

VI.D.6 Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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Objectives

- Synthesize a novel class of porous 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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Weight and Volume
- C. Efficiency

Technical Targets

Porous Hydrogen Storage Systems with Strong Binding of Molecular Hydrogen

This project aims to develop new porous hydrogen storage materials which utilize molecular chemisorption of hydrogen rather than mere physisorption. 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.

Approach

Our approach to the problem of improving the binding strength of hydrogen in hybrid materials includes the use of light metals such as magnesium to support molecular chemisorption of multiple dihydrogen ligands, as well as organic groups with greater charge separation for improved hydrogen binding. In this initial phase of our work on new classes of such materials, we are currently attempting to synthesize new networks for hydrogen adsorption based on oxocarbon dianions (Figure 1). Nearly all of the reported transition metal-oxocarbon structures contain either the squarate or croconate units; there have been no reports of metal deltate (1) compounds, and only two metal rhodizonate (4) compounds exist. Therefore, our work is focused on the attempted synthesis of metal-containing deltate and rhodizonate compounds.

Recently, we also have begun an investigation into the use of di-*tert*-butyl squarate as a starting material to achieve new metal squarate structures. Previous work in our lab has shown that new open-framework metal phosphate structures can be obtained when organophosphorus compounds are used in place of phosphoric acid. One advantage to using alkylated precursors is that they allow the use of organic solvents or biphasic solvent systems. Our current focus in this area is on the synthesis of squarates of magnesium, which have not been explored previously (Figure 2). These have the potential to be sufficiently lightweight that they can meet the constraints of the DOE storage targets. Work at Los Alamos National Laboratory will focus on preparing materials with Fe centers having multiple dihydrogen ligands, and subsequently anchor these in porous supports.

We are particularly interested in extended frameworks of materials containing dicarboxylic acids, such as succinic, glutaric, etc. We have previously made several open-framework materials based upon cobalt(II) and nickel(II) succinates, and there is good reason to believe that the magnesium analogs can be formed. Materials will then be investigated by inelastic neutron scattering studies from the hindered rotational transitions of the sorbed hydrogen molecule in order to determine details of the binding and interaction of hydrogen with our new materials, thereby giving additional direction to our efforts in synthesis. We have previously demonstrated that this technique offers the most detailed and sensitive characterization of guest-host interactions of the adsorbed hydrogen molecule.

Accomplishments

This project is newly initiated and there are no accomplishments to report to date.

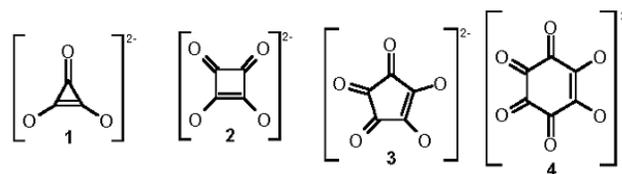


Figure 1. Oxocarbon Anions of the Formula $C_nO_n^{2-}$: Deltate (1), Squarate (2), Croconate (3), Rhodizonate (4)

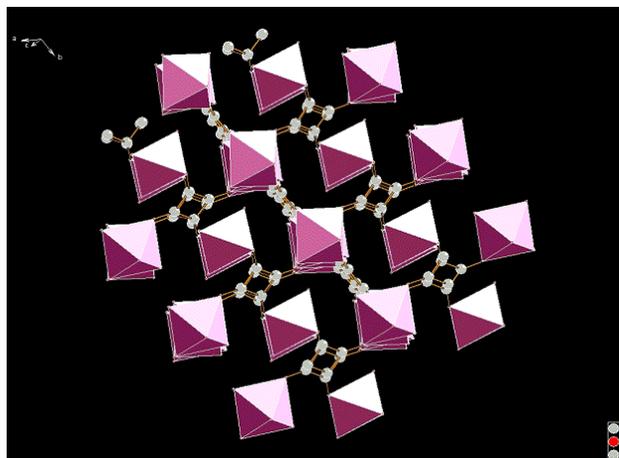


Figure 2. Structure of Manganese Squarate (Squarate ions connect MnO_6 octahedra. Magnesium squarate recently synthesized at University of California Santa Barbara is isostructural.)