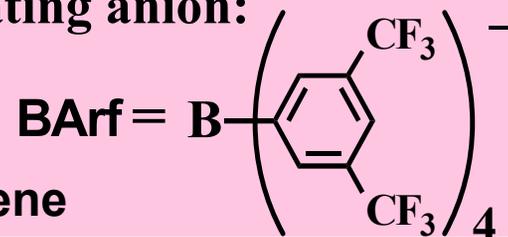
- I $n = 4$, $X = [\text{PF}_6]$; [bmim][PF₆]
- II $n = 4$, $X = [(\text{CF}_3\text{SO}_2)_2\text{N}]$; [bmim][Tf₂N]
- III $n = 2$, $X = [(\text{CF}_3\text{SO}_2)_2\text{N}]$; [emim][Tf₂N]

Iron-aryl complex:

$\text{Fe}_2(\text{mesityl})_4 + \text{H}_2$ gives no reaction

$\text{Fe}_2(\text{mesityl})_4 + \text{H}[\text{BArf}]$ forms oily precipitate in toluene

low coordinating anion:



HYDRIDE

2.7 atm

Linn complex--- soluble in organics!

Linn & Gibbins, *J. Organomet. Chem.*, **554**, 171(1998)

Inorganic Synth. in press

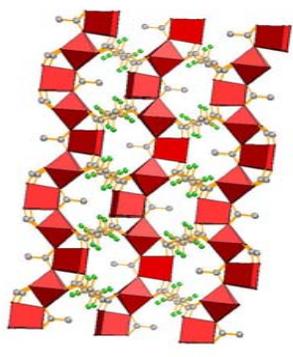
$[\text{FeH}_6]^{4-} + \text{H}[\text{BArf}]$ gives reaction in THF at RT (no gas evolution)

broad NMR signals (paramagnetic impurity?)

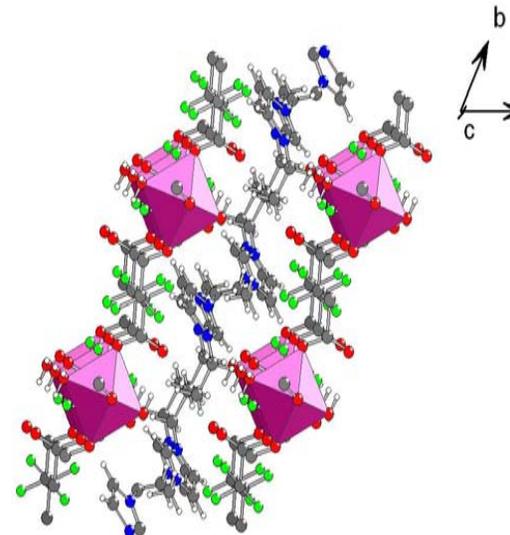
Further reactions will be carried out at low T under H_2

Future Work: further development of fluorinated hybrids (Zeric Hulvey)

FY07: tune synthesis conditions > new phase of
Co-Tetrafluorosuccinate



< crystallized in dry solvents
in presence of some water >



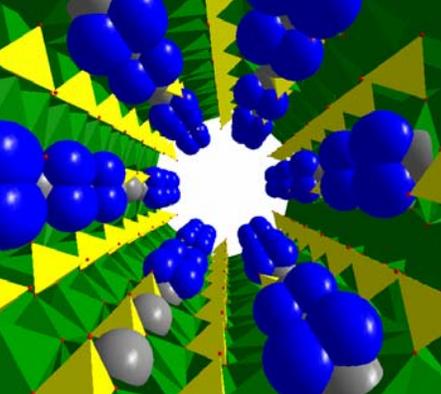
FY08: obtain materials with removable guests
characterize H₂ sorption properties

↓
coordinated (removable ?)
water on Co

+

fluorinated linker

>> strong H₂ binding !



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
- Utilization of INS on the H₂ hindered rotor: most sensitive technique for the study of H₂/host **interactions at specific binding sites**
- Factors in binding at metal sites: oxidation state, accessibility (!)
- Transition metal sites in porous materials \Rightarrow weight penalty addressed by
 - Use of lightweight frameworks: Mg based
 - Binding multiple dihydrogen ligands (needs to be demonstrated)
 - Framework modifications: **$\sim 50\%$ 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
- Investigate if use of chemistry (reversible hydrogenation) on linkers is favorable and can be added to the same material to boost capacity.