

Complex Hydrides for Hydrogen Storage

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Objectives

- Identify complex hydrides containing greater than 6 wt% hydrogen
- Obtain or prepare target compounds
- Investigate hydrogen release and reversibility of target compounds
- Maximize kinetics and reversible content of most promising 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 R,D&D Plan:

- B. Weight and Volume
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Select target compounds with greater than 6 wt% hydrogen
- Purchase or synthesize target compounds
- Determine hydrogen release/uptake characteristics of pure compounds
- Determine effects of ball milling on hydrogen release/uptake characteristics of pure compounds
- Determine effects of catalysts on hydrogen release/uptake characteristics

Accomplishments

- Identified alanates and borohydrides with greater than 6 wt% hydrogen
- Obtained or synthesized most promising compounds
- Studied solvent-free synthetic procedures
- Identified lithium alanate as a promising candidate
- Completed in-depth study of hydrogen release characteristics of lithium alanate
- Identified ball milling as the cause of lowered dehydriding temperature
- Studied effects of incorporation of Ti, TiCl₃, TiCl₄, TiH₂, AlCl₃, Ni, Fe, FeCl₃, C, and V on lithium alanate hydrogen release
- Found that Ti and TiH₂ caused minimal decrease in hydrogen content
- Discovered that elemental titanium, ball milled with sodium alanate, facilitates rehydriding

Future Directions

- Complete investigation of exothermic decomposition of lithium alanate
 - Study the reversibility of catalyzed lithium alanate
 - Synthesize solvent-adduct free magnesium alanate
 - Investigate decomposition products and reversibility of borohydrides
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Introduction

Studies involving complex hydrides of aluminum so far reported in the literature have been primarily restricted to sodium aluminum hydride with a smaller amount of work reported involving lithium aluminum hydride. While these studies are important from a fundamental and mechanistic point of view, they do suffer two serious limitations. One limitation is that the reversible hydrogen capacity of sodium aluminum hydride falls short of the hydrogen content required for practical application. A second limitation arises from the very complex nature of the alanates. Progress in understanding the mechanisms of hydrogen uptake and release and catalyst function in these systems is hampered by data interpretation based on questionable chemistry. For example, in one study,¹ it was reported that the ball milling of TiCl_3 with NaAlH_4 resulted in the reduction of titanium by the Na in NaAlH_4 . This conclusion was supported by the comparison of the TiCl_3 - NaAlH_4 system to an industrial process in which TiCl_4 is reduced by hot elemental Na. These two systems are not comparable. In NaAlH_4 , Na is in the Na^+ form and is incapable of reducing anything. The industrial process utilizes elemental sodium, an excellent reducing agent. This form of sodium is capable of functioning as a reducing agent because it has an electron to lose, forming Na^+ in the process. The work described in that report is excellent from a physics, solids, and materials point of view. However, the mechanistic error punctuates the need for multidisciplinary teams, including chemists as well as physicists and materials scientists, to solve the hydrogen storage problem.

While the recent advances in hydride storage by the research groups of Bogdanovic,² Jensen,³ Zaluski,⁴ and Gross⁵ have illustrated the reversibility of select complex hydrides, none have been shown to

contain the required amount of hydrogen. Additionally, some of the contradictions and inaccuracies in the published work illustrate the need for more in-depth investigations from a chemical viewpoint. Because of the low reversible hydrogen content in the compounds that others are studying, this work has purposely targeted complex hydrides that theoretically contain hydrogen at a higher level than does the sodium aluminum hydride.

Approach

The literature was surveyed for known complex hydrides of aluminum and boron that contain greater than 6% hydrogen. Of the compounds revealed, those that were commercially available were purchased. Those with reported literature syntheses were prepared according to those methods. For those without reported syntheses, procedures were developed. Both wet chemical and solvent free synthetic procedures were investigated.

The compounds were subjected to a baseline study to determine the onset temperatures and rates of hydrogen release, and the reversibility of the process in the uncatalyzed form. This part of the work revealed the need for additional study of lithium alanate due to its unusual characteristic of exothermic dehydrogenation and large hydrogen content.

Following the baseline study, the effects of catalysts on the reversibility of the dehydrogenation were studied. Because the catalysts were incorporated using a high-energy ball milling, the effects of ball milling alone were also investigated.

Results

The primary goal of this project was to investigate a series of complex hydrides of aluminum and/or boron, with large hydrogen contents, as

hydrogen storage media. The compounds originally considered contain a minimum of 7.5% hydrogen by mass. While some of these hydrides have been reported to decompose to compounds that still contain one or more hydrogens, the numbers shown below reflect total hydrogen content. A secondary goal was to identify a catalyst for each hydride that facilitates decomposition while enabling rehydrogenation.

The hydrides originally considered were NaAlH_4 with 7.5% H, $\text{Ca}(\text{AlH}_4)_2$ with 7.7% H, $\text{Zr}(\text{BH}_4)_3$ with 8.8% H, $\text{Ti}(\text{AlH}_4)_4$ and $\text{Mg}(\text{AlH}_4)_2$ both with 9.3% H, NaBH_4 and LiAlH_4 both with 10.5% H, $\text{Ca}(\text{BH}_4)_2$ with 11.4% H, $\text{Fe}(\text{BH}_4)_3$ with 11.9% H, $\text{Ti}(\text{BH}_4)_4$ with 12.9% H, $\text{Mg}(\text{BH}_4)_2$ with 14.8% H, $\text{LiAlH}_4(\text{BH}_4)_4$ with 15.2% H, LiBH_4 with 18.2% H, and $\text{Al}(\text{BH}_4)_3$ with 20.0% H.

Because dehydrogenating is typically endothermic, we decided to investigate the observed exothermic dehydrogenation of LiAlH_4 . The thermogram for LiAlH_4 , Figure 1, shows that three exothermic events, with onset temperatures of 139°C, 157°C,

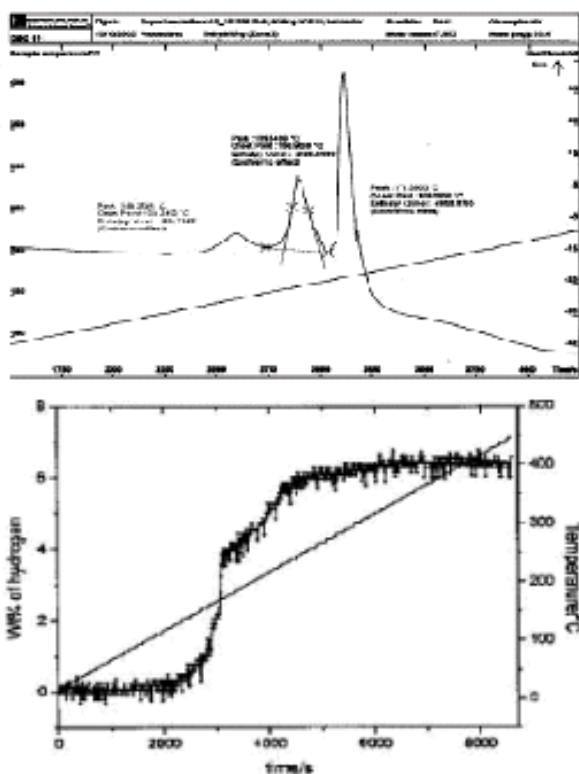


Figure 1. Thermogram (top) and Pressure Plot (bottom) for the Thermal Decomposition of LiAlH_4

and 169°C, respectively, were associated with the decomposition of LiAlH_4 . The pressure data indicate that gas release, most likely hydrogen, began at approximately 110°C but reached a maximum rate at a temperature corresponding to the onset temperature of the first exothermic event in the thermogram. This release continued until approximately 4% of hydrogen was released. Then, the hydrogen release sharply slowed at approximately 170°C, corresponding to the onset temperature of the third exothermic event in the thermogram. This slower hydrogen release continued until approximately 6.3% hydrogen was lost. The first and third exothermic events in the thermogram were thus associated with hydrogen release, and the second event was most likely a phase change that occurs with no gas release.

Catalyst studies were begun with titanium using the mechanical incorporation method suggested by Jensen, et al.³ Ball milling LiAlH_4 with TiCl_4 did decrease the temperature required for dehydrogenation, as was reported by Jensen in his study of NaAlH_4 . As was also reported by Jensen in his work with NaAlH_4 , the hydrogen content was significantly decreased due to the fact that the Ti^{4+} was reduced during the ball milling process, causing loss of a portion of the stored hydrogen. The reducing agent for this process must have been the alanate ion, AlH_4^- , since neither Li^+ nor Na^+ is capable of such a reaction. The resulting NaCl was a difficult-to-remove, non-hydrating contaminant, further decreasing hydrogen capacity.

The pressure plots obtained by dehydrogenating undoped LiAlH_4 , LiAlH_4 milled alone, and LiAlH_4 samples doped with Ti , TiCl_3 , TiCl_4 , and TiH_2 can be seen in Figure 2. Doping with titanium(III) chloride and with titanium(IV) chloride both result in a greatly decreased hydrogen release due to the loss of the first hydrogen release step. Doping with TiH_2 or with elemental titanium causes only a slight decrease in the amount of hydrogen released and does not eliminate the first step of hydrogen release. Thus, it is hoped that incorporation of either of these catalysts will result in allowing lithium alanate to reversibly bind hydrogen while retaining a large hydrogen content.

Ball milling alone results in about the same decrease in the amount of hydrogen released as doping

with either TiH_2 or Ti. Most interesting is the fact that ball milling alone causes the same reduction in the temperature of hydrogen release as does doping.

Figure 3 shows the differential scanning calorimetry (DSC) pressure data for the thermal decomposition of LiAlH_4 samples that were ball milled with AlCl_3 , Ni, Fe, FeCl_3 , carbon black, and with V. Nickel caused a small decrease in the amount of hydrogen released, while vanadium caused a larger decrease. The effect of nickel

appeared to be limited to the first step of hydrogen release, while vanadium appears to have decreased the amount of hydrogen released from both steps of the decomposition. Incorporation of aluminum chloride or elemental iron produced the same effect on the temperature of hydrogen release. However, the iron also appears to have caused a decrease in the amount of hydrogen released in the first step. Iron(III) chloride caused a reduction in the hydrogen release temperature. However, this temperature decrease was accompanied by a significant decrease in the amount of hydrogen released in both decomposition steps.

Conclusions

- Synthesis of a number of alanates and borohydrides investigated
 - Wet chemical methods used for synthesis of magnesium alanate, magnesium borohydride, and calcium borohydride
 - Solvent free methods used for $\text{Mg}(\text{AlH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$, a magnesium hydride/titanium hydride mixture, $\text{Ti}(\text{AlH}_4)_4$ and $\text{Ti}(\text{BH}_4)_4$
 - Synthesis of $\text{Mg}(\text{AlH}_4)_2$ solvent adduct accomplished
 - Wet chemical methods yielded solvent adducts that decomposed upon solvent removal
 - Solvent free synthetic methods identified as having greatest potential
- Lithium alanate is a potentially viable hydrogen storage compound
 - Large hydrogen capacity
 - Decomposition is exothermic
 - Decomposition mechanism varied with material manufacturer
 - Decomposition of ball milled Lancaster sample resembles Aldrich sample
 - Improved kinetics and reduced dehydrogenation temperature result from ball milling
- Effects of catalysts on dehydrogenation of lithium alanate studied
 - Addition of TiCl_3 , TiCl_4 , or FeCl_3 results in large reduction of hydrogen content

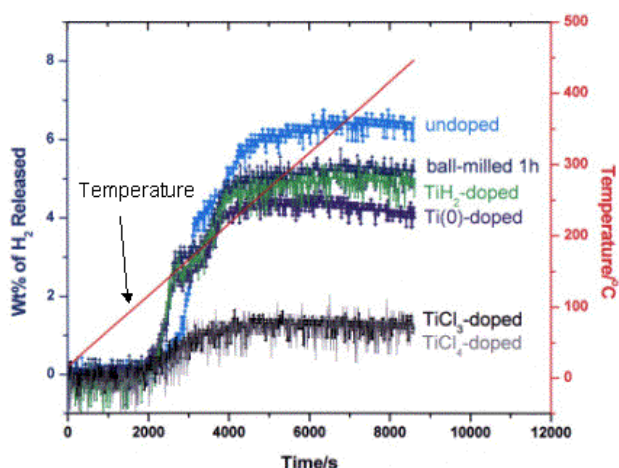


Figure 2. DSC Pressure Data for Dehydrogenating of LiAlH_4 Doped with Ti, LiAlH_4 Doped with TiCl_3 , LiAlH_4 Doped with TiCl_4 , LiAlH_4 Doped with TiH_2 , and LiAlH_4 Ball Milled without Doping

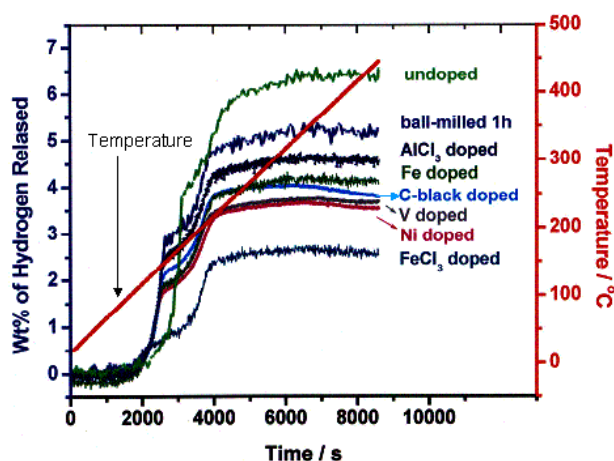


Figure 3. DSC Pressure Data for the Thermal Decomposition of LiAlH_4 Samples That Were Ball Milled with AlCl_3 , Ni, Fe, FeCl_3 , Carbon Black, and with V

- Addition of V results in the same decrease in hydrogen release temperature but with smaller loss in hydrogen capacity
 - Addition of Fe, AlCl₃, Ni, C, Ti, or TiH₂ results in a decrease in the temperature of hydrogen release without a significant loss of H₂ capacity
 - Temperatures similar to those of undoped, ball milled material
 - Mechano-chemical synthetic procedures for complex hydrides studied
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FY 2003 Publications/Presentations

1. Slattery, D.K.; Hampton, M.D., "Complex Hydrides for Hydrogen Storage," presented at the Alanate Working Group meeting at Argonne National Lab, August 15, 2002.
2. Slattery, D.K.; Hampton, M.D.; Lomness, J.K.; Najafi-Mohajeri, N.; Franjic, M., "Hydrogen Storage Using Complex Hydrides," Presented at the 225th National Meeting of ACS, New Orleans, LA, March 25, 2003.
3. Slattery, D.K.; Hampton, M.D., "Complex Hydrides for Hydrogen Storage," Proceedings of the 2003 U.S. DOE Hydrogen and Fuel Cells Annual Program/Lab R&D Review, Berkeley, CA, May 19-22, 2003.