

IV.F.3 Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

Juergen Eckert (Primary Contact) and
Anthony K. Cheatham
Materials Research Laboratory
University of California
Santa Barbara, CA 93106
Phone: (805) 893-8247; Fax: (805) 893-8797
E-mail: juergen@mrl.ucsb.edu
Phone: 011 44 1223 767 061
E-mail: akc30@cam.ac.uk

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

DOE Project Officer: Katie Randolph
Phone: (303) 275-4901; Fax: (303) 275-4753
E-mail: Katie.Randolph@go.doe.gov

Contract Number: DE-FG36-5G01004

Project Start Date: April 1, 2005
Project End Date: September 30, 2010

Objectives

- Synthesize and characterize novel nanoporous hybrid materials with improved affinity for hydrogen.
- Use advanced characterization methods (inelastic neutron scattering spectroscopy, computation, etc.) and thermodynamic data to discern hydrogen binding mechanisms at particular sites.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) 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

- Determined the type of metal site which interacts most strongly with hydrogen by carrying out systematic studies of various types of metal binding sites in zeolites and coordination polymers.
- Investigated intra-framework metal sites in analogs of MOF-74 with Co and Mg substituted for Zn, by inelastic neutron scattering (INS) of the adsorbed H₂, and found Mg to have the strongest interaction among these metals.
- Demonstrated the existence of coordinated molecular hydrogen at an open, and highly accessible metal binding site in Cu-ZSM-5.
- Confirmed evidence for possible binding of two hydrogen molecules at Cu(I) sites in Cu-ZSM-5.
- Completed our investigation of the synthesis of hybrids with a highly functionalized link, 2,5-thiazolo[5,4-*d*]thiazolecarboxylic acid, and several series of metals, including alkali, alkaline earths and first row transition metals, which did not yield a material with appreciable porosity.
- Synthesized a total of 18 new hybrid metal organic frameworks (MOFs) with fluorine-substituted organic linkers.
- Obtained a new hybrid material with a tetrafluoroterephthalate, zinc, and 1,2-bis(4-pyridyl) ethane with substantial porosity.
- INS studies of H₂ in Zn(1,2,4-triazolate) (tetrafluoroterephthalate) reveal three strong binding sites, with interaction much greater than typical MOFs, and serve to understand the relatively high isosteric heat of adsorption of 8 kJ/mol over a wide range of loadings.



Introduction

The vast majority of hydrogen storage materials currently under consideration fall into either of two categories, those with high surface areas, such as carbons of various kinds, MOF materials and other coordination polymers, which bind hydrogen by weak physisorption, or various light metal hydrides, or other

“chemical hydrides” such as aminoborane, which bind hydrogen very strongly, essentially in the form of a chemical compound. 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_2 release characteristics, a lack of reversibility, or cyclability, and potential system deactivation.

There is clearly an urgent need to develop another approach to that hydrogen storage materials which would have the potential to provide superior performance especially in those aspects where current systems have serious shortcomings. We believe this to be a system based on sorption, in which the host-guest interactions are intermediate between those found in the carbons and the metal hydrides, i.e. between physisorption and chemisorption. This must be accomplished by combining in one material several attributes that are known to increase the isosteric heat of hydrogen adsorption. These include the creation of open transition metal binding sites, especially if these can bind multiple dihydrogen ligands, modification of the organic linker by substitution of H with Cl or F, for example, the use of charged, rather than neutral frameworks, and materials with small pores. A suitable combination of these elements could well reach the desired goal of a hydrogen binding energies near 20 kJ/mol, which is necessary for operation at room temperature and modest pressures. The following classes of materials are currently under investigation by us:

- i. Hybrid materials with fluorinated organic linkers.
- ii. Materials with open metal binding sites for molecular chemisorption of hydrogen coupled with functionalized linkers, materials with extra framework metal sites introduced post synthesis by various methods, and anionic frameworks with exchangeable cations.

Approach

The primary focus 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 hybrids 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 adsorbed H_2 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. In the course of this effort we have completed a systematic investigation [1] of hybrid materials which possess one fluorinated (terephthalate, isophthalate, succinate, and hydroxybenzoate), and one non-fluorinated linker (4,4'-bipy, and 2,2'-bipy) (Figure 1a) together with a variety of metals (Zn, Mn, Co, and Cu). We were successful in synthesizing a very large number of novel, previously unknown hybrid materials which incorporate fluorinated links, only one of these compounds [2], $Zn_5(C_2H_2N_3)_6(C_8F_4O_4)_2(H_2O) \cdot 2H_2O$, a three-dimensional coordination polymer containing 1,2,4-triazolate and tetrafluoroterephthalate ligands, was found to be porous with a rather modest surface area of 150 m²/g.

We have previously reported [2] that the isosteric heat of adsorption for hydrogen in this material is more than 50% higher than that in a typical MOF (without F substitution), which is now convincingly supported by our very recent inelastic neutron scattering data on this system obtained on the TOFTOF Spectrometer of the FRM-II reactor at the Technical University of Munich, Germany (Figure 1b). The positions of the three peaks in the INS clearly indicate a much stronger interaction in the presence of the fluorinated linker, as all of them occur well below 10 meV unlike those in MOF-5 (all transitions are above 10 meV), or those of several compounds (e.g. HKUST-1) with so-called open metal sites.

Based on our success in synthesizing a large number of novel hybrid materials which incorporate fluorinated carboxylates along with various triazolate and bipyridine ligands, we have now expanded this work to include the larger bipyridine-based ligands in combination with perfluorinated dicarboxylates in order to achieve significant porosity in these materials. We have now synthesized several phases incorporating the ligands 1,2-bis(4-pyridyl)ethane (bpa) and 1,3-bis(4-pyridyl)

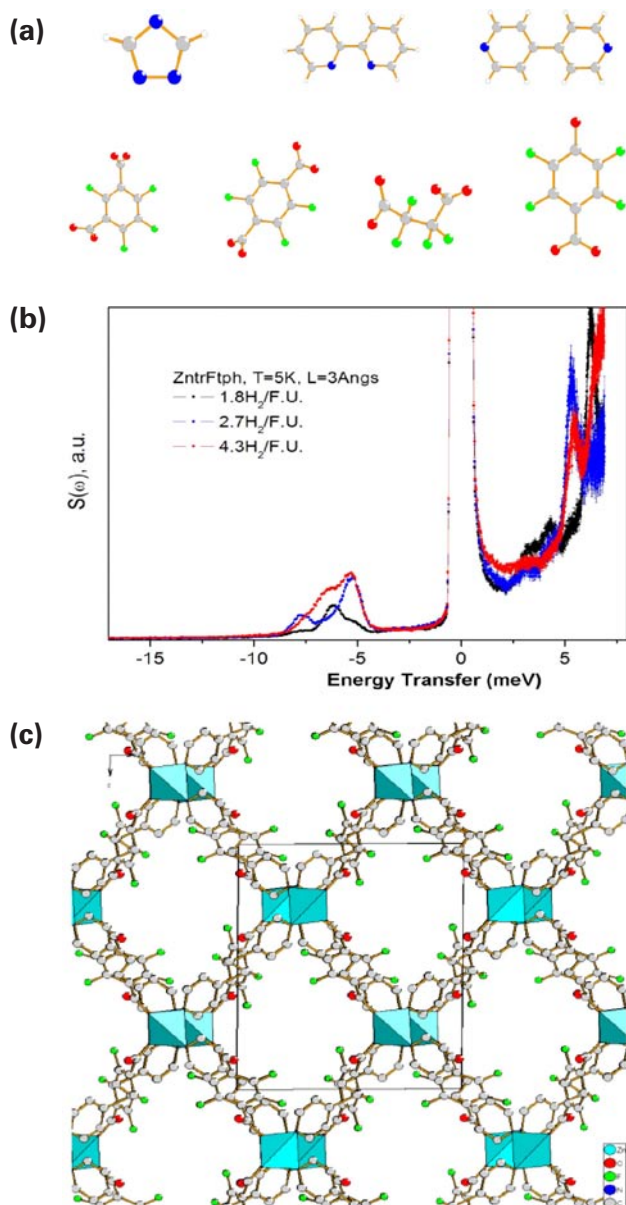


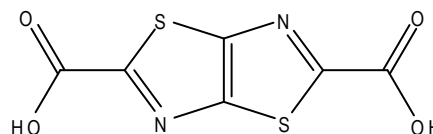
FIGURE 1. (a) Ligands used in the synthesis of partially fluorinated hybrids: (top, from left): 1,2,4-triazole, 2,2'-bipyridine, 4,4'-bipyridine; (bottom, from left): F_4 -isophthalate, F_4 -terephthalate, F_4 -succinate, F_4 -hydroxybenzoate; (b) INS spectra of Zn(1,2,4-triazolate)(tetrafluoroterephthalate); (c) Zn(bis(4-pyridyl)ethane)(tetrafluoroterephthalate) • cyclohexanone.

propane, the most interesting of which is a structure containing zinc, 1,2-bis(4-pyridyl)ethane and tetrafluoroterephthalate (tftpa) (Figure 1c). We were successful in achieving significant porosity in this system by adding a templating molecule to the reaction. This new structure is a four-fold interpenetrated structure with the large pore filled with cyclohexanone molecules formed regardless of this high degree of interpenetration. The unique lattice is built up from tetrahedrally

coordinated Zn^{2+} centers bound to two bpe ligands and two tftpa ligands. The ligands both act as linear linkers between other metal centers, forming a diamond-like net in three dimensions.

(ii) Materials with open metal binding sites:

We have completed our 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. These compounds were synthesized under conditions that could also produce removable ligands on the metal and thereby create 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. Materials with the largest metal cations did have more open structures, but this size effect was insufficient to introduce porosity. The most recent example in this series, a three-dimensional framework with cadmium (Figure 2) features two chemically distinct Cd^{II} centers: a pentagonal bipyramid (7-coordinated) and a distorted octahedron (6-coordinated). Chains of Cd -Thz are connected to form layers with the octahedral Cd^{II} through carboxylate oxygen atoms on axial positions, with potentially removable water molecules occupying the four equatorial positions.

It has become increasingly apparent that the benefit of so-called “open” metal sites in terms of hydrogen binding energies is much more limited than expected, so that the increase in binding energies averages only some 5 kJ/mol relative to MOFs with no such sites. One of the reasons for this is that these sites are not closely accessible to the hydrogen molecule, as has been determined in a few cases by neutron powder diffraction [2]. The formation of a true molecular hydrogen complex with much higher binding energy is thereby prevented.

We have therefore carried out a systematic study of the effect of metal binding sites in porous materials which includes (1) open metal sites that are part of MOFs, (2) extra-framework cations in at various sites in different types of zeolites, and (3) exchangeable, hydrated cations in anionic framework zeolite(-type) MOFs (ZMOF). In the first instance we obtained INS

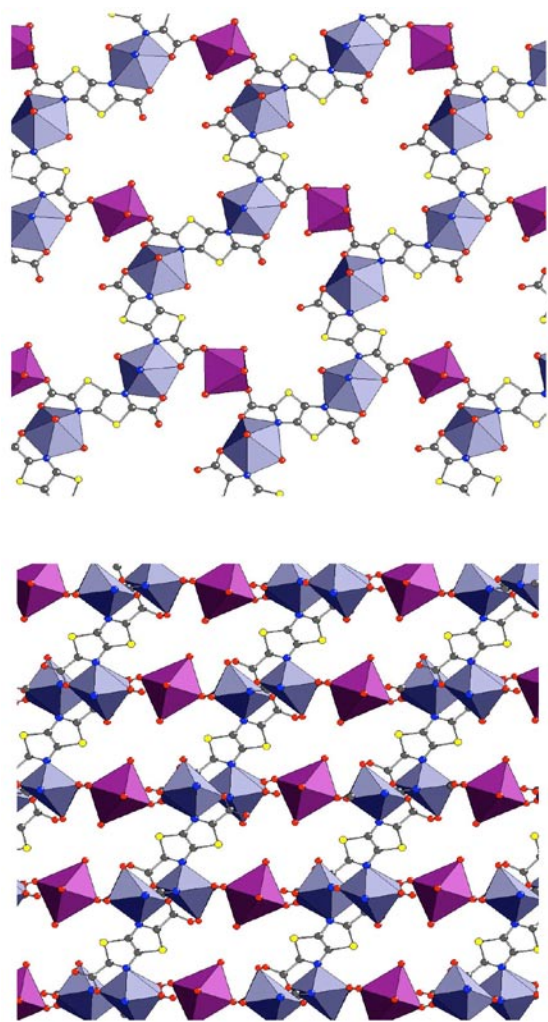


FIGURE 2. Structure of Cd(2,5-thiazolo[5,4-d]thiazole)dicarboxylic acid): (top) view perpendicular to the plane of the layers. Octahedral Cd^{II} in purple, pentagonal bipyramidal Cd^{II} in gray-blue. Guest water molecules omitted for clarity. (bottom): view along the plane of the layers.

spectra for H₂ in two examples (Figure 3) of the more promising materials among neutral MOFs with open intraframework metal sites, namely analogs of MOF-74, where the metal center can be replaced with a variety of other metals. These CPO-27 type materials M₂(dhtp) (H₂O)₂·8H₂O, (H₄dhtp = 2,5-dihydroxyterephthalic acid, M = Mg, Mn, Co, Ni, Zn) [3-5], have been reported to have hydrogen binding energies well in excess of 10 kJ/mol but only at rather low loadings.

The effect of EXTRA-framework metal ions (as opposed to INTRA-framework), on the other hand is much more pronounced. This is clearly demonstrated clearly by our ongoing work on the Fe- and Cu-ZSM-5 system. We have previously reported [6] that the binding of molecular hydrogen to Cu and Fe in these zeolites is by far the strongest of any porous host material, as much as 70 kJ/mol in Cu-ZSM-5, whereas the INTRA-

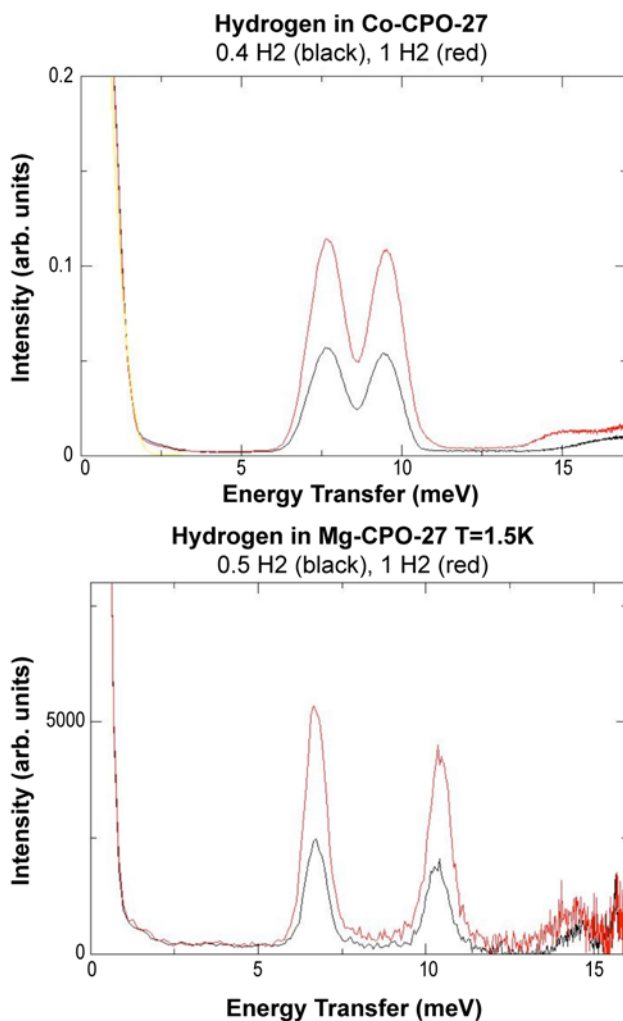


FIGURE 3. INS spectra (T = 5K) of Co- (top) and Mg-coordination polymer Oslo (CPO)-27 (bottom) at hydrogen loadings up to one H₂ molecule per metal site.

framework Cu sites in HKUST-1, for example, only gives rise to binding energies in the range of 6-8 kJ/mol. Our computational analysis of these systems (collaboration with Xavier Solans-Montford and Mariona Sodupe Roure of the Universitat Autònoma Barcelona) unambiguously shows that it is the long-anticipated formation of an actual metal-dihydrogen complex, which results in such strong binding. The metal-dihydrogen coordination in turn is facilitated by the highly open and under coordinated structure of the metal binding site, whereby the Cu ion is bound to just two framework O atoms (Figure 4). In the case of Fe-ZSM-5 we find that the binding site is in fact FeO coordinated to two framework O atoms, and that the interaction with H₂ is much weaker, i.e. 13 kJ/mol. A second H₂ molecule may be bound to the Cu site in ZSM-5, albeit with much lower binding energy. This could, however, be partly responsible for the decrease in isosteric heat of adsorption with increased loading observed by us [6].

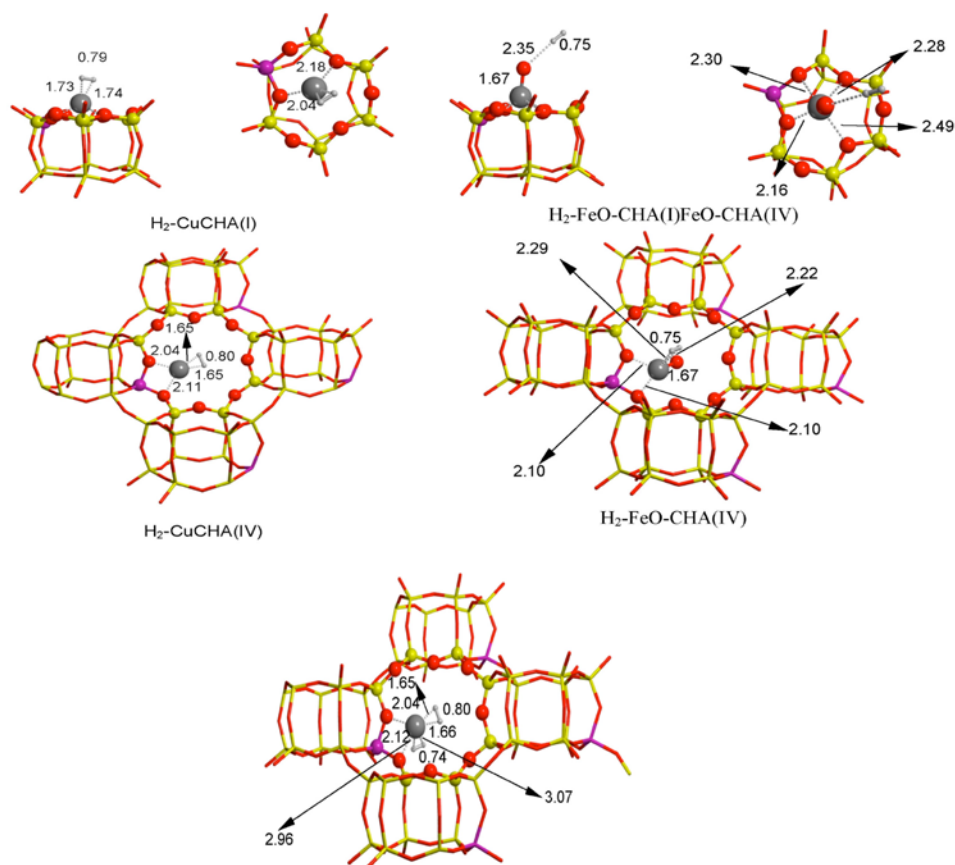


FIGURE 4. Theoretical structures of two binding sites in Cu- (left) and Fe-ZSM-5 (right). The site in the six-ring window (top) is much less favorable than the site in the large cavity. Bis-dihydrogen binding at the Cu-site is shown at the bottom.

Our INS studies on various zeolite model systems [7] provide additional evidence for the efficacy of under coordinated extra-framework metal ions in hydrogen binding. The incorporation of Li⁺ ions in MOFs is widely considered as crucial for obtaining a low-density material with strong H₂ interactions. INS data obtained on zeolite Li-A, however shows, that only the undercoordinated Li site in the 8-ring window binds H₂ strongly (rotational tunneling transition at ~1 meV) whereas the Li site in the six ring window interacts only weakly (~ 8 meV) with the adsorbed hydrogen.

MOF-type porous materials, however, typically have neutral frameworks, which do not lend themselves to simple ion exchange. Our collaboration with the group of Mohamed Eddaoudi (University of South Florida) has included anionic frameworks (ZMOFs) which possess the third type of metal site investigated, namely exchangeable cations in hydrated form. These materials may be viewed as analogues to zeolites with their charged frameworks, and do, in fact exhibit an increase

in binding energy for hydrogen of some 2-3 kJ/mol on account of the electrostatic field in their cavities. The effect of the exchangeable cation, however, does not appear to go much beyond that of the electrostatics, as our INS studies [8] of several forms of this material with different cations show only small differences in hydrogen binding energies. The reason for this is no doubt the fact that the metal cation cannot be closely approached on account of the aquo ligands that surround it.

Conclusions and Future Directions

This project has entered phase II, where the principal emphasis will be on increasing hydrogen binding energies in the most promising materials discovered in phase I based on the results of our investigations described above. More specifically, we aim to achieve post-synthesis introduction of Cu, or Fe (or other metal with high affinity for H₂) into an existing anionic ZMOF with very high surface area in such a way as to create highly under coordinated, open

metal sites. These sites may be expected to be suitable for dihydrogen coordination with the attendant high binding energies. The second, major goal of this phase is to enhance our very promising, partially fluorinated hybrid materials with open metal sites, in addition to other structural enhancements (small pores, anionic frameworks) to achieve hydrogen binding energies well in excess of 10 kJ/mol, along with surface areas exceeding 500 m²/g or greater.

FY 2009 Publications/Presentations

1. “Structural diversity in coordination polymers composed of divalent transition metals, 2,2'-bipyridine, and perfluorinated dicarboxylates”, Z. Hulvey, E. Ayala, J.D. Furman, P.M. Forster, and A.K. Cheetham, *J. Crystal Growth and Design*, 2009 (in press).
2. “Enhanced H₂ adsorption enthalpy in the low-surface area, partially fluorinated coordination polymer Zn_{2.5}(triazolate)₃(tetrafluoroterephthalate)(H₂O) • 2H₂O”, Z. Hulvey,[†] E.H.L. Falcao,[†] J. Eckert,[†] and A.K. Cheetham, *J. Mat. Chem.*, **19**, 4307, 2009.
3. “Tunable zeolite-like metal-organic frameworks (ZMOFs): Lithium and magnesium ion exchange and H₂-(rho-ZMOF) interaction studies”, F.Nouar, J. Eckert, J.F. Eubank, P. Forster, and M. Eddaoudi, *J. Am. Chem. Soc.* **131**, 2864, 2009.
4. “Interaction of Hydrogen with Extraframework Cations in Zeolite Hosts Probed by Inelastic Neutron Scattering Spectroscopy”, J. Eckert, F.R. Trouw, B. Mojet, P.M. Forster, and R. Lobo, *J. Nanosci. Nanotech.*, in press (2009).
5. “Structural and Chemical Complexity in Multicomponent Inorganic-Organic Framework Materials”, R.K. Feller and A.K. Cheetham, *CrystEngComm*, **11**, 980, 2009.
6. “Ionothermal synthesis of inorganic-organic hybrid materials containing perfluorinated aliphatic dicarboxylate ligands”, Z. Hulvey, D.S. Wragg, Z. Lin, R.E. Morris and A.K. Cheetham, *Dalton Trans.* 1131, 2009.
7. “Exceptional stability and high hydrogen uptake in hydrogen bonded Metal-Organic Cubes (MOCs) possessing ACO and ASV zeolite-like topologies”, D.F. Sava, V.Ch. Kravtsov, J. Eckert, J.F. Eubank[†], F. Nouar, and M. Eddaoudi, *J. Am. Chem. Soc.* 2009 (in press).
8. “Hydrogen adsorption in Ti-doped SBA-15”, A.I. Acatrinei, M.A. Hartl, J. Eckert, E.H.L. Falcao, G. Chertkov, and L.L. Daemen” *J. Phys. Chem. C* 2009 (in press).
9. “A Hybrid Cobalt Disulfonate with a Novel Inorganic Layer Architecture Exhibiting a Field-Induced Magnetic Transition”, R.K. Feller, B.C. Melot, P.M. Forster and A.K. Cheetham, *J Mat Chem*, **19**, 2604, 2009.
10. “Tuning the interaction of molecular hydrogen in porous materials from physisorption to metal dihydrogen coordination”, (invited) J. Eckert, ACS National Meeting, Washington, DC, August 16–21, 2009.
11. “Modeling the Hydrogen Storage Materials with Exposed M²⁺ Coordination Sites” Author(s): K.M, Krack, A.K. Cheetham, and M. Parinello, *J. Phys. Chem. C.* **112**, 16171, 2008.
12. “Binding of Molecular Hydrogen in Porous Materials Investigated by Rotational Tunneling Spectroscopy: from Physics to Chemistry”, J. Eckert, Chemistry Department Seminar, New York University, October 2, 2008.
13. “Binding of Molecular Hydrogen in Porous Materials Investigated by Rotational Tunneling Spectroscopy: from Physics to Chemistry”, J. Eckert, Chemistry Department Seminar, Freie Universität Berlin, Germany, October 15, 2008.
14. “Binding of Molecular Hydrogen in Porous Materials Investigated by Rotational Tunneling Spectroscopy: from Physics to Chemistry”, J. Eckert, Physics Department Colloquium, University of Houston, September 16, 2008.

References

1. Z. Hulvey, E. Ayala, J.D. Furman, P.M. Forster, and A.K. Cheetham, *J. Cryst. Growth and Design*, in press, 2009.
2. Z. Hulvey, E.H.L. Falcao, J. Eckert, and A.K. Cheetham, *J. Mat. Chem.*, **19**, 4307, 2009.
3. P.D.C. Dietzel, Y. Morita, R. Blom, H. Fjellvåg, *Angew. Chem., Int. Ed.*, 2005, **44**, 6358.
4. P.D.C. Dietzel, B. Panella, M. Hirscher, R. Blom, H. Fjellvåg, *Chem. Commun.*, 2006, 959.
5. P.D.C. Dietzel, R.E. Johnsen, R. Blom, H. Fjellvåg, *Chem. Eur. J.*, 2008, **14**, 2389.
6. P.A. Georgiev; A. Albinati; J. Eckert, *Chem. Phys. Lett.*, **449**, 182, 2008.
7. J. Eckert, F.R. Trouw, B. Mojet, P.M. Forster, and R. Lobo, *J. Nanosci. Nanotech.*, in press (2009).
8. F. Nouar, J. Eckert, J.F. Eubank, P. Forster, and M. Eddaoudi, *J. Am. Chem. Soc.* **131**, 2864, 2009.