

# Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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April 13, 2007

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)

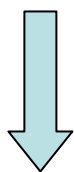
- **Goal is to reach binding energies of 15 - 25 kJ/mol**

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 H<sub>2</sub> binding Energy

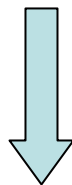
Unsaturated (Transition) Metal Binding Sites

(can reach > 20 kJ/mol)



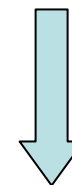
Density too high?

Bind Multiple  
Dihydrogen Ligands  
(Kubas, LANL)

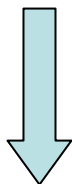


Not enough such sites?

Lighter Metals:  
Mg Hybrids



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



Add "Chemistry": Reversible H<sub>2</sub> addition to C=C Bonds on Linkers

# 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

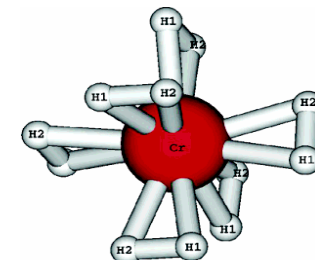
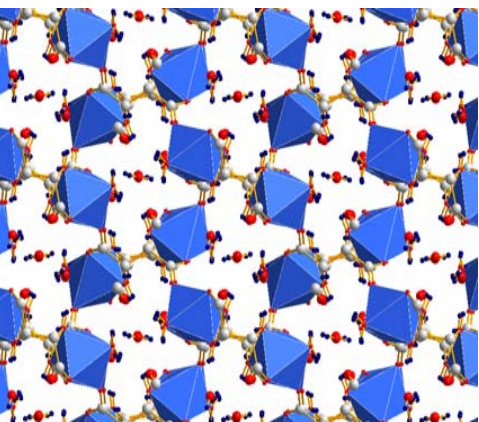
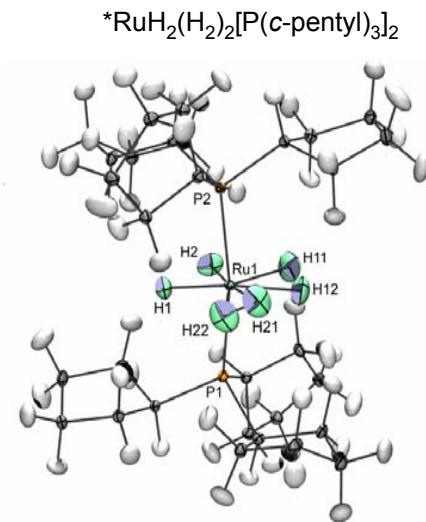
1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes >)

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

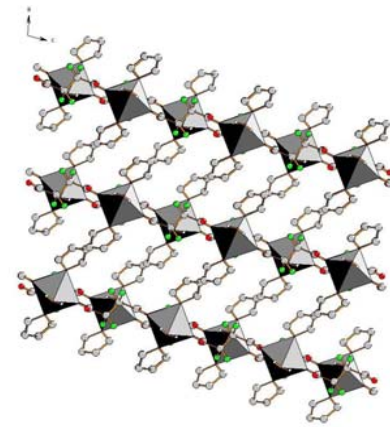
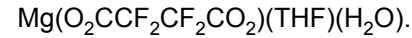
for transition metals: increase H<sub>2</sub> capacity by binding multiple dihydrogen ligands to a metal site -

**OR**

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



# Approach



2. Use **fluorinated organic** linkers:

increase  $\text{H}_2$  binding by **~ 50%** (calc.)

3. (Collaboration\* with M. Eddaoudi, USF): **charged** frameworks increase  $\text{H}_2$  binding energy appreciably (e.g. zeolites: **~ 50%** relative to carbons)

\* Not funded by EERE/DOE

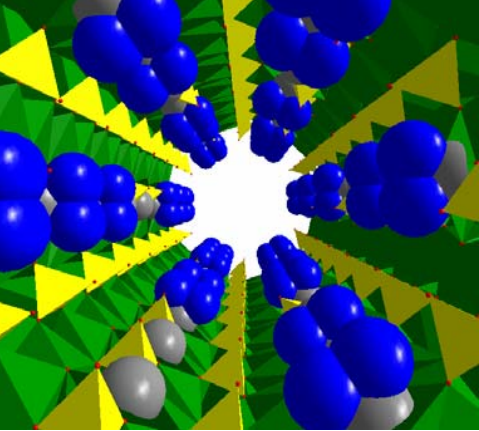
4. Characterize Binding of Hydrogen by Bulk Measurements and Inelastic Neutron Scattering

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  $\text{H}_2$  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 H<sub>2</sub> binding in several promising new Mg based hybrid materials
- Synthesized new hybrids with unsaturated (Co-) binding site
- 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 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

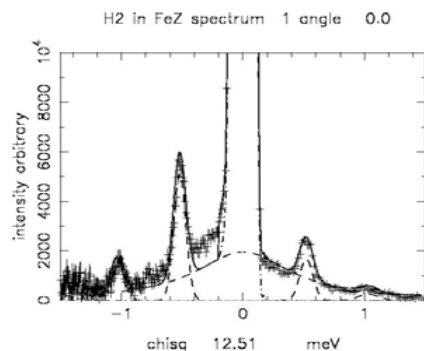
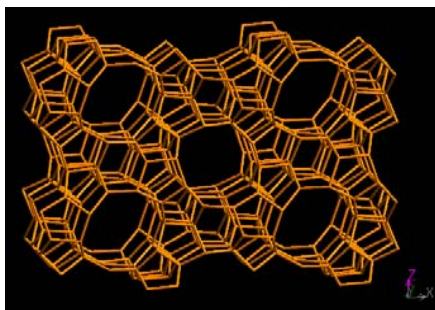
(P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Ferey and A. K. Cheetham J. Am. Chem. Soc. **125**, 1309, 2003)

- 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)



H<sub>2</sub> rotational tunneling  
Spectrum(INS) - analogy with  
Fe-dihydrogen complex

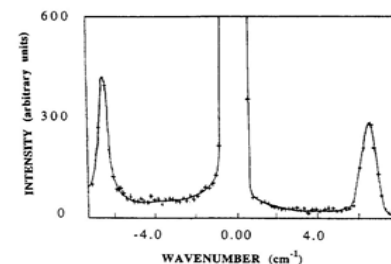
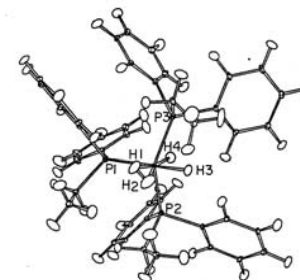
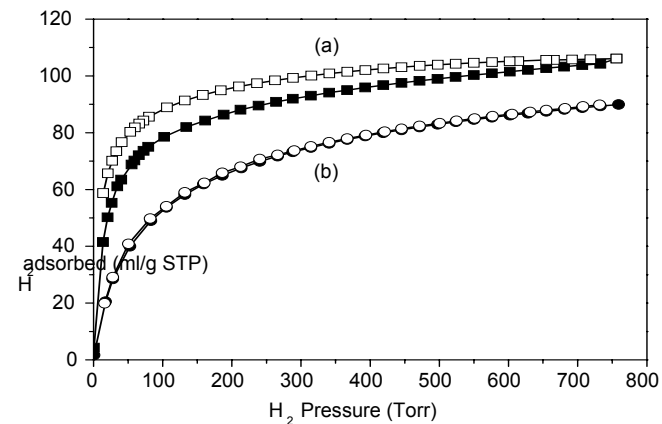
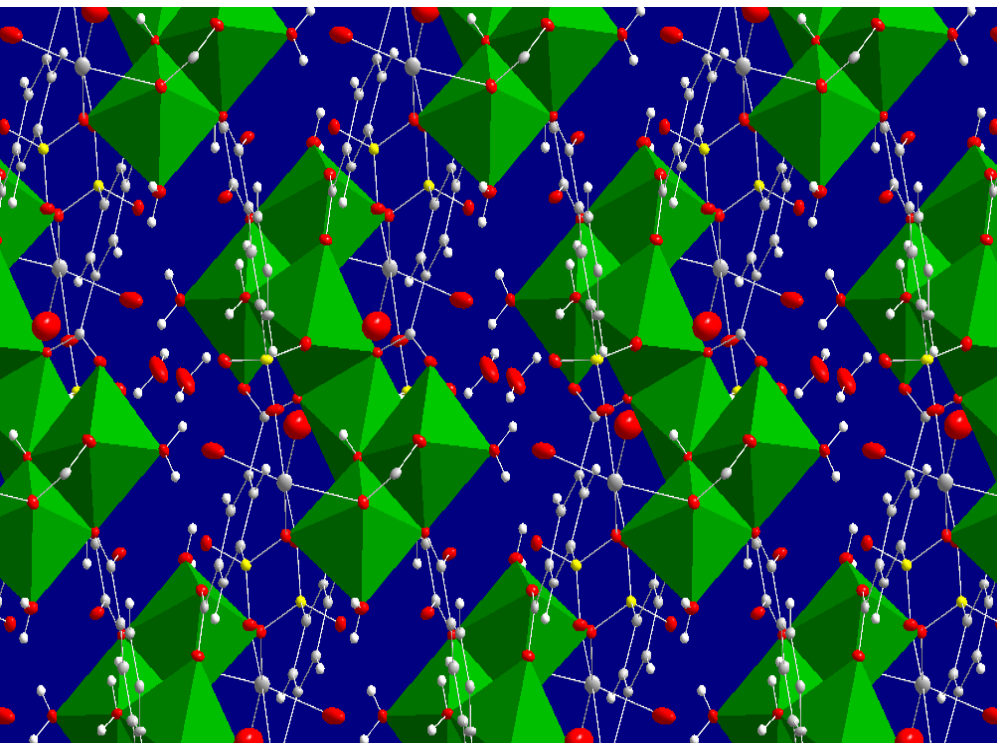


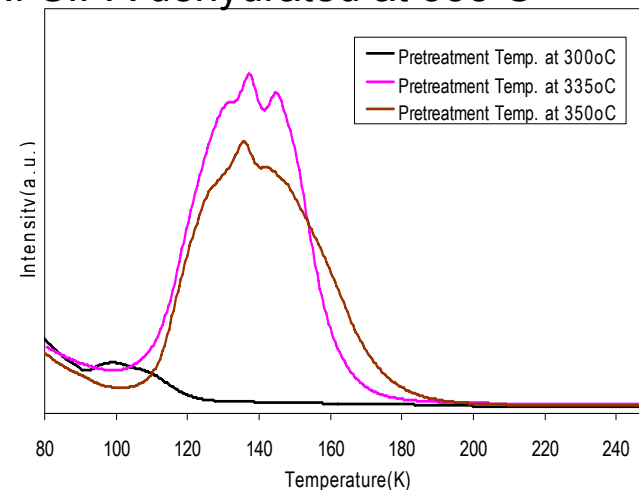
Figure 4. Rotational tunneling spectrum of the H<sub>2</sub> ligand in Fe(H<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>)(PEtPh<sub>2</sub>)<sub>2</sub>, obtained at 1.5 K on the INS spectrometer at the ILL.



# A thermally stable **Nickel 5-Sulfoisophthalate** with remarkable H<sub>2</sub> sorption properties



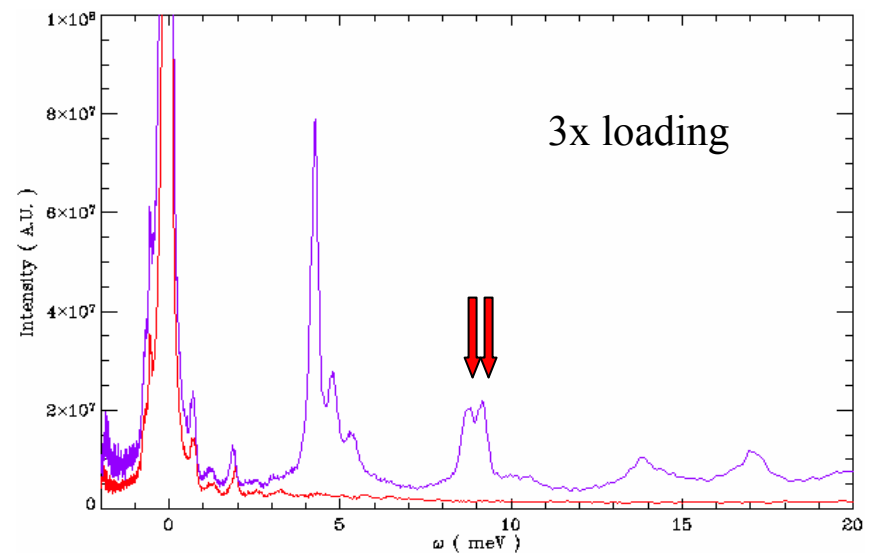
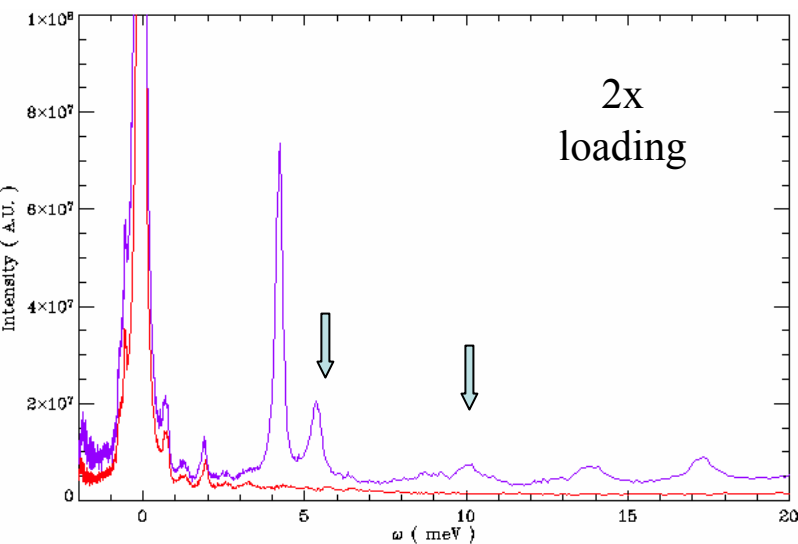
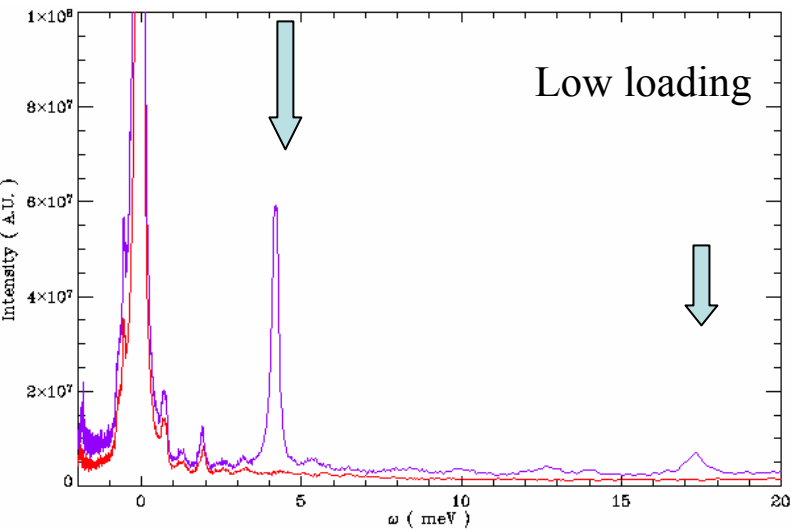
Ni-SIPA dehydrated at 335 C



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

# Rotational tunneling spectra of H<sub>2</sub> 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** H<sub>2</sub> at unsaturated Ni sites)  
and **3-D** rotation **physisorbed** H<sub>2</sub>

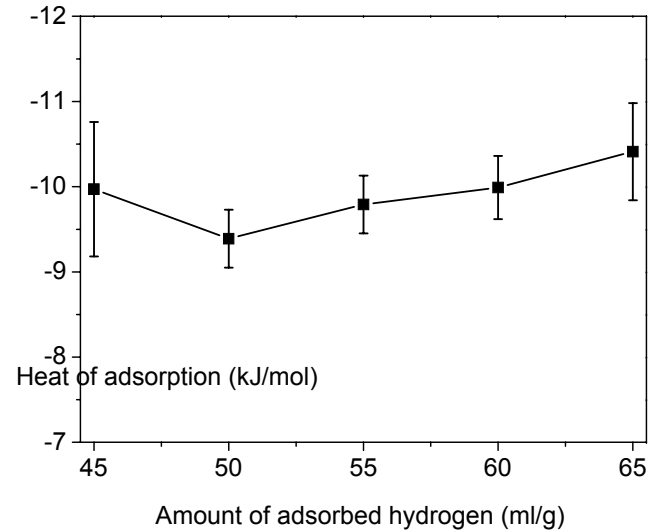


# Nickel 5-Sulfoisophthalate Hydrogen Sorption Properties

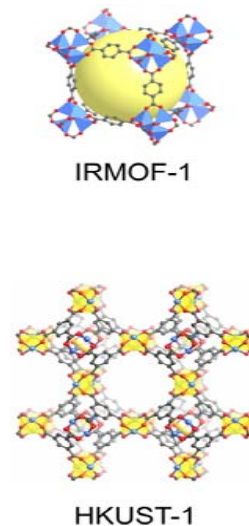
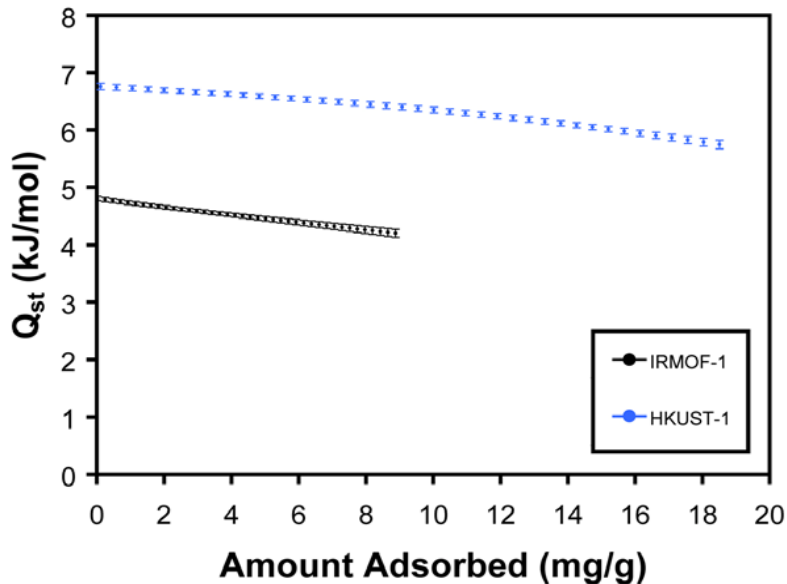
surface area: 743 m<sup>2</sup>/g  
gravimetric capacity (77K) ~ 1 wt. %

>>need more Ni sites, multiple H<sub>2</sub> ligands

binding energy ~ twice that in MOF's



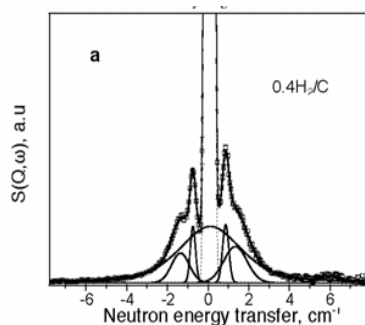
Isosteric heat of hydrogen adsorption estimated using the Clausius-Clapeyron equation and the H<sub>2</sub> adsorption isotherms at 77 K and 87 K (Note: average over ALL sites)



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

# Strong Molecular Chemisorption\* of H<sub>2</sub> on Cu in ZSM-5

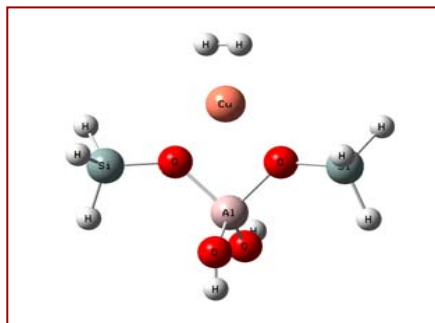
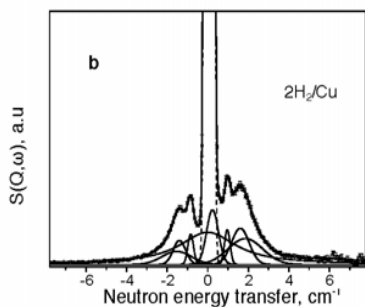
P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert (submitted to JACS); IN5 at ILL(Grenoble, France)



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

**Note:** FIVE times 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



Model for Cu<sup>+</sup> in ZSM-5

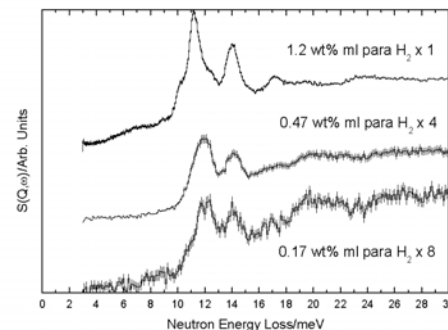


Figure 3. The rotational spectra of para-hydrogen in CuZSM5 at different H<sub>2</sub> loadings.

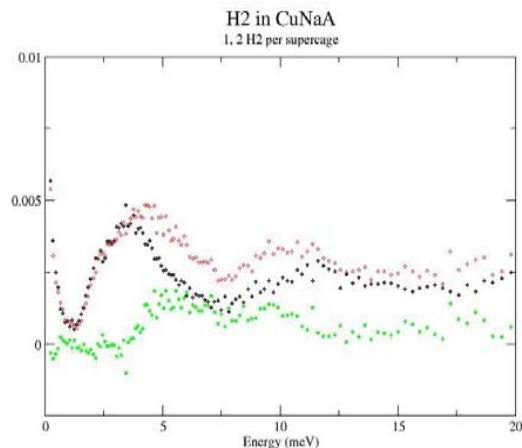
**Calculated binding energy = 56 kJ/mol (!!!)**

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 H<sub>2</sub> binding significantly

Hydrogen adsorption at Cu sites:  
cationic vs. neutral



“0-1” rotational transition\* for H<sub>2</sub> at

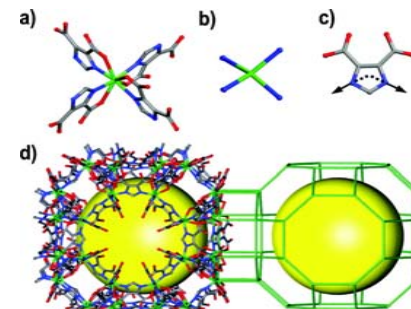
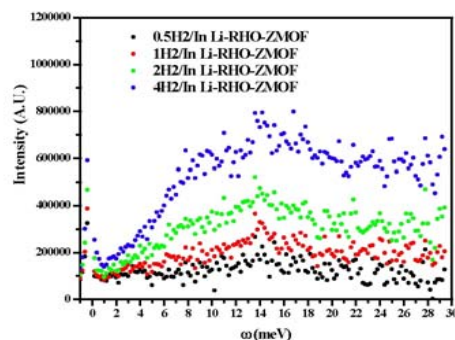
Cu in Cu-ATC: ~ 8 meV

Cu<sup>2+</sup> in zeolite A: ~ 3 meV

Cu<sup>+</sup> in zeolite ZSM-5 ~0.15 meV

Hydrogen in Anionic Framework  
(Collaboration with M. Eddaoudi)

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



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

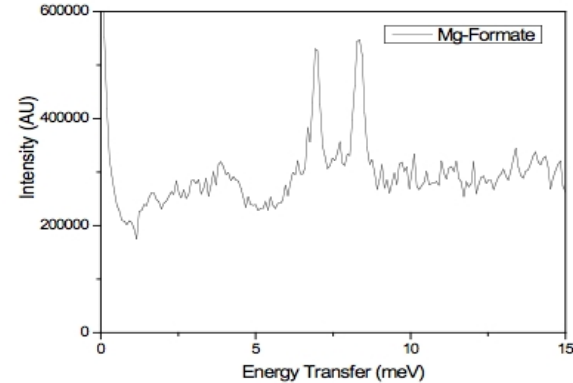
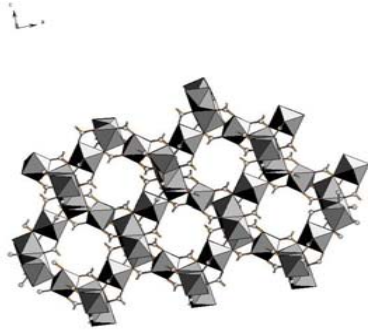
Center of gravity of spectrum shifted to significantly lower energies\*

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

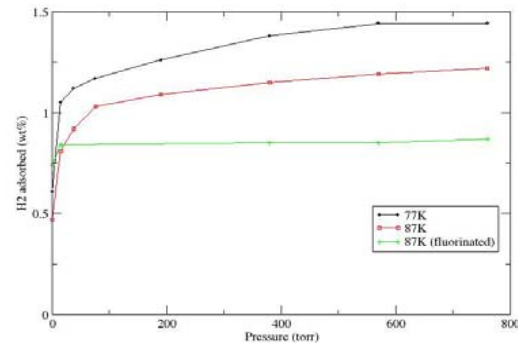
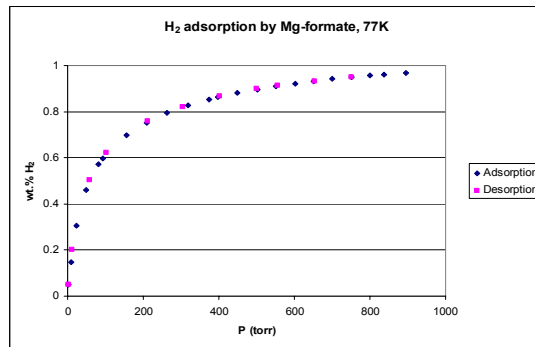
\* **Smaller value > larger barrier**

# 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  $\sim 11$  meV; J. Z. Larese)

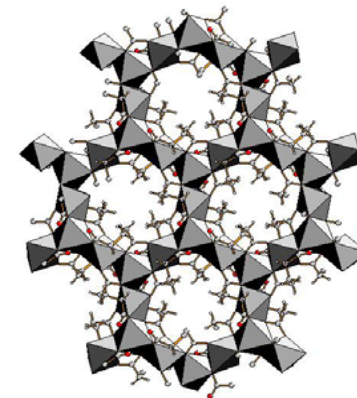
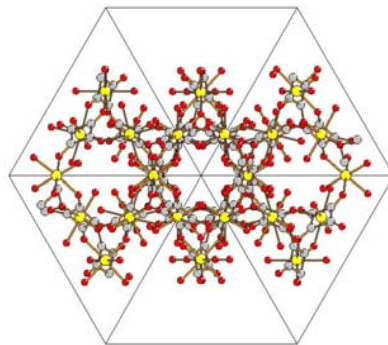
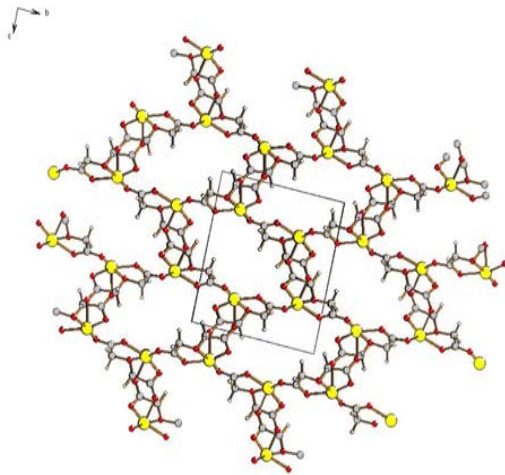


Experimental\* and calculated (GCMC/DIZZY: E. Sullivan)  $H_2$  Isotherms

**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



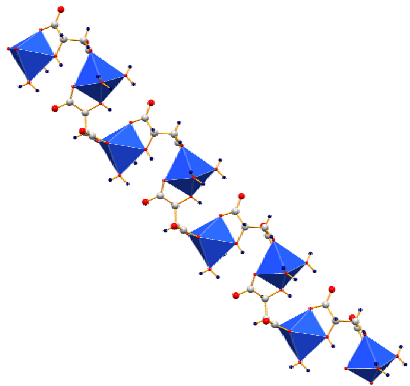
Magnesium Diglycolate:  $\text{Mg}(\text{H}_2\text{O})(\text{C}_4\text{H}_4\text{O}_5) \cdot \text{H}_2\text{O}$   
Shown **without water** guests: **vacant Mg binding site**  
Has  $\sim 9\text{\AA}$  wide channels

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

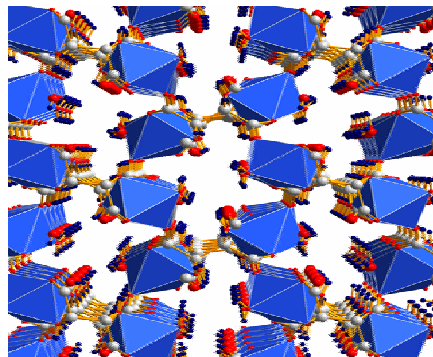
Magnesium Glutarate  
 $\text{Mg}(\text{C}_5\text{H}_6\text{O}_4)$

**BUT: these structures not stable to removal of guests**

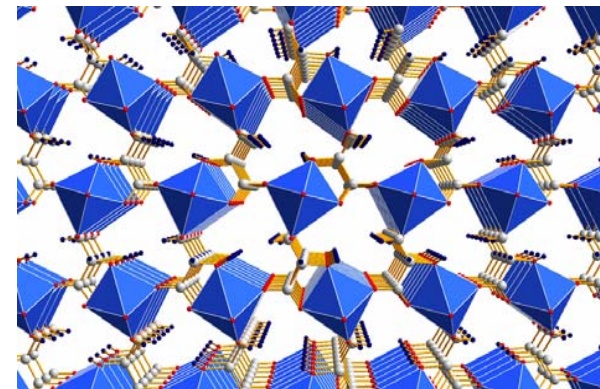
# Synthesis of New, Porous, Mg-based Hybrid Materials Magnesium Tartrate



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

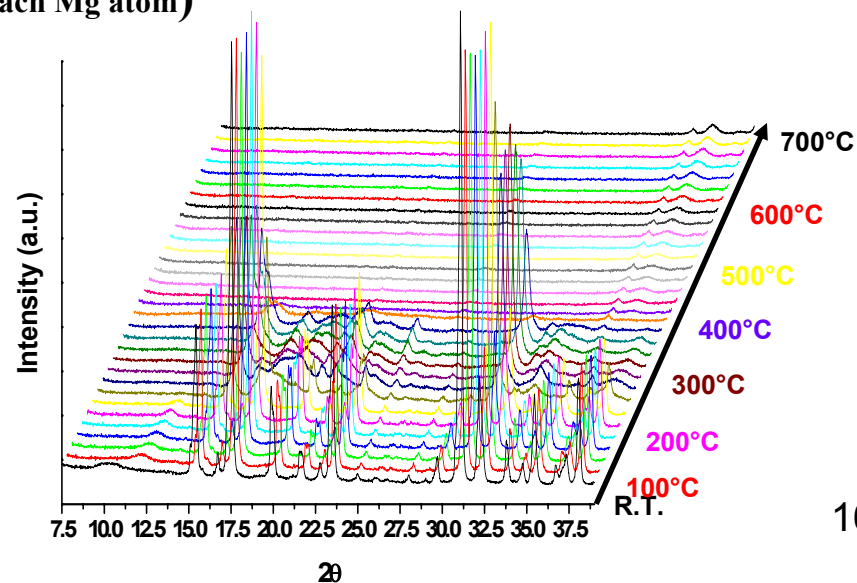


(2D layered structure, pore is 6 membered rings, 1 water coordinated to each Mg atom)



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

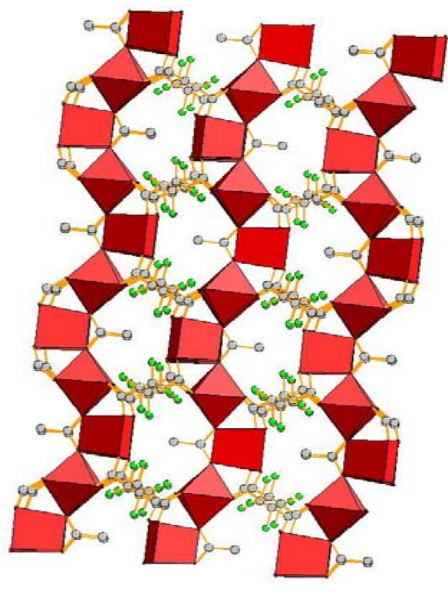
- chain of alternating, corner-sharing octahedral trigonal prismatic  $CoO_6$  units

-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

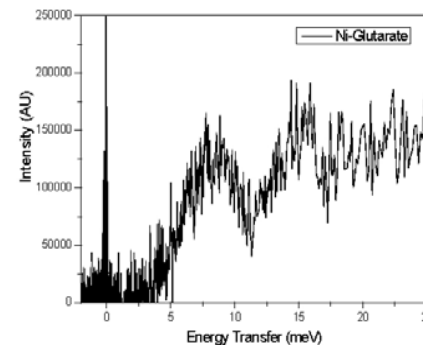
- Recent compounds prepared (E. Falcao)
- Some linkers are chosen to offer the possibility of H<sub>2</sub> addition to C=C bonds

Table 1. Textural characterization of selected frameworks

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

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

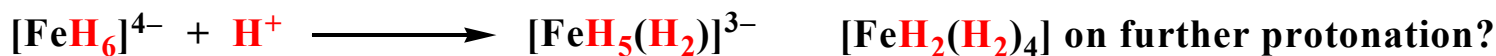
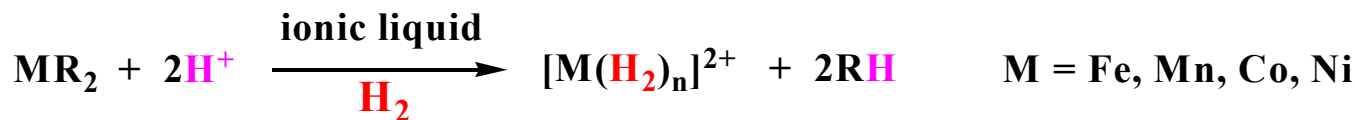
- Characterize H<sub>2</sub> binding\*
- If favorable, synthesize analogs with larger surface area



\*INS spectrum of H<sub>2</sub> 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 H<sub>2</sub>** ligands via metal alkyl, aryl, or hydride complexes



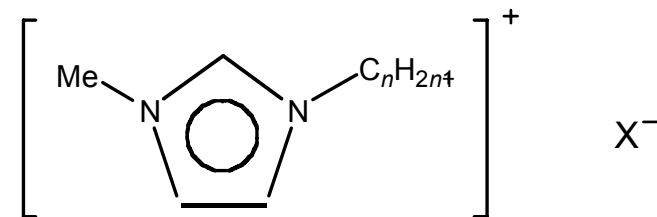
[Linn]

acid with low-coordinating anion

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

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

Molecular complexes can also be grafted to nanoporous materials surfaces



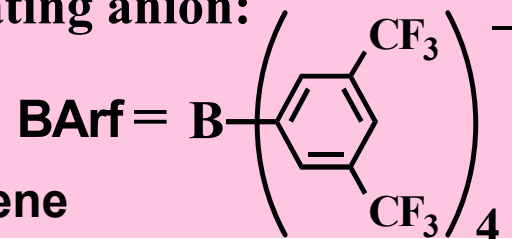
- I  $n = 4$ , X = [PF<sub>6</sub>]; [bmim][PF<sub>6</sub>]
- II  $n = 4$ , X = [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]; [bmim][Tf<sub>2</sub>N]
- III  $n = 2$ , X = [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]; [emim][Tf<sub>2</sub>N]

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

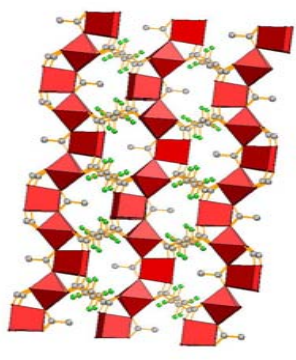
$[\text{FeH}_6]^{4-} + \text{H}[\text{BArf}]$  gives reaction in THF at RT (no gas evolution)

broad NMR signals (paramagnetic impurity?)

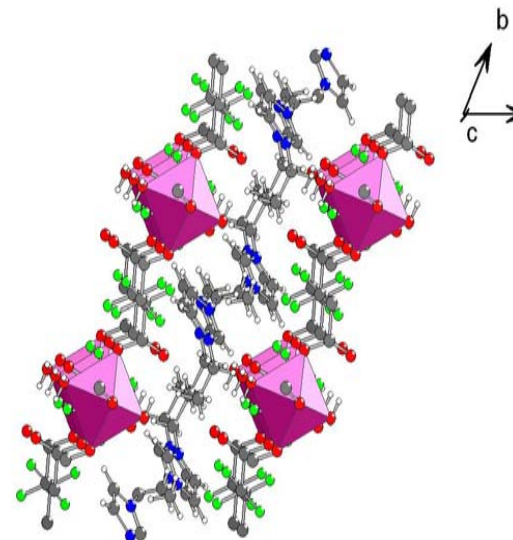
Further reactions will be carried out at low T under  $\text{H}_2$

# 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 >



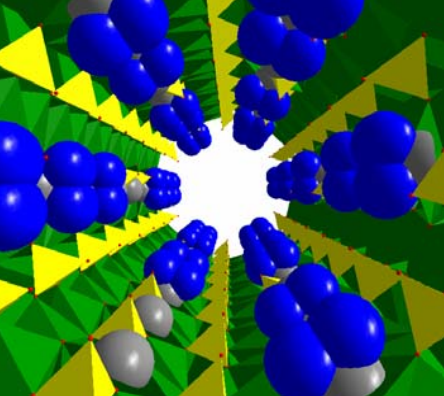
FY08: obtain materials with removable guests  
characterize H<sub>2</sub> sorption properties

↓  
coordinated (removable ?)  
water on Co

+

fluorinated linker

>> strong H<sub>2</sub> 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 H<sub>2</sub> hindered rotor: most sensitive technique for the study of H<sub>2</sub>/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  $\sim 20$  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.