IV.D.2 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 molecular chemisorption of hydrogen.
- 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 Hydrogen Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency

Technical Targets

This project aims to develop new porous hydrogen storage materials which utilize molecular chemisorption of hydrogen rather than mere physisorption, and ultimately do this 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 feasibility of synthesizing hybrid materials containing Mg with four examples of such structures.
- Verified the equivalence efficient microwave synthesis to the conventional hydrothermal method of Ni phosphate nanoporous material synthesis.
- 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.
- Carried out (LANL) initial studies for the synthesis of metal-polydihydrogen complexes of bare metal ions to boost the relative storage capacities of transition metal containing nanoporous 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 carbons (including carbon nanotubes) and metal hydrides. Activated carbons have the attraction that they are very cheap, their capacities on a weight % 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 dihydrogen 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 $NaBH_4$ or on NH_3BH_3, and coordination polymers (the so-called MOF-n series of materials). 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. The three classes of materials that we propose to explore are:

(i) Nanoporous nickel phosphates and related inorganic materials
(ii) Hybrid inorganic-organic open framework materials
(iii) Materials based on metal-dihydrogen complexes (at LANL with Kubas)

Approach

The primary focus of our synthetic work (ii) has been to continue with our efforts to create novel inorganic-organic framework materials based upon magnesium rather than transition metals, while 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. The motivation, of course, is that systems based upon transition metals are unlikely to meet DOE targets due to their high densities. 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. However, only a few magnesium containing metal-organic frameworks [1] have been reported.

Results

(i) We have previously demonstrated [2] the existence of some very strong binding sites for molecular hydrogen in our porous Ni phosphate materials, and have therefore continued to work with our Korean colleague, Dr. Jon-San Chang of the Korea Research Institute of Chemical Technology, Taejon, on an improved synthesis of the nickel phosphate and related molecular sieves (VSB-1 and VSB-5). This has lead to the discovery that these phases, which normally take about 4 days to make in a conventional hydrothermal reaction, can be synthesized in only 2 hours by using microwave methods. Furthermore, this can be achieved without the use of expensive organic templates. This exciting result was published in late 2005 [3]. In Figure 1 we demonstrate the equivalence of the two synthetic approaches for the adsorption-desorption isotherms of nitrogen in Ni glutarate.

(ii) We have succeeded in synthesizing and characterizing four new magnesium containing metal-organic hybrid compounds [1] in an effort to prepare low density materials for hydrogen storage. The compounds were prepared hydrothermally and characterized using single crystal x-ray diffraction. Three of these compounds are analogs of known structures containing transition metals with squarate (**I**),

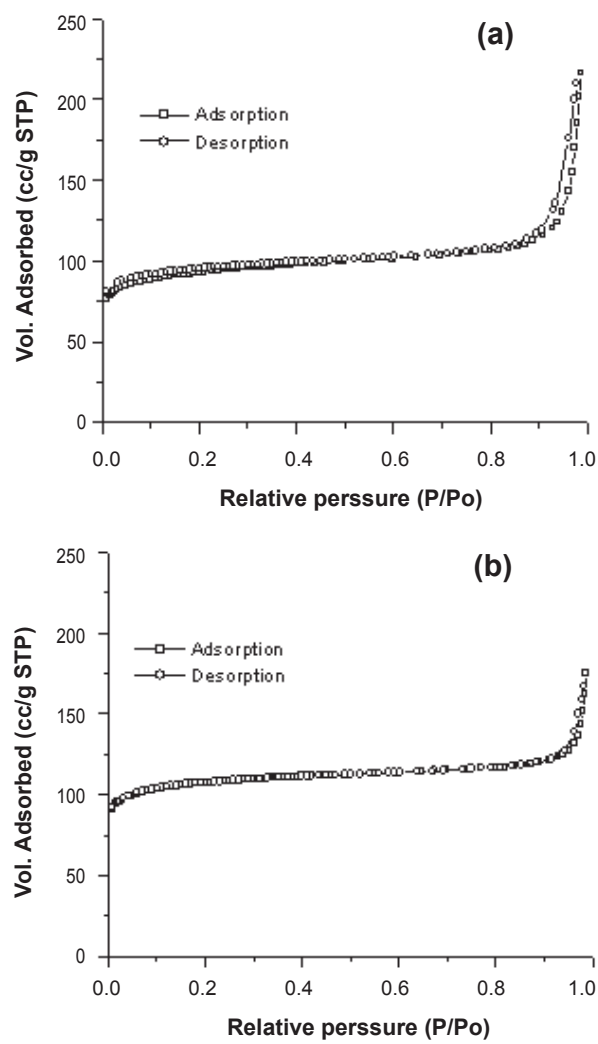

FIGURE 1. Adsorption-desorption isotherms of nitrogen over pure nickel glutarates: (a) nickel glutarate, phase 1, synthesized by a conventional hydrothermal method at 180°C for 48 h and (b) nickel glutarate, phase 2, synthesized by the microwave method at 220°C for 1 min.

diglycolate (**II**), and glutarate (**III**) ligands; the fourth is a novel structure using cyclobutanetetracarboxylate (**IV**) which contains potassium as well as magnesium cations. Although none of these materials have the porosity necessary for gas storage applications, this work does demonstrate that the synthesis of magnesium analogs of some transition metal frameworks is an attractive route for the discovery of new sorbant materials.

Structural Results: In the structure of **I** ($Mg(H_2O)_2(C_4O_4)$) each squarate group is linked to four metal octahedra. The squarate groups lie in perpendicular planes, creating a three-dimensional network (Figure 2). The structure is very open and can be related to the aluminosilicate sodalite, in that the Al_2Si_2 rings of the sodalite are replaced with the squarate ligand, and the oxygen atoms that connect those units are replaced with $Mg(H_2O)_2O_4$ units.

Compound **II** ($Mg(H_2O)(C_4H_4O_5) \cdot H_2O$) is isostructural to previously synthesized Co and Mn containing phases. The structure contains isolated MgO_6 octahedra connected to each other through carboxylate groups on the diglycolate ligand (Figure 3) resulting in a three-dimensional network.

Compound **III** ($Mg(C_5H_6O_4)$) is isostructural to a previously synthesized Mn-glutarate. The structure consists of edge-sharing MgO_6 octahedra that form 12-membered channels lined with methylene units from the glutarate ligands. These rings arrange in a honeycomb manner to form the two-dimensional layers (Figure 4).

The structure of **IV** ($K_2Mg(H_2O)_2(C_8H_4O_8)$) consists of one-dimensional chains of MgO_6 octahedra connected to each other through one cyclobutanetetracarboxylate (cbtc) ligand. Two adjacent carboxylate groups on the ligand bond to the same magnesium, such that each cbtc ligand bridges two magnesium atoms. The chains align parallel to each other and are linked through potassium ions, forming a two-dimensional sheet (Figure 5). The sheets are linked to each other through both the potassium ions and through two hydrogen bonds.

Thermal behavior of the Mg materials: Compound **I** exhibits two distinct mass losses during heating corresponding to dehydration between 200 and 310°C which correspond to the loss of the two water molecules that are coordinated to each magnesium ion. However,

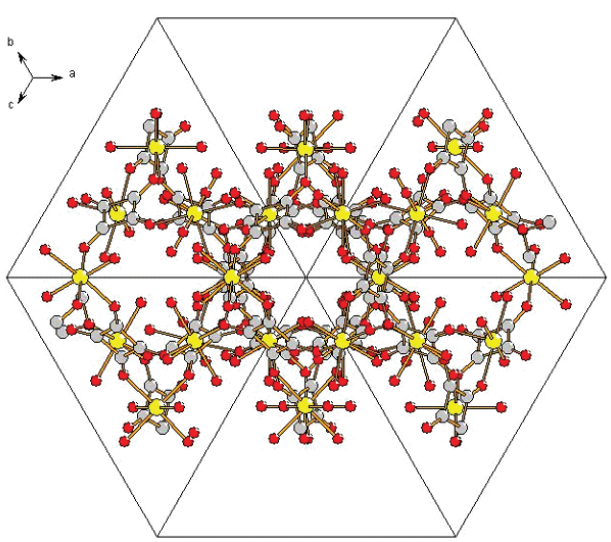

FIGURE 2. The structure of magnesium squarate (**I**) showing channels down the [111] axis.

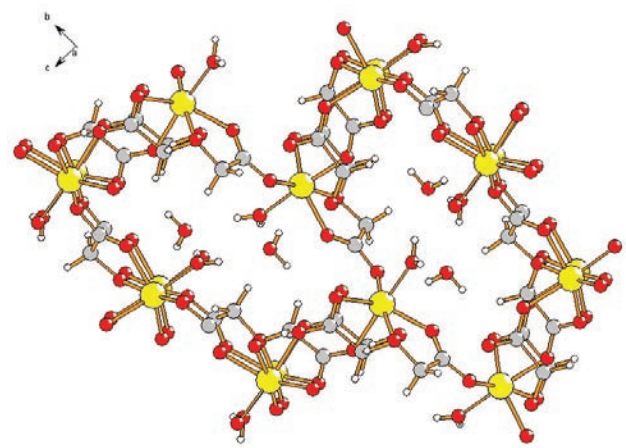

FIGURE 3. The structure of magnesium diglycolate (**II**) viewed down the *a*-axis showing the cavities filled with uncoordinated water molecules.

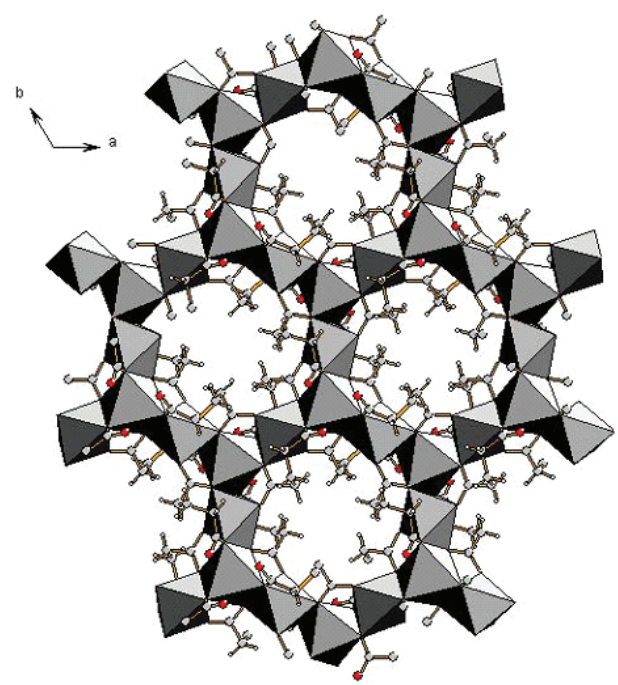

FIGURE 4. One layer of magnesium glutarate (**III**) viewed down the *c*-axis, with 12 MgO_6 octahedra edge-sharing to form the channels.

we find that the structure collapses between 200 and 300°C during this dehydration process. Compound II exhibits similar behavior corresponding to loss of both the coordinated and the uncoordinated water molecules, between 120 and 240°C. The diglycolate units begin to decompose at 370°C. Compound **III** shows a single mass loss between 370 and 520°C (found 72.5%; calcd, 73.8%) corresponding to the decomposition of the glutarate units to form MgO. Efforts to synthesize a pure sample of **IV** for thermal and elemental analysis failed.

Reversible hydrogenation on organic linking groups: We have taken up a new and very exciting idea to make hybrid materials, which would function as the solid state analog of the reversible hydrogenation of unsaturated liquid hydrocarbons patented by Air Products (423648100; USPTO) by making the organic molecule part of one of our nanoporous hybrid inorganic-organic frameworks. This approach should have the advantage that the capacity should be substantially higher than what we have obtained to date. Our strategy is also more attractive than Air Products' approach since it is generally easier to work with solids than liquids for practical applications. In addition, the kinetics of our proposed process should be more facile. We are investigating possible materials in which to explore this approach, such as those containing frameworks with all-carbon saturated organic bridges, e.g. glutarates, adipates, 1,3-cyclohexanedicarboxylates. These frameworks are of interest because they often feature significant porosity and consequent surface area, and some are known to strongly bind H_2. In addition, conditions may be found that allow for the formation of double bonds in the organic moiety, thus releasing H_2.

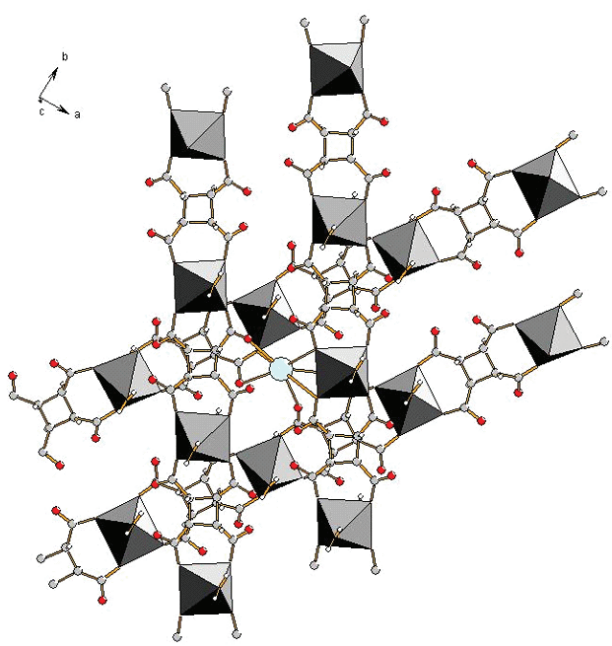

FIGURE 5. The structure of **IV** viewed down the *c*-axis showing the four chains connected to each other through one potassium atom. The potassium atom connects two parallel chains on two neighboring sheets.

Examples of such framework compounds that we have synthesized include a nickel framework with 1,3-cyclohexanedicarboxylic acid, a nickel-2,6-naphthalenedicarboxylate with a significant surface area (~250 m^2/g) as well as novel frameworks with Quinone-containing bridges have been synthesized through the hydrothermal or solvothermal method, as well as zinc-, nickel-, iron- and manganese-anthraquinonedisulfonates have also been produced. These quinone-containing frameworks are of interest because the quinone group is prone to undergo hydrogenation to hydroxyl under reducing conditions.

(iii) Several new potential synthetic routes were devised in our LANL collaboration to generate hydrogen-rich first-row transition metal complexes of the type $[M(H_2)_y]^+$ (cationic) or $MH_x(H_2)_y$ (neutral) that contain multiple reversibly-bound dihydrogens. Approaches now being taken include protonating a first-row transition metal alkyl or aryl with an acid that has a noncoordinating anion such as $B[C_6F_5]_4$ in an inert solvent such as an ionic liquid. We have prepared a dinuclear complex, $Fe_2(mes)_4$ (mes = mesityl), and reactions with hydrogen and protons have been carried out., and have protonated anionic light metal polyhydrides such as known $Mg_2[FeH_6]$ to directly make multi-dihydrogen species such as $FeH_4(H_2)_2$ [4]. This difficult synthesis involves reaction of iron(II) bromide with Grignard reagents (PhMgBr) under pressure of several atmospheres of hydrogen. We have been successful in reproducing the synthesis and have reacted the hexahydride with protonic acids.

Even simpler routes to multiply-bound dihydrogen complexes have been devised that involve the synthesis of classical coordination complexes such as $[Fe(H_2O)_6][triflate]_2$, in which the aquo ligand can be replaced with H_2 simply by pressurizing it with hydrogen at about 10 atmospheres in solution [5]. We have assembled a high pressure infrared spectroscopy apparatus for reacting hydrogen under several atmospheres pressure with iron salts in sulfolane and analyzing the spectrum of the products to determine if hydrogen binds to iron in place of one or more water ligands. The apparatus is now undergloing testing.

Conclusions and Future Directions

Our efforts in terms of the synthesis of new lightweight hybrid storage materials based upon magnesium has shown great promise and will now continue with the aim of finding porous magnesium-based systems with high surface areas, along with our parallel approach to increase (a) the binding strength

of hydrogen by molecular chemisorption of multiple dihydrogen ligands at transition metal sites and (b) the capacity of such materials by pursuing the novel idea of reversible hydrogenation of the organic groups in these frameworks. Beamtime has been obtained at the Intense Pulsed Neutron Source at Argonne National Laboratory to perform inelastic neutron scattering studies later this year on hydrogen binding in some of the new materials synthesized under this project.

FY 2006 Publications/Presentations

1. "Facile Synthesis of Nanoporous Nickel Phosphates without Organic Templates under Microwave Irradiation", S.H. Jhung, J.W. Yoon, J-S. Hwang, A.K. Cheetham, and J-S. Chang, Chem. Mater. **17**, 4455-4460 (2005).

2. "Characterization of H_2 Binding Sites in Prototypical Metal Organic Frameworks by Inelastic Neutron Scattering" J. L. C. Rowsell, J. Eckert, O. M. Yaghi, J. Am. Chem. Soc. 127, 14904, 2005.

3. "Adsorption of Molecular Hydrogen on Coordinatively Unsaturated Ni(II) Sites in a Nanoporous Hybrid Material", Paul M. Forster, Juergen Eckert, Brandon Heiken, John B. Parise, Ji Woong Yoon, Sung Hwa Jhung, Jong-San Chang, and Anthony K. Cheetham. (submitted to JACS, 2006).

4. "Hybrid Inorganic-Organic Frameworks Containing Magnesium; Synthesis and Structures of Magnesium Squarate, Diglycolate, and Glutarate, and Potassium Magnesium Cyclobutanetetracarboxylate", Zeric Hulvey and Anthony K. Cheetham (submitted to Solid State Sciences, 2006).

Invited Presentations

1. "Metal (Poly)Dihydrogen Complexes for Hydrogen Storage", G. J. Kubas, J. Cross, and J. Eckert, Materials Research Society Spring Meeting, San Francisco, CA, April 17-21, 2006.

2. "Modes of Binding of Molecular Hydrogen and their Implications for Hydrogen Storage", J. Eckert, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 15-20, 2005.

3. "Characterization of the Interaction of Molecular Hydrogen with Porous Materials by Rotational Tunneling Spectroscopy", J. Eckert, XIIIth Int.'l Workshop on Quantum Atomic & Molecular Tunneling in Solids, Santiago de Compostela, Spain, July 27-31, 2005.

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