IV.D.1 Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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Objectives

- Synthesize a novel class of hybrid hydrogen storage materials which utilize <u>molecular</u> chemisorption of hydrogen.
- Synthesize and characterize new lightweight (first-row) transition metal compounds capable of binding more than one dihydrogen molecule; incorporate these compounds/materials into nanoporous hybrid materials for hydrogen storage.
- Characterize binding of hydrogen by inelastic neutron scattering methods.
- Utilize these results to optimize new materials.
- Demonstrate improved hydrogen storage properties of these materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section 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

This project aims to develop new porous hydrogen storage materials which utilize molecular chemisorption of hydrogen rather than mere physisorption, and do so along with framework modifications to enhance hydrogen binding, all in low weight hybrid materials. Stronger binding of hydrogen should result in greater capacity and lower operating pressures at room temperature. These studies should lead to the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage system targets, especially those for specific energy, energy density and operating conditions.

Accomplishments

- Demonstrated the existence of coordinated molecular hydrogen at open metal binding sites in several porous materials.
- Demonstrated the feasibility of synthesizing hybrid materials containing Mg including several which are porous and thermally stable.
- Synthesized several hybrid metal organic frameworks with fluorine-substituted organic linkers in ionic liquids. The use of F in place of H should increase H_2 binding energies.
- Synthesized several hybrid metal organic frameworks with organic linkers that are promising candidates for reversible hydrogenation, which would offer much greater capacity for strongly bound hydrogen.
- The known $[FeH_6][MgBr(\text{tetrahydrofuran}, \{THF\})_2]_4$ complex was synthesized as a starting material. $[FeH_6]^{4-}$ was reacted with the strong acid H[BArf] in THF under H_2 at room temperature to attempt protonation to a dihydrogen complex.
- A known dinuclear iron aryl complex, $Fe_2(\text{mesityl})_4$, was synthesized. Reactions with H_2 and with strong acids under H_2 were carried out.
- An apparatus for high pressure infrared spectroscopic measurements was designed and assembled to study reactions of H_2 with for example simple hexaaquo iron(II) salts such as $[Fe(H_2O)_6][BF_4]$.

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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 carbons (including carbon nanotubes) and metal hydrides. Activated carbons have the attraction that they are very cheap, their capacities on a weight percent basis are very good at low temperatures due to their very low densities, and the adsorption process is readily reversible. Their shortcomings stem from the fact that the fundamental interactions between carbons and hydrogen are non-bonding in nature (i.e. they involve physisorption) and are therefore rather weak. It therefore seems unlikely that they will meet the capacity and working pressure targets set by the DOE. Metal hydrides, on the other hand, adsorb hydrogen by a chemisorption process that is accompanied by dissociation of the hydrogen molecules. The interaction is much stronger, but facile reversibility is a problem in many cases and such systems are often prone to irreversible poisoning by oxygen.

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 L-N-Al-Mg-H alloys, or on NH_3BH_3, coordination polymers (the so-called MOF-n series of materials), or liquid organic carriers which can be reversibly hydrogenated. Our highly promising strategy is aimed at the development of new hybrid materials 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 hybrid materials based on lightweight metals such as Mg. Modification of the linker may also be necessary to reach the desired goal of a binding energy near 20 kJ/mol, and we are 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)   Materials with open metal binding sites for molecular chemisorption of hydrogen
(ii) Magnesium based hybrid materials
(iii) Hybrid materials with fluorinated organic linkers
(iv) Bind multiple dihydrogen ligands at open metal sites

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, or the development of hybrids based on lightweight magnesium. The motivation, of course, is that systems based simply upon transition metals are unlikely to meet DOE targets due to their high densities. Efforts by our LANL collaborator G. J. Kubas are directed at finding synthetic routes to poly-dihydrogen complexes of Fe to be incorporated into framework compounds. Divalent magnesium has a number of similarities to the transition metal ions typically used to make metal-organic frameworks (e.g. cobalt, nickel, and zinc) in that it prefers octahedral coordination, has a comparable ionic radius, and a similar hydration energy. Either of these approaches is likely to require additional improvements of hydrogen binding as the number of open metal sites cannot be increased without limitations. We are attempting to accomplish this by one or both innovative methods, namely the use of fluorinated organic linkers, or with unsaturated linkers that could be reversibly hydrogenated.

Results

(i) Open Metal Binding Sites We have now been successful in demonstrating 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.

From our inelastic neutron scattering spectroscopy on the hindered rotation of the sorbed hydrogen molecule in Ni-SIPA we have concluded that there exist at least two sites where H_2 coordinates to Ni, and that these become available only when the material is first evacuated at 325°C or higher. Under these conditions hydrogen desorbs only at temperatures around 140-150 K. Binding energies for hydrogen in this material are between 10 and 11 kJ/mol over a wide range of loading, i.e. approximately 50% of the target for room temperature operation of a sorption-based storage system.

The formation of the first isolable dihydrogen complex with Cu in the Cu-exchanged zeolite ZSM-5 was recently reported by us [4] with much strongest binding of *molecular* hydrogen found to date in any porous material. While zeolites themselves are not likely candidates as hydrogen storage materials on

account of the high density of their framework, they are in some ways ideal for testing interactions of H_2 with various metal cations with which the usual Na^+ can be exchanged. We have in fact earlier observed that the interaction of H_2 with Cu in CuNaA is appreciably stronger than that with open Cu sites in MOFs. In the case of ZSM-5, however, neither the site geometry nor the oxidation state of Cu are known with a great deal of certainty, although the latter is taken to be Cu(I). A simple model for this site was therefore used to calculate a binding energy for dihdyrogen in Cu-ZSM-5 of 56 kJ/mol. While this value is well above the practical goal of approximately 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.

We have continued to synthesize metal containing frameworks by hydrothermal or solvothermal methods with a particular emphasis on those containing Ni, as it has been shown that the Ni ion can serve as a strong binding site for molecular hydrogen [2,3]. We have chosen some of the organic linkers to be potentially useful for reversible hydrogenation in the solid state to boost hydrogen storage capacity in a similar manner as has been demonstrated in the liquid phase by Air Products. To date, none of the materials prepared by us has sufficient porosity to attempt this type of reaction. Our work includes the known Ni-adipate, -glutarate and -cyclohexanedicarboxylate materials following reported procedures. We also prepared several new hybrid framework materials with other metals including zinc anthraquinonedisulfonate (Zn-AnQDS), cobalt and magnesium 2,6-naphthalenedicarboxylate (Co-2,6NDC and Mg-2,6NDC). All of these feature the diffraction peaks at low angles that are characteristic of large unit cells and possible open structures. Co-2,6NDC dehydrates readily at about 100°C with a reversible change in color from pink to gray. While is compound has a rather small surface area we have nonetheless obtained evidence (a very low energy transition at

1.3 meV) by our inelastic neutron scattering studies that H_2 may indeed coordinate to the vacant Co site.

(ii) Mg-Based Hybrid Materials We have now synthesized several additional, new hybrid structures based upon magnesium, some of which do in fact retain porosity after removal of the guest species. For example, the systematic variation of the synthesis conditions for obtaining Mg Tartrate have resulted in three different structures with 1-, 2- and 3-D arrangements of MgO_6 octahedra, which are shown in Figure 1. On the one- and two-dimensional chains the Mg has, respectively, two or one water molecules coordinated to it, while in the three-dimensional structure Mg is fully coordinated to tartrate linkers. The 2-D structure is layered with the pores being formed by 6-membered rings, whereas the 3-D structure has pores made up of three-membered rings. Both the 2-D and 3-D structures are stable to removal of guest molecules and retain their integrity up to at least 300°C. We note that the 2-D porous compound also has a coordinated water molecule. If this can be removed without compromising the structure it could provide a rather strong binding site for molecular hydrogen.

As part of our effort to design new lightweight Mg-based hybrid porous materials we are also investigating the previously synthesized, and known compound magnesium formate [7]. The structure consists of a three-dimensional network of corner-sharing MgO_6 octahedra with formate groups pointing into the channels. The surface area has been determined with variable results up to about 180 m^2/g. It is therefore remarkable that this compound was found to store nearly 1 wt% of H_2 at 77K (Figure 2a). In fact, such a capacity can only **be reached by going well beyond** monolayer coverage, i.e. by filling the pores. The binding hydrogen in some of this material has been characterized by new isotherms (Figure 2a), which yields a binding energy of 6.5 kJ/mol, as well as an inelastic neutron scattering (INS) experiment (Figure 2b) at the Intense Pulsed Neutron Source of Argonne National Laboratory. The INS spectrum reveals several well-defined binding
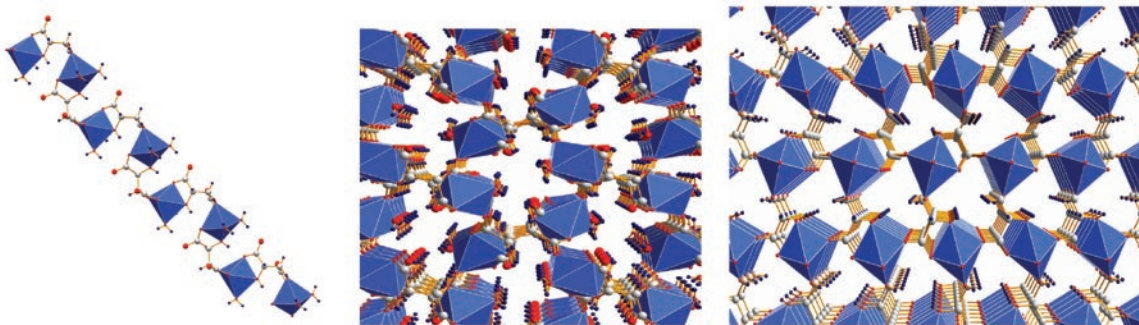
FIGURE 1. Synthesis of New, Porous, Mg-Based Hybrid Materials Magnesium Tartrate: (a) 1-D Chains, Two Waters Coordinated to Each Mg Atom, (b) 2-D Layered Structure, Pore is Six-Membered Rings, One Water Coordinated to Each Mg Atom (c) 3-D Framework, Three-Membered Rings

(a)

(b)
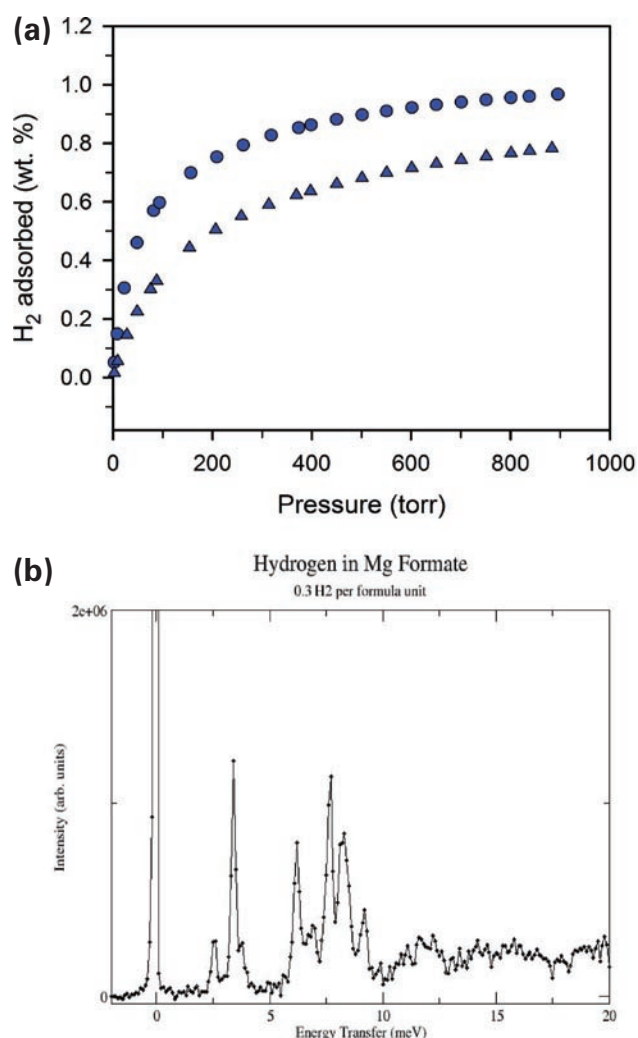
FIGURE 2. Magnesium Formate: Hydrogen Adsorption Isotherms (a) at 77K and 87K; (b) INS Spectrum for a Loading of 0.3 H_2 per Formula Unit

sites for hydrogen, all of which exhibit considerably stronger interactions than those with the (100) surface of MgO, or in MOF-5. The reason for this difference may lie in the fact that H_2 in the small pores of Mg formate can interact with multiple surfaces as opposed to just one external surface on MgO. This conclusion further demonstrates that Mg-based hybrids may have significant advantages for hydrogen storage applications.

　　(iii) 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 recently begun to attempt 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 normal (H-) organic linkers. In fact, our Grand Canonical Monte Carlo (GCMC) calculations on H_2 in

Mg formate demonstrate that the fluorinated form binds hydrogen about 50% more strongly that the H- form.

　　The synthesis of materials containing fluorinated ligands differs greatly from traditional synthesis of hybrid materials. In collaboration with Russell Morris (St. Andrews, UK) we have developed the 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 more soluble in some of the solvents we would normally use. Our initial attempts to crystallize a Co-fluorosuccinate were carried out in a 1:1 molar mixture of ethylmethylimidazolium (emim) bromide and emim-triflimide. These two ionic liquids have very different purposes: the triflimide is strongly hydrophobic and yet still solubilizes the fluoro-organics, while the bromide is strongly hydrophilic and easily solubilizes the metal. When the synthesis is carried out in simply the bromide ionic liquid, no reaction occurs; and since the triflimide is noncoordinating, it cannot dissolve the metal. The correct mixture of the two solvents produced the Co-fluorosuccinate structure I shown in Figure 3a. It contains a unique chain of alternating, corner-sharing octahedral and trigonal prismatic CoO_6 units, with acetate ions kinking the chain and bridging the trigonal prism while the tetrafluorosuccinate anions are linking the chains. The main problem with this structure is the fact that a cationic species from the solvent remains in the pore which cannot be removed without destroying the structure. Nonetheless, this first example of a fluorinated coordination polymer obtained by us constitutes an important proof of principle.
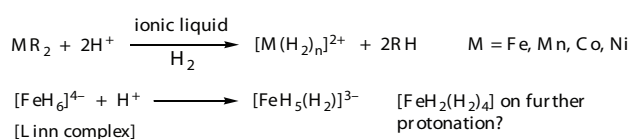
　　Slight changes in the amounts of water in the reaction mixture were subsequently found to result in significant differences in the structure obtained in the synthesis. Co-fluorosuccinate I (above) was anhydrous and utilized dry emim-Br, while the new form of Co-tetrafluorosuccinate (Figure 3b) was carried out with emim-Br that was not completely dry. This structure II is a 2-D coordination polymer with layers of CoO_6 octahedra connected in the b and c directions by the tetrafluorosuccinate dianions. Two

(a)　　　　　　　　　　　**(b)**
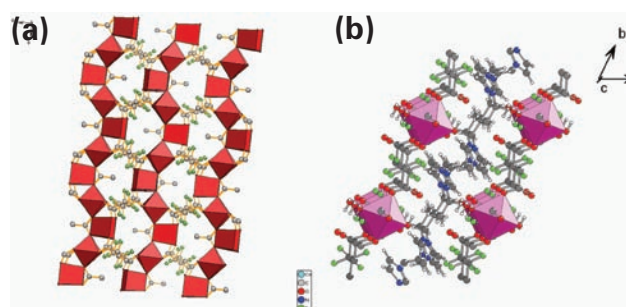
FIGURE 3. Co-Tetrafluorosuccinate Synthesized in Ionic Liquids (a) Without Water, (b) in The Presence of Some Water

water molecules are coordinated to the Co center. The 1-ethyl-3-methylimidazolium cations are found between these layers. The structure has a large pore which unfortunately is packed full of the imidazolium cations that seem to be too difficult to remove. Nonetheless, it is clear from these examples that it should be possible to produce hybrid materials using fluorinated organics, along with potentially open metal binding sites, if the water can be removed from the Co. Such a material would have significantly enhanced binding energies for sorbed hydrogen.

(iv) Multiple Dihydrogen Ligands Our efforts to experimentally demonstrate the feasibility of binding multiple molecular hydrogen ligands to open metal sites in hybrid materials presently employ the strategy shown by the following two reactions:

$$MR_2 + 2H^+ \xrightarrow[\;H_2\;]{\text{ionic liquid}} [M(H_2)_n]^{2+} + 2RH \qquad M = Fe, Mn, Co, Ni$$

$$[FeH_6]^{4-} + H^+ \longrightarrow [FeH_5(H_2)]^{3-} \qquad [FeH_2(H_2)_4] \text{ on further}$$
[Linn complex]　　　　　　　　　　　　　　　　protonation?

For the first reaction shown above, a known dinuclear iron aryl complex, $Fe_2(mesityl)_4$, was synthesized, which contains two bridging mesityl groups and two terminal mesityl ligands. The reaction with H_2 gave no reaction but the reaction with H[BArf] in toluene under H_2 gave an oily precipitate. Although the product was intractable, it appears that this and similar systems have some promise and further reactions will be carried out under different conditions. The second, more promising reaction involves protonation of Linn's complex, $[MgBr(thf)_2]_4[FeH_6]$, a rare example of a first-row metal homoleptic polyhydride [8]. Multiple protonations could yield iron species with multiple H_2 and or hydride ligands with >6 wt% H_2. We prepared the $[FeH_6]$ complex, which required a special apparatus was designed, built, and rigorously checked for required safety issues for use at Los Alamos National Laboratory since the reaction requires hydrogen pressures greater than 1 atmosphere. The $[FeH_6]^{4-}$ complex was then reacted with the strong acid H[BArf] in THF at room temperature to attempt protonation to a dihydrogen complex. No gas evolution was observed which is indeed encouraging. The reactions are now being carried out at the lowest accessible temperatures for solvent systems that will include fluorocarbons (e.g. Freon-dichloromethane mixtures) to avoid decomposition and solvent binding.

An apparatus for high pressure infrared spectroscopic measurements was designed and assembled to study reactions of H_2 with for example simple hexaaquo iron(II) salts such as $[Fe(H_2O)_6][BF_4]$. Ruthenium analogues are known to react with H_2 under pressure to give substitution of H_2O by H_2 to form $[Ru(H_2)(H_2O)_5]^{2+}$ [9] and the iron system may do the same, possibly giving multiple substitutions by H_2.

A low-coordinating polar solvent, sulfolane, was planned for initial studies (so as to dissolve ionic complex), although difficulties were encountered since its freezing point is near room temperature.

Conclusions and Future Directions

We have clearly demonstrated the pronounced effect on the binding of molecular hydrogen offered by the presence of open metal sites which can in fact coordinate the H_2 molecule. 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 value of the rotational tunneling splitting for the bound H_2 molecule are about 8 meV for the Cu site in HKUST-1, 3 meV in zeolite CuNaA, and 0.15 meV in Cu-ZSM-5 (where a smaller energy implies a stronger interaction). We therefore expect to be able to optimize our synthetic strategy involving open metal sites to make use of these findings.

The open Ni sites in our compounds VSB-5 and Ni-SIPA are created by removal of water ligands, and contribute critically to an overall binding energy of nearly 11 kJ/mol in the latter case, or about 50% of the target for a room temperature, sorption base system. As it is not clear how many additional open metal sites can be introduced into this kind of structure, we are at the same time pursuing complementary strategies to increase hydrogen storage capacity as well binding energies: first, we have synthesized some hybrid materials with unsaturated organic linkers that may be suitable for reversible hydrogenation and thereby increase the amount of hydrogen bound in the system, while we have also synthesized some of the first hybrid materials using fluorinated organic linkers. The latter will bind hydrogen more strongly (by as much as 50% based on our calculations) than its H- containing counterpart. A third method for increasing hydrogen binding energies is to synthesize charged, rather than neutral frameworks, as has been demonstrated in our collaboration with the group of Eddaoudi (University of South Florida). A suitable combination of these approaches clearly holds the promise of reaching the necessary binding energies of 15–25 kJ/mol.

The principal issue in following up on our success in producing several novel coordination polymers including fluorinated organics, or highly functionalized linkers is to modify synthesis conditions and strategies to turn these into porous materials and demonstrate the expected improvement in their hydrogen sorption properties.

We have already successfully synthesized a considerable number of Mg-based hybrid materials with porosity, and have determined that hydrogen binding in these frameworks is improved over that in Zn- and Cu-based MOFs. As our knowledge of the

magnesium chemistry increases, we feel more confident that we shall succeed in producing such materials with the larger surface areas as well. We will continue our synthesis efforts of hybrids materials containing highly functionalized linkers in conjunction with open metal binding sites and attempt to make compounds with Ca, Sr and trivalent ions.

The approaches for synthesizing and isolating complexes with reversibly bound multiple dihydrogen ligands now appear to be feasible, and should be successful within the next year. However, the stability of such complexes will need to be determined, as well as their transferability to porous host materials.

FY 2007 Publications/Presentations

1. "Observation of exceptionally strong binding of Molecular Hydrogen in a porous material: formation of an η^2-H$_2$ complex in a Cu-exchanged ZSM-5 zeolite", P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert , J. Am. Chem. Soc. **2007**, 129, 8086.

2. "Hybrid inorganic–organic frameworks containing magnesium: Synthesis and structures of magnesium squarate, diglycolate, and glutarate, and potassium magnesium cyclobutanetetracarboxylate", Z. Hulvey, A.K. Cheetham, Solid State Sciences, **2007**, 9, 137.

3. "Assembly of Metal-Organic Frameworks Based on Indium Trimer Building Blocks with Unprecedented "soc" Topology and High Hydrogen Uptake", Y. Liu, J. F. Eubank, A. Cairns, J. Eckert, V. Ch. Kravtsov, R. Luebke and M. Eddaoudi, Angew. Chem. Int. Ed**., 2007**, 46, 3278.

4. "Adsorption of Molecular Hydrogen on Coordinatively Unsaturated Ni(II) Sites in a Nanoporous Hybrid Material", P. M. Forster, J. Eckert, B. Heiken, J. B. Parise, Ji Woong Yoon, S. H. Jhung, J.-S. Chang, and A. K. Cheetham J. Am. Chem. Soc., **2006** 128, 16846, 2006.

5. "Metal-Dihydrogen Complexes. Prototypes for The Coordination Chemistry of Saturated Molecules", G. J. Kubas, *PNAS* **2007**, 104, 6901. [invited Perspectives article]

6. "Hydrogen Storage gets a Boost", Feature in C&E News **2007**, 85, 11, which includes our results on H2 in Ni-SIPA (ref. 3).

7. "The Problem of Hydrogen Storage for Mobile Applications: Showstopper for the Hydrogen Economy?", Chemistry Department Lecture, University of Santiago de Compostela, Spain, June 21, 2007.

8. "Modes of Binding of Molecular Hydrogen in Porous Materials for Hydrogen Storage", J. Eckert, Invited Plenary Lecture, ANL Users Week, Argonne National Laboratory, May 7–11, 2007.

9. "Hydrogen Storage Materials with Binding Intermediate Between Physisorption and Chemisorption", J. Eckert, 2007 DOE Hydrogen Program Annual Review, Arlington, VA, May 14–18, 2007.

10. "Synthesis, Structure, and Bonding Aspects of the Reversible Binding of Dihydrogen to Materials for Hydrogen Storage and Production", G. J. Kubas, University of Oregon, October 2006.

11. "Hydrogen Storage Materials with Binding Intermediate Between Physisorption and Chemisorption", J. Eckert, Freedom Car Team Meeting, USCAR, Southfield, MI, August 17, 2006.

12. "Will Porous Materials be the Hydrogen Storage Medium in your Fuel Tank?", J. Eckert, ICMR Summer Program in Porous Materials, UCSB, Santa Barbara, CA, August 7, 2006.

13. "Binding of Molecular Dihydrogen to Metal Complexes and Materials for Hydrogen Storage and Production", G. J. Kubas, Lujan Seminar Series, Los Alamos National Laboratory, April 24, 2007.

14. "Hydrogen Storage Materials with Binding Intermediate Between Physisorption and Chemisorption", G. J. Kubas, 2007 DOE Hydrogen Program Annual Review, Arlington, VA, May 14–18, 2007.

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