

## IV.D.2 Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

Juergen Eckert (Primary Contact) and  
Anthony K. Cheetham  
Materials Research Laboratory  
University of California  
Santa Barbara, CA 93106  
Phone: (805) 893-8247; Fax: (805) 893-8797  
E-mail: juergen@mrl.ucsb.edu

DOE Technology Development Manager:  
Monterey R. Gardiner  
Phone: (202) 586-1758; Fax: (202) 586-9811  
E-mail: Monterey.Gardiner@ee.doe.gov

DOE Project Officer: Jim Alkire  
Phone: (303) 275-4795; Fax: (303) 275-4753  
E-mail: James.Alkire@go.doe.gov

National Laboratory Collaborator:  
Gregory J. Kubas, Los Alamos National Laboratory

Contract Number: DE-FG36-5G01004

Start Date: April 1, 2005  
Projected End Date: March 31, 2010

### Objectives

- Synthesize and characterize novel nanoporous hybrid materials with improved affinity for hydrogen.
- Evaluate storage capacities of the above materials on an on-going basis and model adsorption isotherms.
- Use advanced physical characterization methods (nuclear magnetic resonance, neutron spectroscopy etc.) and thermodynamic data to discern hydrogen binding mechanisms.
- Down-select optimum materials.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

The objective of the project is to develop hydrogen storage materials for reversible on-board applications with hydrogen binding energies intermediate between physisorption and chemisorption. Such materials need to reach a binding energy for hydrogen in the range of 15–25 kJ/mol averaged over all sorption sites.

### Accomplishments

- Demonstrated the existence of coordinated molecular hydrogen at open, and highly accessible metal binding sites in several porous materials.
- Found evidence for *bis*-dihydrogen coordination at Cu(I) in Cu-ZSM-5.
- Measured room temperature, molecular hydrogen adsorption isotherms in Cu-ZSM-5; obtained values for the isosteric heat of adsorption between 74 and 38 kJ/mol.
- Synthesized a total of nine new hybrid metal organic frameworks with fluorine-substituted organic linkers, more than the total number previously known.
- The use of F in place of H was shown to increase H<sub>2</sub> binding energies by some 50%.
- Completed a systematic exploration of hybrid materials composed of a highly functionalized organic link (2,5-thiazolo[5,4-*d*]thiazolecarboxylic acid) and three series of metal centers, i.e. transition metals, alkaline earth and alkali metals in search of a new porous material with open metal sites combined with an attractive linker.
- Demonstrated the synthesis a series of mixed transition metal (Mn, Cu, Zn, Ni), mixed organic link (bipyridyl and hydroxyisophthalic acid) hybrid materials.



### Introduction

Recent work in the field of hydrogen storage has been overwhelmingly dominated by the use of a narrow range of materials, specifically high surface area materials, such as carbons of various kinds, metal organic framework (MOF) materials and other coordination polymers, and, on the other hand, various light metal hydrides, or so-called chemical hydrides. Many sorption-based systems approach sufficiently high capacities at low temperatures and

high pressures, but not under ambient conditions, while the hydride compounds have impressive capacities at room temperature but suffer from various problems, such as undesirable H<sub>2</sub> release characteristics, a lack of reversibility, or cyclability, and potential system deactivation.

There is clearly an urgent need to develop new classes of materials that have the potential to provide superior performance for hydrogen storage. Some of the more recent developments in this area include the use of chemical hydrides based upon lightweight Li-N-Al-Mg-H alloys, or on NH<sub>3</sub>BH<sub>3</sub>, and a wide variety of coordination polymers, such as MOFs. Our highly promising strategy is aimed at the development of new hybrid materials for sorption-based systems where the host-guest interactions are intermediate between those found in the carbons and the metal hydrides. This must be accomplished either by binding multiple dihydrogen ligands to a transition metal site in the material, or by the synthesis of new materials based on lightweight metals such as Mg, alkali or alkaline earths. Modification of the organic linker will also be necessary to reach the desired goal of a binding energy near 20 kJ/mol. We are therefore exploring the use of fluorinated organics to improve binding energies on the organic components. The three classes of materials currently under investigation by us are as follows:

- (i) Hybrid materials with fluorinated organic linkers.
- (ii) Materials with open metal binding sites for molecular chemisorption of hydrogen coupled with functionalized linkers.
- (iii) Bind multiple dihydrogen ligands at open metal sites or metal clusters introduced into porous hosts.

## Approach

The primary focus of our work has been to improve the binding energies for hydrogen in porous materials into the range of 15–25 kJ/mol needed for a room temperature sorption-based storage system given the fact that it has already been demonstrated the necessary surface areas can be achieved. Our synthetic work therefore is aimed at creating novel inorganic-organic framework materials either based on transition metals with the ability to bind more than one molecular hydrogen ligand by molecular chemisorption, and/or the development of hybrid materials that combine a number of strategies, each of which may improve binding energies by some 50% relative to those of standard, neutral MOFs. We are attempting to accomplish this by one or both innovative methods, namely the use of fluorinated organic linkers, in combination with open metal sites, small pore systems and charged frameworks. The key experimental component in this effort is the use of inelastic neutron scattering of the hindered rotation of the sorbed H<sub>2</sub> molecule, which makes it possible

to associate improvements in binding energies from thermodynamic measurements with specific binding sites. Once a promising material is identified and characterized it will be modified to increase its surface area to achieve capacity goals.

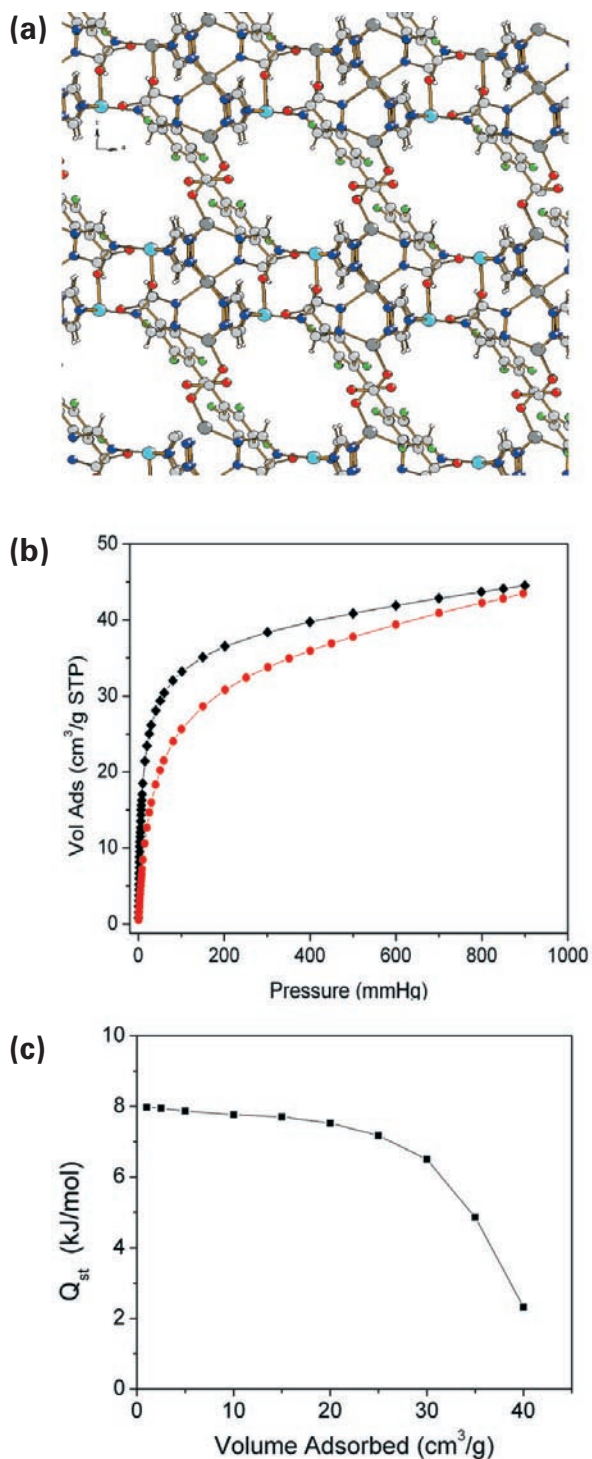
## Results

**(i) Hybrid materials with fluorinated organic linkers:** Because of the fact that we must improve the binding energy of hydrogen in these sorption-based systems, we have been developing the synthesis of hybrid organic-inorganic structures using fluorinated organic ligands as linkers. We anticipate the molecular hydrogen will interact more strongly with fluorine than with hydrogen, so that the storage properties of such a material should be improved compared with one which employs unsubstituted organic linkers.

The synthesis of materials containing fluorinated ligands differs greatly from traditional synthesis of hybrid materials. Our initial attempts involved use of ionic liquids as solvents in the synthesis to address the solubility issues regarding the fact that the fluorinated carboxylates are more acidic and therefore less soluble in some of the solvents we would normally use. We were successful in obtaining several new fluorinated hybrid materials using first a 1:1 molar mixture of ethylmethylimidazolium (emim) bromide and emim-triflimide, and later with added water. It was not possible, however, to obtain porosity as the ionic guest molecules could not be removed.

We have therefore been using alternate synthetic routes to obtain structures with fluorinated carboxylates. One successful method has proven to be the use of additional ligands, specifically 1,2,4-triazolates, in conjunction with the fluorinated carboxylates. A porous hybrid containing partially fluorinated cavities still has great potential to have interesting sorption properties but would not suffer as much of the weight penalty that perfluorination causes. We have indeed been successful in synthesizing Zn<sub>5</sub>(C<sub>2</sub>H<sub>2</sub>N<sub>3</sub>)<sub>6</sub>(C<sub>8</sub>F<sub>4</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O) · 2H<sub>2</sub>O, a three-dimensional coordination polymer containing 1,2,4-triazolate and tetrafluoroterephthalate ligands (Figure 1). This phase can be dehydrated without losing its crystallinity, with the non-coordinated water molecules being removed between 50 and 70°C and the coordinated water molecules being removed around 150°C. The resulting anhydrous analog begins to decompose above 275°C. While this material has a rather modest surface area of 150 m<sup>2</sup>/g, the H<sub>2</sub> adsorption isotherm exhibits a very steep rise along with saturation at relatively low pressure. This observation indicates that a large fraction of the binding sites in this material have a very strong affinity for H<sub>2</sub>.

We have derived the isosteric heats of hydrogen adsorption for these materials in the standard way from



**FIGURE 1.** Synthesis and thermodynamic  $H_2$  adsorption properties of  $Zn_{2.5}(1,2,4\text{-triazole})_3(\text{tetrafluoroterephthalate})(H_2O) \cdot 2H_2O$ ; (a) structure (top) (b) isotherms at 77 K (black) and 87 K (red); (middle) (c) isosteric heat of adsorption (bottom).

isotherms at 77 and 87 K, and find (Figure 1) a maximum value of about 8 kJ/mol at low coverage, which drops only slightly until a point close to the maximum loading of the material. We cannot conclude, at this point, if this

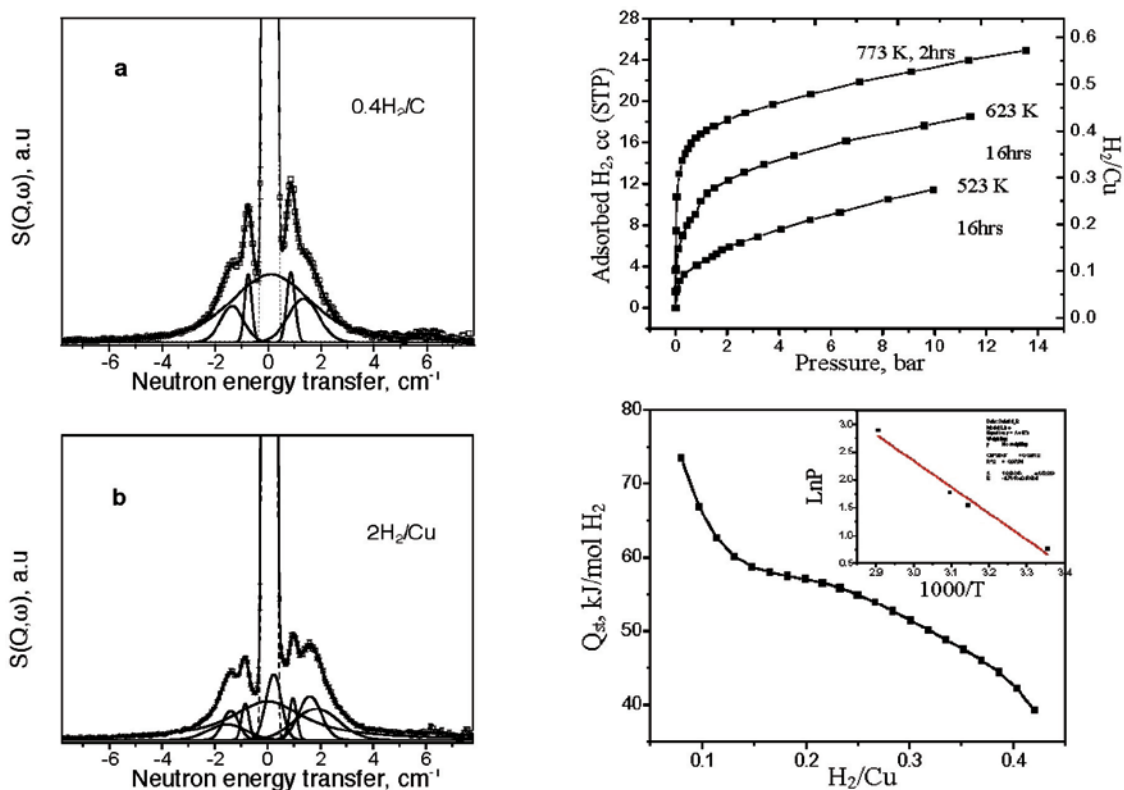
increase of about 3 kJ/mol relative to hybrid materials with hydrogen instead of fluorine on the linkers, and no open metal sites (e.g. MOF-5,  $Q_{st} \sim 5$  kJ/mol) results from binding sites at the Zn, or near the fluorinated organic. Our proposed inelastic neutron scattering (INS) studies are urgently needed to decide this question, and thereby guide future synthesis strategies.

We have synthesized several additional, very promising hybrid materials with mixed linkers, where one is fluorinated and offers a relatively uniform surface of F binding sites. One of these,  $Zn(\text{bipy})(\text{tetrafluorohydroxybenzoate}) \cdot \text{bipy}$ , also exhibits infinite inorganic connectivity in one dimension, a property which ought to lead to more strong binding sites in much the same way as the catenated clusters in MOF-74.

**(ii) Open metal binding sites:** We have successfully demonstrated the existence of *coordinated* molecular hydrogen at unsaturated metal binding sites in four porous systems, namely Fe-ZSM-5 [1], the Ni-phosphate VSB-5 [2], the hybrid material Ni-SIPA [3], and most recently Cu-ZSM-5 [4]. The importance of open metal sites for improving the binding energies of molecular hydrogen in porous materials is now widely recognized. However, several other systems [5,6] have been reported with apparently open metal (Cu, Mn) sites, which are non-coordinating as indicated by relatively modest improvements in hydrogen binding energies, and other experimental evidence. The main problem with those systems appears to be that the site is partially blocked by surrounding atoms, and thereby prevents the  $H_2$  molecule from approaching the metal to within about 1.7-1.8 Å to form a coordination complex. This is also evident from our work on ion exchanged zeolites, where the common six ring site is often partially obstructed by surrounding O atoms.

The formation of the first isolable dihydrogen complex with Cu in the Cu-exchanged zeolite ZSM-5 (Figure 2) was recently reported by us [4], and its isosteric heats of adsorption have been determined (Figure 2) from room temperature adsorption isotherms [7]. The values ranging from a high of 74 kJ/mol at the lowest loadings to about 38 kJ/mol are, of course, well above the practical goal of around 20 kJ/mol. It should be viewed as a proof-of-principle that the properties of porous host materials can be tuned to yield the necessary binding energies for molecular hydrogen. These results do, however, demonstrate that highly exposed metal binding sites may well be necessary to reach the goal for room temperature operation, and do in fact suggest, that these may have to be created by a post-synthesis method as in Fe- and Cu-ZSM-5.

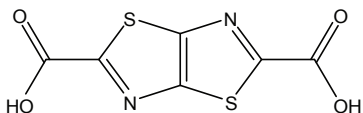
Upon comparison the above results with those on Fe-ZSM-5 we note that the rotational tunnel splitting in the latter is about six times greater, which implies a smaller barrier to rotation, and usually a lower binding energy. We are extending our computational effort to



**FIGURE 2.** Rotational tunneling spectra for two different  $H_2$  loadings in Cu-ZSM-5 (IN5, Institut Laue-Langevin, Grenoble, France) (left); room temperature  $H_2$  adsorption isotherms for Cu-ZSM-5 heated to three successive different temperatures to reduce Cu to Cu(I) (top, right); isosteric heat of adsorption for  $H_2$  in Cu-ZSM-5 (bottom, right).

the Fe system, as this may come rather close to the goal of 15–25 kJ/mol.

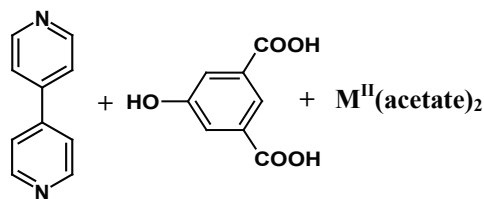
*Materials with open metal binding sites coupled with functionalized linkers.* We have undertaken a systematic search for new hybrid materials that are composed of a highly functionalized link, 2,5-thiazolo[5,4-*d*]thiazoledicarboxylic acid (Thz) (shown below).



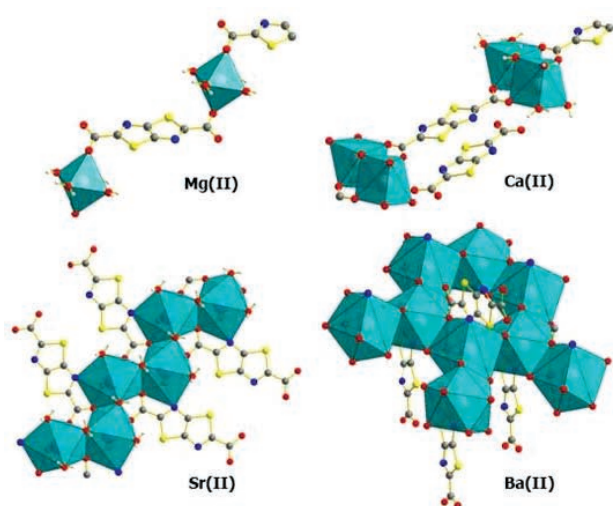
and three series of metal centers, namely transition metals, alkaline earths and alkali metals, which are synthesized under conditions that could also produce some removable ligands on the metal and therefore open metal binding sites. These efforts resulted in a considerable number of interesting new structures that were found to be governed by some well defined trends in the dimensionality of metal-ligand chains and metal polyhedra connectivity, but none of these materials exhibited appreciable porosity. The reason for this was found to be in the nature of the heteroatoms on the organic, which can also coordinate to the metal, and hence produce more compact structures. As an

example we show in Figure 3 the structures obtained with  $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$  and  $Ba^{2+}$ , which exhibit a well-defined progression. However, only one compound in this series,  $[Ba(Thz)(H_2O)_5]_8$ , the one with the largest cation, has a dimensionality greater than one, and was found to consist of layers of  $Ba^{2+}$  ions connected to three others through three neighboring polyhedra, without any appreciable porosity, however. While work on the alkali metal analogs is still in progress, a similar pattern has emerged in that the system with the largest cation,  $Rb^+$ , was found to have a dimensionality of three. These findings may open up a new set of possibilities for creating frameworks with some of the lighter alkaline metals, if a second type of linker is incorporated to open up these structures.

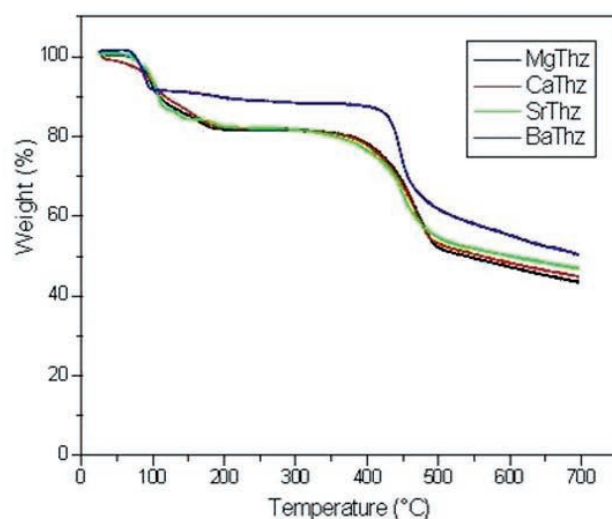
In a similar vein we have obtained a considerable number of novel hybrid materials with transition metals combined with the linkers bipyridyl and hydroxyisophthalic acid,







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



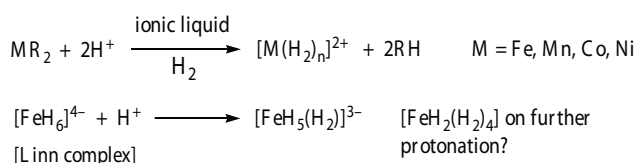
**FIGURE 3.** Hybrid Materials with alkaline earth metal (Mg, Ca, Sr, Ba) centers and the highly functionalized organic link 2,5-thiazolo[5,4-*d*]thiazole-5-carboxylic acid: select views of the structures (top), structural properties (middle) and thermal gravimetric analysis curves (bottom).

These include materials which incorporate  $\text{Mn}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  as well as mixed metals in the same material. These materials do not, however, exhibit adequate porosity for studying their hydrogen sorption

properties, but demonstrate the feasibility of producing ordered hybrids with mixed metal, which could be an important strategy in designing materials where the functional metal sites are of heavier metals, and structural metal sites of lighter ones.

**(iii) Multiple Dihydrogen Ligands.** As part of effort to investigate the possibility of binding multiple dihydrogen ligands to a metal, or metal cluster in a porous host material, we have tentatively concluded that based on the combined use of our rotational tunnelling spectra [2], thermodynamic measurements and theoretical modelling that the binding of multiple dihydrogen ligands to some Cu sites<sup>4</sup> in porous ZSM-5 is indeed possible, if not likely. Density functional theory calculations (carried out in collaboration with Mariona Sodupe Roure at the Unversitat Autnoma Barcelona, Spain) using a model of the open Cu site in chabazite do, in fact find that a second  $\text{H}_2$  molecule can be bound to the Cu site. The overall binding energy is thereby reduced, something they could explain the gradual reduction in the isosteric heat of adsorption (Figure 2) with increased hydrogen loading. We are currently investigating a similar possible scenario for  $\text{H}_2$  in Fe-ZSM-5, which again, is suggested by the INS rotational tunnelling spectrum.

We have continued our effort to experimentally demonstrate the feasibility of binding multiple molecular hydrogen ligands to open metal sites in hybrid materials and presently employ the strategy shown by the following two reactions:



We prepared the  $[\text{FeH}_6]^{4-}$  and a similar Co complex, which required a special apparatus was designed, built, and rigorously checked for required safety issues for use at Los Alamos since the reaction requires hydrogen pressures greater than 1 atmosphere. Attempts to protonate these complexes yielded an unstable material for Fe, and a Co polyhydride anion that could not be characterized because the crystals were of insufficient size.

## Conclusions and Future Directions

We have clearly demonstrated the pronounced effect on binding energies (<74 kJ/mol) of *molecular* hydrogen offered by the presence of unsaturated metal sites, which can in fact form a chemical bond with  $\text{H}_2$  molecules, and we have in fact obtained indirect evidence of *bis*-dihydrogen coordination. The interaction with such sites depends very strongly on accessibility to the hydrogen molecule as well as the oxidation state of the metal ion:

the values of the rotational tunneling splitting for the bound H<sub>2</sub> molecule are about 8 meV for the Cu site in HKUST-1 (and in several other coordination polymers containing the so-called Cu-paddlewheel SBU), 3 meV in zeolite CuNaA, and 0.15 meV in Cu-ZSM-5 (where a smaller energy implies a stronger interaction). These trends suggest that very open metal sites can only be created by post-synthesis introduction (as in Fe- and Cu-ZSM-5) and that it is important to develop such synthetic strategies for lightweight host materials rather than zeolites.

The goal in H<sub>2</sub> binding energies of 15–25 kJ/mol over the entire range of H<sub>2</sub> loadings may well only be realized in a material which combines several approaches to improved H<sub>2</sub> interactions. Two of these (open metal sites, fluorinated linkers) are combined in one of the nine new hybrid materials using fluorinated organic linkers synthesized by us, a significantly greater number than what was known prior to our efforts. Moreover, we have obtained evidence for the expected increase in binding energy of some 50% (relative to H-containing organic links) has been demonstrated, and now plan to combine these properties in compounds with more attractive (than Zn) open metal sites. We have also explored a large range of compounds synthesized with a given, highly functionalized link (2,5-thiazolo[5,4-*d*]thiazolecarboxylic acid), and three series of metal centers in the search for new materials that also combine these two strategies for improved H<sub>2</sub> binding. A third method for increasing hydrogen binding energies is to utilize charged, rather than neutral frameworks, as has been demonstrated in our collaboration with the group of Eddaoudi (University of South Florida).

### FY 2008 Publications/Presentations

1. “Investigation of Hydrogen Binding in MOF Catenation Isomers by Inelastic Neutron Scattering and High Pressure Hydrogen Adsorption”, Shengqian, Ma, Juergen Eckert, Paul M. Forster, Ji Woong Yoon, Young Kyu Hwang, Jong-San Chang, Christopher D. Collier, and Hong-Cai Zhou\* (submitted to *J. Am. Chem. Soc.* 2008).
2. “Strengthening the framework-H<sub>2</sub> interaction by “close-packing” alignment of coordinatively unsaturated metal centers in metal-organic frameworks”, X.-S. Wang, S. Ma, P.M. Forster, D. Yuan, J.W. Yoon, Y.K. Hwang, J.-S. Chang, J. Eckert, B.J. Murphy, J.B. Parise, H.-C. Zhou (submitted to *Angew. Chem. Int. Ed.*, 2008).
3. “Room temperature isosteric heat of dihydrogen adsorption on Cu(I) cations in ZSM-5”, P.A. Gregoriev, A. Albinati and J. Eckert, *Chemical Physics Letters* 449, 182 2008.
4. “Ionothermal synthesis of inorganic-organic hybrids materials containing perfluorinated aliphatic dicarboxylate ligands”, Z. Hulvey, D. S. Wragg, Z. Lin, R. E. Morris, and A. K. Cheetham, *J. Mat. Chem.* (in press, 2008).
5. “Hybrid Organic-Inorganic Framework Structures: Influence of Cation Size on Metal-Oxygen-Metal Connectivity in the Alkaline Earth Thiazolothiazolecarboxylates”, E.H.L. Falcao, Naraso, R.K. Feller, G. Wu, F. Wudl and A.K. Cheetham, *Inorganic Chemistry* 2008, in press.
6. “Polytypism, homochirality, interpenetration, and hydrogen-bonding in transition metal (Mn(II), Ni(II), Cu(II), Zn(II)) 5-hydroxyisophthalate coordination polymers containing 4,4'-bipyridyl”, R.K. Feller and A.K. Cheetham, *Dalton Trans.*, 2008, DOI: 10.1039/b716454h.
7. “Two coordination polymers created via in-situ ligand synthesis involving C-N and C-C bond formation”, R.K. Feller, P.M. Forster, F. Wudl, F. and A.K. Cheetham, *Inorg. Chem.* 2007, 46, 8717.
8. “Strategies for Strengthening the Interaction of Molecular Hydrogen in Porous Materials for Hydrogen Storage”, J. Eckert, 24<sup>th</sup> Meeting of the Catalan Theoretical and Computational Chemistry Reference Network, Girona, Spain, June 26-27, 2008.
9. “Hydrogen Storage Materials with Binding Intermediate Between Physisorption and Chemisorption”, J. Eckert, 2007 DOE Hydrogen Program Annual Review, Arlington, VA, June 11, 2008.
10. “Interactions of Molecular Hydrogen with Metal Organic Frameworks Studied by Inelastic Neutron Scattering”, American Chemical Society National Meeting, New Orleans, April 6-11, 2008.
11. “Modes of Binding of Molecular Hydrogen in Porous Materials for Hydrogen Storage”, J. Eckert, Condensed Matter Physics Seminar, University of Florida, April 14, 2008.
12. “Modes of Binding of Molecular Hydrogen in Porous Materials for Hydrogen Storage”, J. Eckert, Physics Department Colloquium, University of Nevada Reno, February 22, 2008.

### References

1. B. Mojet, J. Eckert, R. van Santen, A. Albinati and R. Lechner, *J. Am. Chem. Soc.* 2001, 121, 8147.
2. P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Ferey and A. K. Cheetham *J. Am. Chem. Soc.* 2003, 125, 1309.
3. P.M. Forster, J. Eckert, B. Heiken, J.B. Parise, Ji Woong Yoon, S.H. Jhung, J.-S. Chang,<sup>†</sup> and A.K. Cheetham. *J. Am. Chem. Soc.* 2006, 128, 16846.
4. P.A. Georgiev, A. Albinati, B.L. Mojet, J. Olivier and J. Eckert, *J. Am. Chem. Soc.* 2007, 129.
5. J.L.C. Rowsell and O. Yaghi, *J. Am. Chem. Soc.* 2006, 128, 1304.
6. M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann, and J.R. Long, *J. Am. Chem. Soc.* 2006, 128, 16876.
7. P. A. Gregoriev, A. Albinati and J. Eckert, *Chem. Phys. Letters* 449, 182 2008.