IV.A.4h Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage

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Start Date: April 2005
Projected End Date: September 30, 2010

Introduction

ORNL is conducting research both on the development of synthetic methods and on the discovery of new hydrides, chosen mostly from alanates, amides, and borohydrides of the light elements in the periodic table. ORNL research on chemical synthesis takes advantage of expertise in solution-based synthesis to develop novel light weight compounds. The synthetic approach that is being followed incorporates strategies such as the use of solvents, catalysts, modifiers, and complexation agents that lead to the production of reversible hydrogen storage materials. ORNL work is exploring the synthesis of new and known materials using synthetic methods appropriate for scale-up to production and practical application.

Approach

ORNL is conducting research on the development of synthetic methods based on solution chemistry since these methods offer the most potential for scaling to kg and greater lot size. Work is being carried out under two general tasks: (1) the development of synthetic methods in support of Metal Hydride Center of Excelence (MHCoE) collaborators, and (2) discovery of new complex metal hydrides and amides. Within these two general tasks synthetic methods are being developed for two types of target materials for hydrogen storage: complex anionic materials (MHCoE Project B) and amide/imide (M-N-H) systems (MHCoE Project C). For both types of materials ORNL is seeking (a) methods to scale-up synthesis of known materials or new materials identified by MHCoE partners, and (b) development of new materials. The primary method used to follow the progress of reactions which release hydrogen is to follow temperature programmed pressure measurements where reaction products other than hydrogen are analyzed using a mass spectrometer. Hydrogen uptake is investigated in a traditional Sieverts apparatus. Fourier transform infrared (FTIR), Raman, and x-ray diffraction (XRD) are available to characterize solid reaction products.

Results

Technical progress in the latter part of FY 2005 and the first quarter of FY 2006 was focused on $LiAlH_4$ and the lithium-magnesium amide-imide systems. In particular, we investigated the effect of additives on the decomposition of $LiAlH_4$. The preparation of organometallic compounds of Ti for use as catalysts for liberation and uptake of hydrogen from $LiAlH_4$ were also investigated.

1. Additives generally increase temperature for conversion of $LiAlH_4$ to Li_3AlH_6.
2. Addition of $NaBH_4$ or $LiBH_4$ increases temperature for conversion of $LiAlH_4$ to Li_3AlH_6 and no decomposition of borohydride observed at temperatures less than 200°C.
3. Investigated the preparation of titanium-aluminum catalysts by the decomposition of organometallic complexes of the form $TiR_{(4-n)}(AlH_4)_n$ where R is an alkyl or aryl group that is thermally labile.
4. Investigated methods of preparing imide/amide system Li-Mg-N-H using liquid ammonia as a solvent.
5. Ammonolysis product of $Ti(NR_2)_4$ was prepared for investigation as a catalyst for metal imide/amide systems.

In January 2006 there was a transition to focused projects within MHCoE. In this new alignment ORNL is participating in two general projects: Project B – Complex Anionic Materials (borohydrides and alanates) and Project C – Amides/Imides (M-N-H systems). Within this new alignment, ORNL began work on borohydrides under Project B and focused work more closely on the development of general synthetic methods to make metal amide-imides under Project C.

1. Plans made to develop the chemistry of liquid and volatile metal borohydrides such as $Al(BH_4)_3$, $Ti(BH_4)_3$, and $Zr(BH_4)_4$ for hydrogen storage materials.

2. Planning conducted to attempt the development an organic amide/ammonia analog of the traditional sol-gel process, used to make metal oxides, for the preparation of metal imide/amides using liquid ammonia as the solvent.

ORNL has discussed joining Project D – Alanes with the project point of contact, and Brookhaven National Laboratory and ORNL have agreed to informally collaborate in the remainder of FY 2006.

Conclusions and Future Directions

We are making progress toward meeting the center's objective of developing a storage material that will meet the 2010 goals. At the present, designing a nanostructured catalyst/support to achieve fast cycling at the desired temperature appears to be the most challenging goal. Research to be conducted in FY 2007 is subdivided according to the MHCoE project it falls under. The focus will be materials that have the capacity to meet the 2010 DOE storage goals and collaboration with MHCoE partners.

MHCoE Project B – Complex Anionic Materials (borohydrides and alanates)

Liquid and volatile metal borohydrides such as $Al(BH_4)_3$, $Ti(BH_4)_3$, and $Zr(BH_4)_4$ are covalent molecular compounds with bridging M-H-B bonds. The concept is that volatile (or liquid) $M(BH_4)_n$ can be transported to heated zone containing a catalyst for hydrogen production and deposition of a spent boron containing metal solid. The application of high pressure hydrogen in presence of a catalyst regenerates the hydrogen storage compound which is transported to a cool zone of the reactor. Borohydride complexes of Al, Ti, and Zr have been shown to be precursors for the chemical vapor deposition of metal borides with the evolution of H_2 as a by-product – the formation of crystalline ceramic-like metal boride product requires much higher temperature and our work will focus on making the reaction reversible. Volatile or liquid hydrogen storage materials are anticipated to have some engineering advantages for scale-up including ease of heat and mass transfer. New materials development will focus on making $LiM(BH_4)_4$ where M = Al, Ti by the reaction of $M(BH_4)_3$ with $LiBH_4$ in a solvent.

MHCoE Project C – Amides/Imides (M-N-H systems)

The initial focus is on methods of preparing the mixture Li_3AlH_6 plus $LiNH_2$ that is a promising material identified by our collaborators. The chemistry for preparation and thermal decomposition of $LiAl(NH_2)_4$ will also be investigated. The decomposition of samples will be briefly investigated at ORNL, and if the characteristics are satisfactory samples will be provided to MHCoE partners.

ORNL will attempt to develop general method for the preparation metal amides in support of MHCoE goals. To this end ORNL will attempt to develop an organic amide/ammonia analog of the traditional sol-gel process used to make metal oxides. Metal dialkylamides will be reacted with ammonia to form metal amide/imide, liberating a dialkylamine as illustrated for magnesium

$$Mg(NR_2) + 2\,NH_3 \rightarrow Mg(NH_2)_2 + HNR_2$$

Surfactants form micelles in liquid ammonia analogous to micelles formed by detergents in aqueous solution. The use of an inverted micelle provides a method of limiting reaction to materials in the ammonia "pocket;" and this provides a method of controlling particle size. Inverted micelles in liquid ammonia are relatively poorly defined, and investigation is needed to determine appropriate surfactants and concentrations.

MHCoE Project D – Alanes

In FY 2007, ORNL will begin working with the alane focus group, concentrating on the chemistry of making the process reversible. The effort at ORNL will be in two general areas: (1) the traditional organometallic chemistry approach in which aluminum is activated with reagents such as AlR_3 where R is an alkyl group. The role of this activating reagent will be investigated. (2) The chemistry of regenerating spent alane in solution will be investigated using salts of AlH_4^- as the catalyst for the uptake of hydrogen.

FY 2006 Publications/Presentations

"Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage," G. M. Brown and J. H. Schneibel, Poster presentation at the DOE 2006 Hydrogen Annual Review, Washington, D.C., May 16-19, 2006.