

IV.A.2 Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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developed a system of for the full reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ to MgB_2 that has shown a record, >12 wt% reversible hydrogen capacity but requires further development to meet kinetic performance targets within the target temperature.

FY 2012 Accomplishments

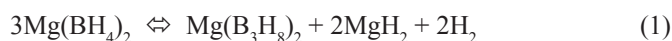
During the past year we have provided the first example of the reversible, solid-state dehydrogenation of a borohydride at temperatures below 250°C (200°C dehydrogenation, 100°C, 50-atm re-hydrogenation).



Introduction

The development of high capacity, hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the utilization of hydrogen as an onboard energy carrier. Towards this end we have examined mixed metal borohydride complexes as hydrogen storage materials. Our initial focus was on anionic transition metal complexes. Our structural characterizations of these complexes have shown that they are best viewed as Group I and II salts anionic transition metal borohydride complexes. Through studies utilizing X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and vibrational spectroscopy, we have clearly established the coordinative interaction between the BH_4^- anions and the metal centers. The anionic character of these borohydrides has been found to result in an increased stability and a reduced volatility when compared to neutral transition metal borohydride complexes. Our efforts are currently focused on determining whether the thermodynamic parameters of these complexes will allow them to undergo reversible dehydrogenation.

In the course of these investigations we have found that that ball-milled mixtures of MgB_2 and catalytic additives undergo full hydrogenation to $\text{Mg}(\text{BH}_4)_2$ at high pressures. In consideration of the >14 wt% hydrogen that is potentially cyclable with this system, it has become the focus of our efforts in the area of borohydride complexes. More recently, we have studied the dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ under mild conditions and observed the, clean, reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ to $\text{Mg}(\text{B}_3\text{H}_8)_2$ as seen in equation 1 (dehydrogenation, 200°C; re-hydrogenation, 250°C under 120 atm of H_2). Our findings have provided



Fiscal Year (FY) 2012 Objectives

The objective of this project is to develop a new class of reversible materials that have the potential to meet the DOE kinetic and system gravimetric storage capacity targets. During the past year, our investigations have focused on the study of novel, high hydrogen capacity, borohydrides that can be reversibly dehydrogenated at low temperatures.

Technical Barriers

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

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (J) Thermal management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

During the past year, work on this project was currently exclusively devoted borohydride materials that have demonstrated available hydrogen capacities of >10 wt% hydrogen. In our previous work on this project we have

the first example of the **reversible**, solid-state dehydrogenation of a borohydride occurring at temperatures below 300°C.

Our studies of the mixed metal borohydride complexes showed that they evolve high weight percentages of hydrogen at low temperatures (100-150°C). Our finding of the reversible dehydrogenation of magnesium borohydride at moderate temperatures suggested that reversibility of our novel anionic transition metal borohydrides which previously thought to be “irreversible” should be investigated under the same conditions found for the reversible cycling of $\text{Mg}(\text{BH}_4)_2$ to $\text{Mg}(\text{B}_3\text{H}_8)_2$.

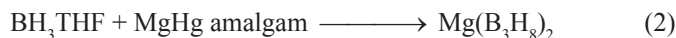
Approach

Having demonstrated the reversible elimination of >12 wt% hydrogen from $\text{Mg}(\text{BH}_4)_2$, we sought to develop methods for hydrogen cycling in this system under less forcing conditions. In order to accomplish this, we required a more detailed understanding of the dehydrogenation reaction pathway. Thus we have monitored both the dehydrogenation and re-hydrogenation reactions by XRD and magic angle spinning boron-11 (MAS ^{11}B) NMR spectroscopy and conducted quantitative thermal volumetric pressure-composition-temperature measurements. In order to further explore the low temperature reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$, we planned to prepare $\text{Mg}(\text{B}_3\text{H}_8)_2$ through an alternative method and examine the hydrogenation of mixtures of the triborane and two equivalents of MgH_2 under the conditions we have previously utilized in our re-hydrogenation studies. Furthermore, we have hypothesized that stability of the corresponding metal hydride formed in the dehydrogenation of Group I borohydrides may explain in part the trend in barriers to their reversibility. In order to probe these possibilities we planned to explore hydrogenation $\text{Mg}(\text{B}_3\text{H}_8)_2$ in mixtures containing MgH_2 , LiH, and NaH.

Results

Synthesis and Evaluation of Novel Borohydrides

As discussed above, our previous studies have indicated that the dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ at 200°C results in selective dehydrogenation to $1/3 \text{Mg}(\text{B}_3\text{H}_8)_2 + 2/3 \text{MgH}_2$ and that this process can be reversed at 250°C under 120 atm of H_2 . In order to verify this finding, we sought to prepare $\text{Mg}(\text{B}_3\text{H}_8)_2$ through an alternative method, and examine the hydrogenation of mixtures of the triborane and MgH_2 under the conditions we have previously utilized in our re-hydrogenation studies. Finding the syntheses reported in the literature for $\text{Mg}(\text{B}_3\text{H}_8)_2$ to be irreproducible, we have developed a reliable, high yield synthesis for $\text{Mg}(\text{B}_3\text{H}_8)_2$. In accordance with equation 2, our method entails the reaction of the tetrahydrofuran (THF) adduct of borane, 25°C



$\text{BH}_3\cdot\text{THF}$ with magnesium-mercury amalgam in THF solution at room temperature which results in the immediate precipitation of pure $\text{Mg}(\text{B}_3\text{H}_8)_2$ as a white crystalline powder in >95% yield.

Our synthesis of pure $\text{Mg}(\text{B}_3\text{H}_8)_2$, allow us to explore the hydrogenation the triborane with stoichiometric quantities of different metal hydrides. The metal hydrides (LiH, NaH, and MgH_2) were chosen for their varying degrees of thermodynamic stabilities. Mixtures of the triborane and hydride were hydrogenated under 7 MPa H_2 at 200°C for 2 days and the resulting products were analyzed by solid-state ^{11}B NMR spectroscopy. Surprisingly, hydrogenation of the mixtures of $\text{Mg}(\text{B}_3\text{H}_8)_2$ and either LiH and NaH resulted in the exclusive formation of $[\text{BH}_4]^-$. Initial attempts at the hydrogenation of a 2:1 mixture of MgH_2 and $\text{Mg}(\text{B}_3\text{H}_8)_2$ were found to instead give rise to $\text{MgB}_{12}\text{H}_{12}$ and other boranes. However, we found if mixtures of MgH_2 and $\text{Mg}(\text{B}_3\text{H}_8)_2$ are ball-milled prior to reaction, that the predominant product is $\text{Mg}(\text{BH}_4)_2$ and that $\text{MgB}_{12}\text{H}_{12}$ is obtained in only minor amounts. The production of the $\text{MgB}_{12}\text{H}_{12}$ side product can be completely eliminated by increasing the $\text{MgH}_2:\text{Mg}(\text{B}_3\text{H}_8)_2$ ratio to 4:1. The speed at which the triborane species hydrogenates to borohydride was investigated and found to occur within 2 hours at 100°C.

We also studied the hydrogenation of mixtures of $-\text{Mg}(\text{B}_3\text{H}_8)_2$ and either LiH, NaH, or MgH_2 by differential scanning calorimetry (DSC) in collaboration with Dr. S. Orimo at the Institute for Materials Research at Tohoku University. A hydrogen pressure of 5 MPa was applied as the temperature was ramped to 200°C at a rate of 5°C/s. Regardless of metal hydride species, all experiments with $\text{Mg}(\text{B}_3\text{H}_8)_2$ exhibited a quick endothermic step beginning at about 60°C (Figure 1). ^{11}B NMR analysis of the material immediately after this step confirmed that

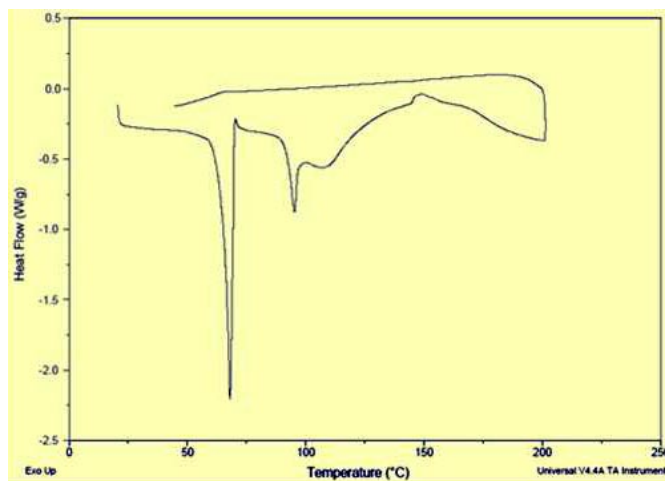


FIGURE 1. DSC scan of $\text{Mg}(\text{B}_3\text{H}_8)_2 + 2 \text{MgH}_2$ heated under 5 MPa H_2

the $[\text{B}_3\text{H}_8]^-$ anions were still intact. Next, a large broad exothermic peak was consistently observed with a maximum at about 130°C. ^{11}B NMR analysis after this step showed that the boron in the sample had converted predominantly to $[\text{BH}_4]^-$. Hydrogenation of $\text{Mg}(\text{B}_3\text{H}_8)_2$ (Figure 2) without any metal hydride present displayed the same endothermic peak at around 60°C, suggesting that it may be attributed to the melting of the triborane. For comparison, NaB_3H_8 was hydrogenated under the same conditions in mixtures containing either NaH or MgH_2 . NaB_3H_8 was found to melt at a lower temperature and two overlapping exothermic steps were observed at higher temperature. The detection of $\text{Na}_2\text{B}_{12}\text{H}_{12}^-$ along with NaBH_4^- in the MAS ^{11}B NMR analysis of the NaB_3H_8 hydrogenation reaction products implies that while $\text{Mg}(\text{B}_3\text{H}_8)_2$ + metal hydride readily forms $\text{Mg}(\text{BH}_4)_2$ in a single step after melting, the hydrogenation of NaB_3H_8 is somewhat more complex, resulting in the formation of more than one boron species.

In addition, to releasing high weight percentages of hydrogen at low temperatures (100-150°C), our studies have indicated that the alkali metal salts of anionic manganese and zirconium borohydride complexes undergo elimination of hydrogen with little or no tandem production of diborane. However, there have been conflicting reports regarding the levels diborane that are released during the thermal dehydrogenation of the scandium borohydride complexes, $\text{MSc}(\text{BH}_4)_4$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$). In order to resolve this controversy, we established a collaboration with the group of Prof. Zuetzel at EMPA to quantify the amount of diborane produced during the thermal decomposition of $\text{MSc}(\text{BH}_4)_4$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$). The dehydrogenation of samples of the scandium borohydrides that were synthesized at the University of Hawaii was studied by specialty infrared equipment at EMPA that was designed for the detection and quantification of diborane emission from borohydrides. This method has proven much more reliable and reproducible

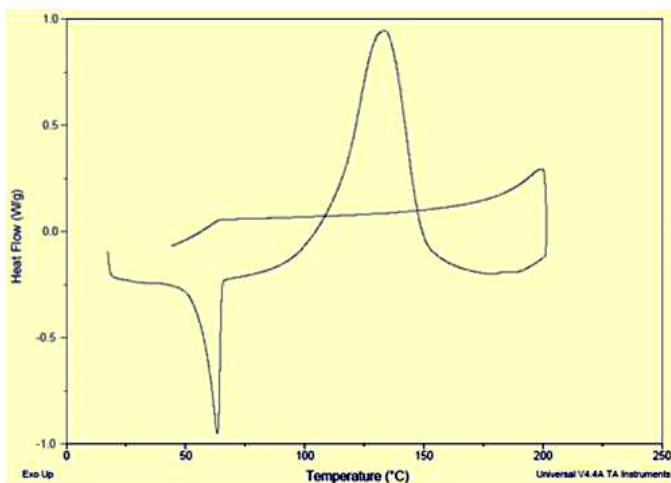
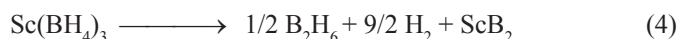
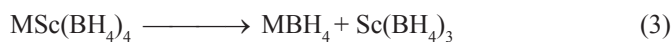


FIGURE 2. DSC scan of $\text{Mg}(\text{B}_3\text{H}_8)_2$ heated under 5 MPa H_2

than determinations that have been made using flow meter/mass spectrometer equipment. These studies have shown that about 0.5 equivalents of diborane are released during the dehydrogenation of $\text{MSc}(\text{BH}_4)_4$ ~150°C. Our previous studies have shown that a second hydrogen release occurs at higher temperatures that match the characteristic hydrogen release temperatures of the corresponding simple alkali metal borohydride, MBH_4 . These results indicate thermal decomposition of the scandium borohydrides proceeds according to equations 3 and 4.



Conclusions

We have established that $\text{Mg}(\text{BH}_4)_2$ is selectively dehydrogenated to $\text{Mg}(\text{B}_3\text{H}_8)_2$ 200°C while cleanly releasing 2.9 wt% H_2 . This reaction has now been demonstrated to be reversible at 100°C under 50 atm of H_2 thus provides the first example of direct hydrogen cycling of a borohydride under mild conditions. The rapid re-hydrogenation kinetics are, at least in part, due to the fact that $\text{Mg}(\text{B}_3\text{H}_8)_2$ is in the liquid state above 60°C. This finding points to the possibility of finding mild, proton exchange membrane fuel relevant conditions for the reversible dehydrogenation of borohydrides that avoid the thermodynamic sinks such as $[\text{B}_{12}\text{H}_{12}]^{2-}$.

We have also found that the thermal decomposition of $\text{MSc}(\text{BH}_4)_4$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) at 150°C gives rise to MBH_4 and $\text{Sc}(\text{BH}_4)_3$. The resulting neutral, $\text{Sc}(\text{BH}_4)_3$ is unstable and rapidly decomposes to produce diborane. Thus the $\text{MSc}(\text{BH}_4)_4$ family of borohydrides will not undergo reversible dehydrogenation and can be excluded as potential application as reversible hydrogen storage materials.

Future Directions

We plan to explore the adjustment of conditions to maximize trade off between cycling capacity and temperature/pressures required for reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ under moderate conditions.

FY 2012 Publications/Presentations

Publications

1. "Reversible Dehydrogenation of Magnesium Borohydride to Magnesium Triborane in the Solid State Under Moderate Conditions", Marina Chong, Ahbi Kamkamkar, Tom Autrey, Shin-ichi Orimo, Satish Jalihatgi, and Craig M. Jensen; (invited contribution for themed issue on Hydrogen) *Chem. Commun.* **2011**, 47, 1330.
2. "Homogeneous Dehydrogenation of Liquid Organic Hydrogen Carriers Catalyzed by an Iridium PCP Pincer Complexes",

Zhouhui Wang, Jack Belli, and Craig Jensen, *Faraday Discuss* **2011**, *151*, 297.

3. “High-Yield Direct Synthesis of LiAlH_4 from LiH and Al in the Presence of TiCl_3 and Me_2O ”, Xiangfeng Liu, Henrietta W. Langmi, Shane D. Beattie, Felix F. Azenwi and G. Sean McGrady, and Craig M. Jensen, *J. Am. Chem. Soc.* **2011**, *133*, 15593.

Presentations

1. ”Development of Processes for the Reversible Dehydrogenation of High Capacity Hydrogen Carriers”; Craig Jensen; Peking University; Beijing, China.; October 20 2011.

2. ”Development of Processes for the Reversible Dehydrogenation of High Capacity Hydrogen Carriers”; [Craig Jensen](#), Godwin Severa, Marina Chong, Zhouhui Wang, Ewa Rönnebro, Tom Autrey, and Ahbi Kamkamkar; Symposium on Complex Hydrides for Hydrogen Storage, Low Carbon Earth Summit 2011.; Dalian China, October 23–24, 2011.

3. “Development of Processes for the Reversible Dehydrogenation of High Capacity Hydrogen Carriers”; Craig Jensen; Nankai University; Tainjin, China; October 26 2011.

4. ”Development of Processes for the Reversible Dehydrogenation of High Capacity Hydrogen Carriers”; Craig Jensen; Yanshan University; Qinhuangdao, China; October 27 2011.

5. “Development of Processes for the Reversible Dehydrogenation of High Capacity Hydrogen Carriers”; Craig Jensen; Institute of Metals Research; Chinese Academy of Science; Shenyang, China, October 31, 2011.