

IV.A.1r Lightweight Metal Hydrides for Hydrogen Storage

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Objectives

The objective of this project is to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. The current focus of the project is on Mg-containing borohydrides and their complexes as well as aluminoborane compounds which have very high capacities and attractive properties. The key is to make them reversible. To accomplish this, we are working on detailed characterization of their decomposition mechanism and their amine complexes as well as new borohydrides.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan:

- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies of the decomposition mechanism of $\text{Mg}(\text{BH}_4)_2$. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Accomplishments

- Explored the synthesis of pure $\text{MgB}_{12}\text{H}_{12}$ in order to study the stability of this very important intermediate phase that is key to the reversibility of $\text{Mg}(\text{BH}_4)_2$. We found that the literature claim of anhydrous $\text{MgB}_{12}\text{H}_{12}$ synthesis was incorrect. We studied the stability H_2O and OH complexes of $\text{MgB}_{12}\text{H}_{12}$ and gained clear understanding of their relative stabilities.
- Synthesized $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ and other compounds during the synthesis of $\text{MgB}_{12}\text{H}_{12}$ and we are studying their properties to explore suitability for hydrogen storage.
- Explored synthesis of analogy compounds $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ and $\text{Mg}(\text{NH}_3)_6\text{B}_{10}\text{H}_{10}$ based on a consideration that the $\text{B}_{10}\text{H}_{10}$ compounds may be less stable than their $\text{B}_{12}\text{H}_{12}$ counterparts – thus potentially more suitable for hydrogen storage.
- Studied a “new” class of hydrides – aluminoborane compounds for hydrogen storage in collaboration with Oak Ridge National Laboratory (ORNL), the Jet Propulsion Laboratory (JPL), and the California Institute of Technology (Caltech). These compounds such as $\text{AlB}_4\text{H}_{11}$ have low desorption temperatures, high wt% hydrogen, low amounts of diborane, and at least partial reversibility at mild conditions (200°C, 90 bar H_2).
- Synthesized $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and provided the material to Metal Hydride Center of Excellence partners for encapsulation into aerogels and other studies.
- Re-synthesized $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$ and have gained much better understanding of its desorption process via high-resolution nuclear magnetic resonance (NMR) studies in collaboration with ORNL, JPL and Caltech.



Introduction

The U.S. Department of Energy (DOE) defines on-board hydrogen storage for mobile vehicles as a “Grand Challenge”. It is one of the biggest hurdles to the implementation of hydrogen-powered vehicles. Metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty. Metal borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, desorption temperature, reversibility and diborane formation during desorption are challenging issues for these materials. This project attempts to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

Approach

- Explore two classes of materials: Mg-containing borohydrides and aluminoborane compounds such as $\text{AlB}_4\text{H}_{11}$ and their amine complexes.
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted pressure-concentration-temperature tests, NMR, infrared (IR), differential scanning calorimetry (DSC), and residual gas analysis.
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes (such understanding is crucial for reversibility of all borohydrides);
- Synthesize new hydrides and complexes in collaboration with ORNL, JPL, Caltech, Sandia National Laboratories, and the National Institute of Standards and Technology (NIST).

Results

Our previous results clearly showed that during decomposition of $\text{Mg}(\text{BH}_4)_2$, an intermediate phase $\text{MgB}_{12}\text{H}_{12}$ appears and this phase is believed to be detrimental to reversibility [1-3]. In order to devise a viable reversibility strategy, it is very important to understand the properties of this phase. Thus, we decided to synthesize the pure compound $\text{MgB}_{12}\text{H}_{12}$ for detailed characterization. A literature reported procedure was followed and the intended product was obtained [4]. However, when NMR was performed on the powders, it was clear that the product still had H_2O attached to it. A careful examination of the published thermogravimetric analysis (TGA) curve clearly showed that the authors made a mistake in computing the weight loss and there should be three H_2O molecules

still attached to the compound. Thus, the claimed anhydrous $\text{MgB}_{12}\text{H}_{12}$ was never really synthesized. Several different ways were attempted to remove the three residual H_2O molecules, but none of them was completely successful. For instance, the powders were heated up to 900°C ; there was still OH signals in the IR spectrum. A study was subsequently performed using both TGA and NMR to monitor the loss of H_2O and H_2 from $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}\cdot 6\text{H}_2\text{O}$ to $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$ to $\text{Mg}(\text{H}_2\text{O})_3\text{B}_{12}\text{H}_{12}$ to $\text{Mg}(\mu\text{-OH})_3\text{B}_{12}\text{H}_x$. A manuscript is in preparation to report the results in detail.

During the process of synthesizing anhydrous $\text{MgB}_{12}\text{H}_{12}$, an attempt was made to use NH_3 to replace the residual H_2O in $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{12}\text{H}_{12}$. The replacement was successful and the corresponding amine complex $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ was obtained. This compound decomposes with an endothermic peak in the DSC curve (Figure 1) and it has very high hydrogen content. We are studying it as a potential hydrogen storage material. An attempt was made to grow a single crystal of $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ in CH_3OH for crystal structure identification. The obtained single crystal was found to be $\text{Mg}(\text{CH}_3\text{OH})_6\text{B}_{12}\text{H}_{12}\cdot 6\text{CH}_3\text{OH}$. Thus CH_3OH was able to replace NH_3 in $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$. Powders of $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ was sent to NIST (Dr. J.H. Her) for crystal structure analysis using both X-ray diffraction (XRD) and neutron diffraction.

In a separate route to anhydrous $\text{MgB}_{12}\text{H}_{12}$, we first synthesized $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$ from $\text{Cs}_2\text{B}_{12}\text{H}_{12}$. Subsequent NH_3 treatment of $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}$ resulted in a pure $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ compound. Its DSC curve also showed an endothermic peak and the desorbed gas was very likely hydrogen – careful tests are in progress. Thus, this compound is also an attractive candidate for hydrogen storage. We were able to grow a single crystal of this compound and have refined its crystal structure as shown in Figure 2. Careful study of its properties is currently underway. We are ball milling $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ with MgH_2 to try to make $\text{MgB}_{12}\text{H}_{12}$. This process is H_2O free

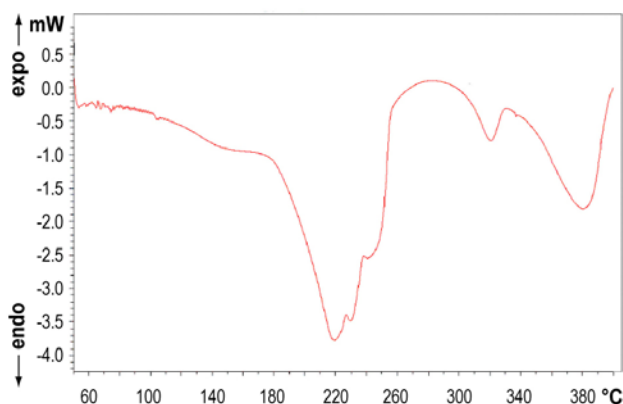


FIGURE 1. DSC Curve of $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$ Showing Endothermic Desorption

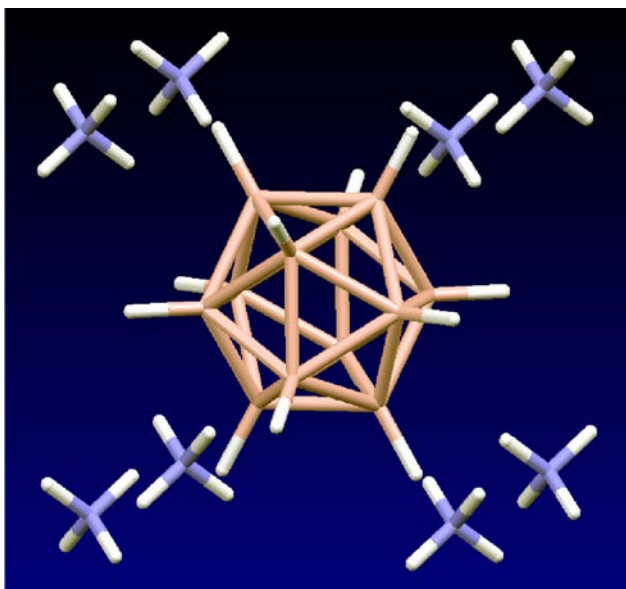


FIGURE 2. Crystal structure of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ based on single crystal XRD showing the $\text{B}_{10}\text{H}_{10}$ cage sits in the middle of a cubic NH_4 lattice.

and OH free, thus we hope to be able to make anhydrous $\text{MgB}_{12}\text{H}_{12}$.

Experience indicates that $\text{MB}_{10}\text{H}_{10}$ compounds are usually less stable than the analogy $\text{MB}_{12}\text{H}_{12}$, thus $\text{MB}_{10}\text{H}_{10}$ compounds may be good candidates for hydrogen storage considering that $\text{MgB}_{12}\text{H}_{12}$ is too stable. Attempts to synthesize anhydrous $\text{MB}_{10}\text{H}_{10}$ faced a similar hurdle as the synthesis of $\text{MgB}_{12}\text{H}_{12}$: difficulty to remove the $\text{H}_2\text{O}/\text{OH}$. In the process, we made $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}\cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}$ compounds. We were able to identify the crystal structure of the first compound. Powders of the second compound were also sent to NIST for structure identification. $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}\cdot 4\text{H}_2\text{O}$ was synthesized in water by ion exchange method by converting $[\text{NEt}_3\text{H}]_2[\text{B}_{10}\text{H}_{10}]$ to the acid form and reacting the acid with MgCO_3 . The product was characterized by DSC, NMR, IR and single crystal X-ray diffraction. Efforts to replace the water molecule from $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}$ with ammonia resulted only in partial ammonia substitution. Also, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}\cdot 1.5\text{H}_2\text{O}$ was synthesized by the reaction of $[\text{H}_3\text{O}]_2[\text{B}_{10}\text{H}_{10}]$ with ammonia gas in water solution. The product was characterized by DSC, TGA, NMR, IR and single crystal XRD. The water containing compound $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}\cdot 1.5\text{H}_2\text{O}$ was heated at 70°C for 2 hours to give $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ as evident from the IR spectrum. The XRD pattern of anhydrous $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ is shown in Figure 3. Heating of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ at 70°C for 2 hours resulted in no change in the $[\text{B}_{10}\text{H}_{10}]^{2-}$ boron structure, but heating at 130°C for 2 hours resulted in conversion of small amount of $[\text{B}_{10}\text{H}_{10}]^{2-}$ to $[\text{B}_{12}\text{H}_{12}]^{2-}$. Heating at 250°C resulted in change of color from white to yellow brown and $[\text{B}_{12}\text{H}_{12}]^{2-}$ formation from ^{11}B NMR.

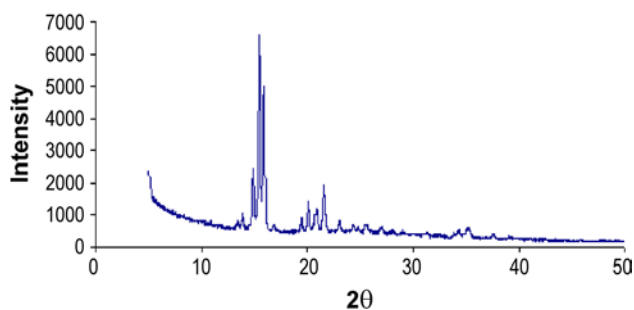


FIGURE 3. XRD Pattern of Anhydrous $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$

More efforts are under way to heat the anhydrous product $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ at different temperatures and characterize the heated residue and gaseous products.

In order to be prepared for a comparative study of the relative stability of $\text{MB}_{12}\text{H}_{12}$ compounds ($\text{M} = \text{Li}, \text{Mg}, \text{Na}, \text{Ca}$), we synthesized $\text{Li}_2\text{B}_{12}\text{H}_{12}$ following a literature route. $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 7\text{H}_2\text{O}$ was first prepared by cation exchange. Anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was obtained by heating the compound at 250°C under vacuum for 12 hours. (We provided gram quantity $\text{Li}_2\text{B}_{12}\text{H}_{12}$ to HRL for nano-framework encapsulation.) We studied the anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$ using DSC, XRD, and NMR. The ammine complex then was synthesized by condensing ammonia onto anhydrous $\text{Li}_2\text{B}_{12}\text{H}_{12}$. The complex was soluble in tetrahydrofuran (THF) as indicated by boron-NMR. Two types of single crystals from the THF solution were analyzed using XRD. The first batch of single crystals were picked out from the THF solution after 24 hours, the second were picked out after one week. The structure derived from the single-crystal XRD shows that the first batch of crystals is $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 7\text{NH}_3$. There are two types of Li cations, one coordinated by three ammonias, the other four ammonias. The second batch of crystals was identified as $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 6\text{THF}$. Thus, the $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 7\text{NH}_3$ was only stable in the THF solution for a limited amount of time. After one week, it transformed into $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 6\text{THF}$. Ammonia was replaced by THF completely. In this compound, both Li cations are identical, each coordinated by three THFs. The boron cage was connected to Li cations. TGA and NMR study shows that $\text{Li}_2\text{B}_{12}\text{H}_{12}\cdot 7\text{NH}_3$ decomposes by giving off NH_3 instead of H_2 , thus it is not a viable candidate for hydrogen storage.

$\text{Mg}(\text{B}_3\text{H}_8)_2$ was synthesized as a precursor for chemical vapor deposition of MgB_2 [5]. The authors reported a melting and desorption temperature of 120°C , thus it can potentially be an interesting candidate for hydrogen storage material if it is reversible. The synthesis of this compound requires the use of NaB_3H_8 as a starting material. NaB_3H_8 will also be a useful compound for a comparison study of the stability of MB_3H_8 compounds ($\text{M} = \text{Li}, \text{Mg}, \text{Na}, \text{and Ca}$). In this

regards, we have developed new method for better synthesis of NaB_3H_8 .

In collaboration with JPL and Caltech, we employed high resolution NMR to compare the desorption products of $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2 + n\text{LiBH}_4$ ($n = 1, 2$). Disordered boron-nitrogen is identified as the initial desorption product of $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$. $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion is the primary intermediate species during desorption of LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2 + n\text{LiBH}_4$ ($n = 1, 2$). A manuscript is in the process for submission for publication.

Attempts have been made to synthesize the complex metal hydride $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ using modified procedures reported by Ashby and Goel [6]. Earlier preliminary work at General Electric on $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ synthesis didn't separate it from the by-product salt. However, the desorption temperature was significantly lower than that of $\text{Mg}(\text{BH}_4)_2$. We have tested four different methods trying to make the pure $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ compound. $\text{Mg}(\text{BH}_4)(\text{AlH}_4)\cdot\text{THF}$ was found to decompose slowly at room temperature to very nice colorless crystals of $\text{Mg}(\text{AlH}_4)_2\cdot 4\text{THF}$ and $\text{Mg}(\text{BH}_4)_2\cdot 3\text{THF}$ powders. Characterization of the other products is still in progress.

Our work on aluminoborane compounds such as $\text{AlB}_4\text{H}_{11}$ was on hold waiting for a new batch of materials from ORNL. The new batch has now arrived at OSU and more exploration of its reversibility conditions is currently underway.

We built a specialized glovebox around a Mettler Toledo high-pressure DSC unit to allow inert transfer of sample from the large glovebox to the DSC. This DSC unit will be the workhorse equipment for us since heat absorption and desorption (thermodynamics) is the key indicator of potential reversibility.

Conclusions and Future Directions

The OSU hydrogen storage materials research team has synthesized and tested several new compounds for hydrogen storage. This was made possible by the availability of four vacuum wet-chemistry synthesis lines in Prof. Sheldon Shore's laboratory, a group of dedicated researchers, the unique boron chemistry expertise in the group, and a dedicated hydride testing facility established in Dr. J.-C. Zhao's laboratory. Close collaboration with ORNL, JPL, Caltech, and NIST made possible effective synthesis and characterization of these compounds.

The materials we are synthesizing and studying including $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$, $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{CH}_3\text{OH})_6\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{H}_2\text{O})_5(\text{CH}_3\text{OH})_3\text{B}_{12}\text{H}_{12}$, $\text{Li}_2\text{B}_{12}\text{H}_{12}(\text{NH}_3)_7$, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, $\text{Na}(\text{NH}_3)_x\text{B}_{12}\text{H}_{12}$, $\text{Mg}(\text{H}_2\text{O})_6\text{B}_{10}\text{H}_{10}$,

$\text{Mg}(\text{NH}_3)_x\text{B}_{10}\text{H}_{10}$, $\text{AlB}_4\text{H}_{11}$, and $\text{Mg}(\text{B}_3\text{H}_8)_2$. Several of these compounds are new compounds that were not reported before. A few of these compounds showed endothermic desorption at low temperatures, thus they are good candidates for further study as potential hydrogen storage materials. The following compounds are very worthy of further studies: $\text{Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$, $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, $\text{Mg}(\text{NH}_3)_x\text{B}_{10}\text{H}_{10}$, $\text{AlB}_4\text{H}_{11}$, and $\text{Mg}(\text{B}_3\text{H}_8)_2$.

We will perform more detailed study of these compounds for hydrogen storage in collaboration with ORNL, JPL/Caltech, Sandia, and NIST. We will focus on more promising candidates as the properties of these compounds are tested.

Special Recognitions & Awards/Patents Issued

1. J.-C. Zhao was named by the National Academy of Engineering (NAE) as one of eight-two brightest young engineers to attend the NAE 2008 Frontier of Engineering Symposium: <http://www8.nationalacademies.org/onpinews/newsitem.aspx?RecordID=06172008>

FY 2009 Publications/Presentations

- MH2008 International Conference on Hydrogen-Metal Systems, Reykjavik, Iceland, June 24–28, 2008, "Mg(BH₄)₂ and Its Complexes for Hydrogen Storage", Grigori Soloveichik, Sergei Kniajansky, Job Rijssenbeek, Yan Gao, Robert C. Bowman, Jr. and Son-Jong Hwang, J.-C. Zhao.
- IEA Task 22 International Experts Meeting, Villa Mondragone, Italy, October 7–10, 2008. "Hydride Research at OSU", J.-C. Zhao.
- Lehigh University, October 14th, 2008. "Hydrogen Storage Materials" (Invited talk), J.-C. Zhao.
- International Energy Agency (IEA) Task 22 Hydrogen Storage Experts' Meeting, The Shilla Jeju Hotel, Jeju Island, Korea, April 19-23, 2009. "Lightweight Borohydrides for Hydrogen Storage", J.-C. Zhao*, S. Shore, X. Chen, Z. Huang, H. Kumar, T. Yisgedu, B. Billet, and J. Hoy.
- North American Solid State Chemistry Conference, Columbus, OH, June 17–20, 2009. "Borohydrides for Hydrogen Storage", X. Chen*, Z. Huang, H. Kumar, T. Yisgedu, B. Billet, J. Hoy, S.G. Shore, J.-C. Zhao (Poster).
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