

IV.A.5e Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Introduction

The development of high capacity, hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the realization of a hydrogen economy. Recently, lithium and other Group I and II borohydrides have been explored as hydrogen storage materials. However, the dehydrogenation of these compounds is plagued by severe kinetic limitations, competing side reactions, and/or irreversibility, that preclude the practical utilization of these compounds as components of a hydrogen carrier for vehicular applications. Many transition metal borohydride complexes have highly attractive gravimetric hydrogen densities (7-11 wt% hydrogen). However, most well known transition metal borohydride complexes such as $Zr(BH_4)_4$ and $Zn(BH_4)_2$ are inadequate hydrogen absorbants, as they volatilize under the conditions required for dehydrogenation. Additionally, the elimination of diborane often competes with dehydrogenation and typically highly stable, transition metal borides are obtained upon dehydrogenation that cannot be directly hydrogenated under practical conditions.

In addition, kinetics limit the practical potential of many borohydrides, amides, and “destabilized metal

hydrides.” An “assault on kinetics” is required but there is no clear guide as to the approach to be taken. Determination of the mechanism by which dopants enhance the dehydrogenation and re-hydrogenation of complex hydrides could provide guidance for this effort. Anelastic spectroscopy has established that Ti promotes the formation of highly mobile, hydrogen containing point defects in $NaAlH_4$. However, chemical nature of the point defects could not be determined.

Approach

In an attempt to circumvent the problems with neutral borohydrides, we have synthesized Group I salts of anionic transition metal borohydride complexes. These materials maintain a high hydrogen capacity (9–13 wt% hydrogen) while the anionic character offers reduced volatility and increased stability. In addition, different thermodynamic parameters might allow reversibility and eliminate production of diborane during dehydrogenation.

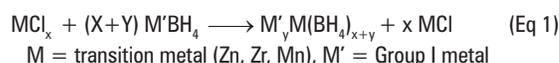
Additionally, muon spin resonance is a proven method for determination of the immediate chemical environment of point defects. A collaborative effort was established with Prof. Kadono of KEK-IMSS, Japan to apply this technique for the elucidation of the chemical nature of the point defects that are responsible for the remarkable hydrogen cyclic kinetics observed for Ti-doped $NaAlH_4$.

Results

Anionic transition metal borohydrides

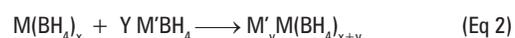
We have synthesized anionic borohydride complexes of zinc, manganese, and zirconium by ball milling the transition metal chlorides with Group I borohydrides, as seen in Equation 1:

Ball milling 1 h



We have also synthesized anionic borohydride complexes of the same three elements by ball milling of neutral transition metal borohydrides with Group I borohydrides as seen in Equation 2. The above reactions were monitored by infrared spectroscopy (Figure 1).

Ball milling 1 h/ 77 K



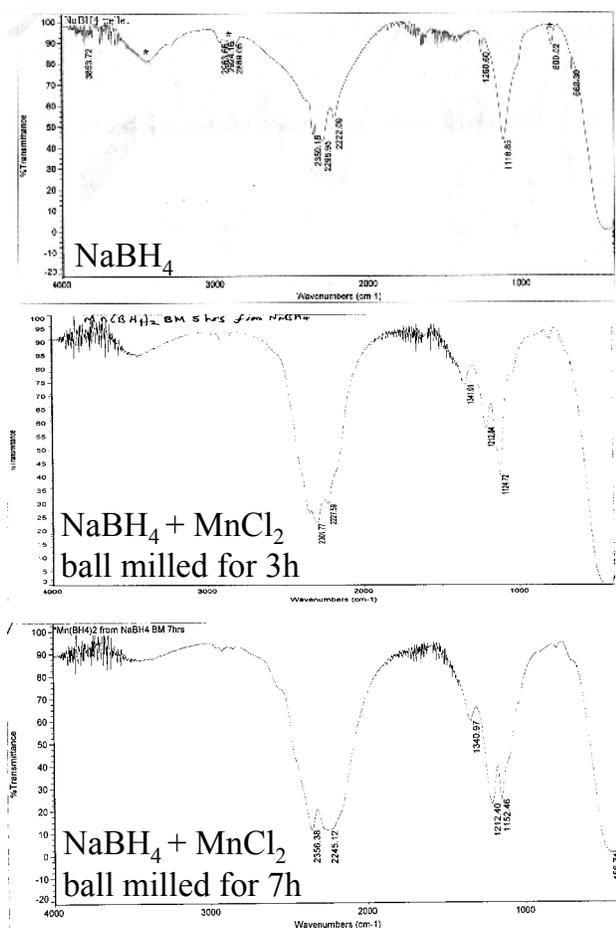


FIGURE 1. Borohydride Synthesis Monitored by IR (New peaks appear at 1,213 and 1,341 cm^{-1} together with shoulders at 2,150 and 2,400 cm^{-1} , which increase with ball milling time.)

Transition metal borohydrides are generally highly amorphous and cannot be observed by powder X-ray diffraction. However, characterization of the products was possible by magic angle spinning ^{11}B -nuclear magnetic resonance (NMR) spectroscopy (Figure 2).

Thermal desorption mass spectroscopy studies were conducted on these materials to examine the evolved gases. It was found that tandem hydrogen/diborane evolution occurs with anionic zinc borohydride complexes. On the other hand, hydrogen evolved from $\text{M}^{\text{Mn}}\text{Mn}(\text{BH}_4)_3$ at low temperatures with little or no diborane production. For example, gases eliminated from $\text{NaMn}(\text{BH}_4)_3$ exhibited a 50:1 $\text{H}_2/\text{B}_2\text{H}_6$ molar ratio. Furthermore, no diborane was observed with hydrogen evolved from anionic zirconium borohydrides. These studies also showed that the $\text{M}_2\text{Zr}(\text{BH}_4)_6$ compounds are much less volatile than $\text{Zr}(\text{BH}_4)_4$. Anionic Zr complexes eliminated 2-3 wt% hydrogen at 40-100°C without undergoing sublimation. It was also found that the nature of the cation influences the desorption temperature of complexes like $\text{M}_2\text{Zn}(\text{BH}_4)_4$. For

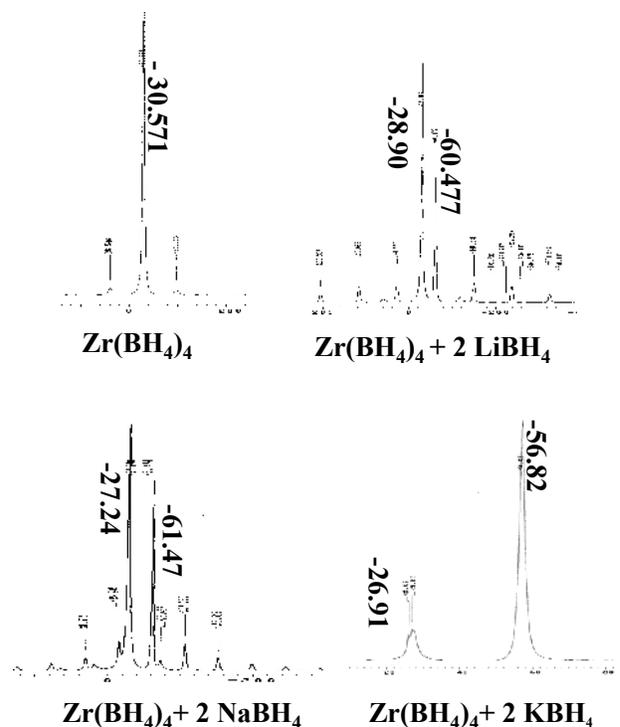


FIGURE 2. Characterization of Borohydride Products by ^{11}B NMR (New peaks appear corresponding to the formation of new borohydride materials. Chemical shifts in ppm of Group I borohydrides: LiBH_4 , -60.5; NaBH_4 , -61.5; KBH_4 , -56.81).

example, the exchange of Li with Na in the complex $\text{M}_2\text{Zn}(\text{BH}_4)_4$ lowers the desorption temperature from 140°C to 110°C.

The dehydrogenation properties of the synthesized complexes were studied. The complexes all eliminated 2-7 weight percent hydrogen at around 100°C. In addition, complexes like $\text{LiMn}(\text{BH}_4)_3$ undergo rapid dehydrogenation kinetics at 100°C.

Characterization of Point Defects in Ti-Doped NaAlH_4

Our collaborative study with the KEK group was successful, as a fraction of positive muons implanted in NaAlH_4 form a muonium state that selectively substitutes for hydrogen in point defects. Since muons have a nuclear spin (hyperfine parameter of ~420 MHz), information about the immediate chemical environment of the hydrogen in the point defects can be determined from the hyperfine interaction of the muonium state with surrounding spin active nuclei.

Positron decay (muon polarization) is asymmetric because of overlap of the Gaussian damping with a sinusoidal oscillation (Figure 3). NaAlH_4 is a non-magnetic, insulator, so the origin of the oscillation is the

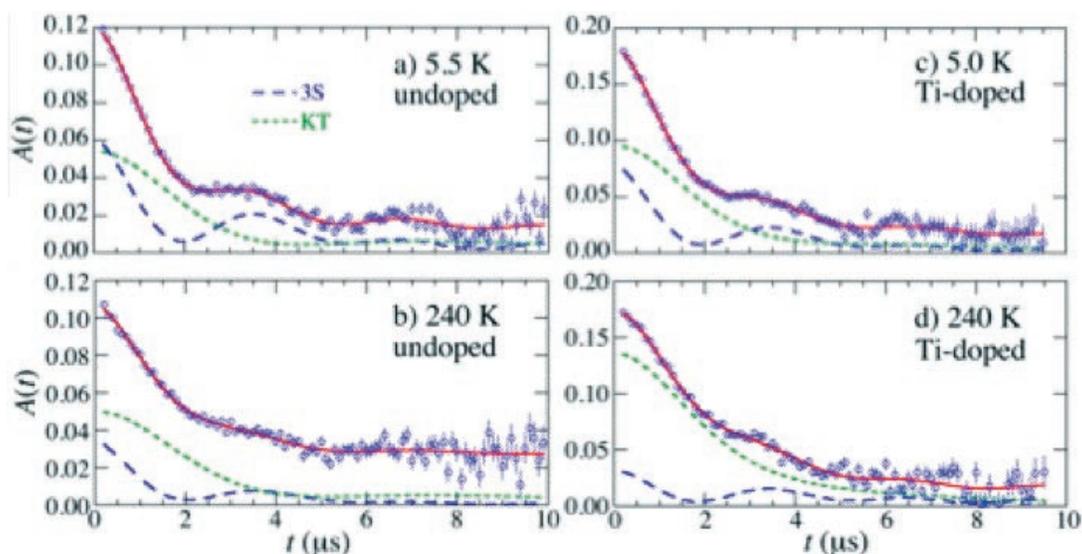


FIGURE 3. Time-dependent μ -e decay asymmetry (muon polarization) observed in pure (a, b) and Ti-doped (c, d) NaAlH_4 , respectively at about 5 K and 240 K under zero external field (color online). The full polarization corresponds to -0.18 for a), b) (PSI data), and -0.26 for c), d) (TRIUMF data). Solid curves are those obtained by fitting analysis.

formation of local atomic cluster consisting of μ^+ and small number of atoms.

χ^2 -minimization fits of temperature dependent muon spin resonance data indicates the point defect is $\text{AlH}_4^- - \mu^+ - \text{AlH}_4^-$. Titanium reduces the activation energy required to form the point defect (Figure 4). The composition of the point defect suggests that proton transfer catalyzes the intake/release of hydrogen in NaAlH_4 . This effect might be common to other complex hydrides.

Conclusions and Future Directions

In summary, anionic transition metal borohydride complexes can be conveniently prepared from the ball milling of alkali metal borohydrides with transition metal chlorides or transition metal borohydrides. Also, anionic transition metal borohydride complexes, unlike most neutral transition metal borohydride complexes, are non-volatile and highly stable at ambient temperatures. These complexes have been found to undergo rapid elimination of 2-7 weight percent hydrogen at relevant ($\sim 100^\circ\text{C}$) temperatures. In addition, anionic manganese and zirconium borohydride complexes have been found to undergo elimination of hydrogen at low temperatures with little or no elimination of diborane.

Muon polarization studies have helped to identify the point defect composition in titanium doped sodium alanate in the detection of an $\text{AlH}_4^- - \mu^+ - \text{AlH}_4^-$ complex. Titanium reduces the activation energy required to form the muon-bialanate state. These results suggest that proton transfer catalyzes the intake/release of hydrogen in NaAlH_4 . While these studies will not continue in our efforts, this effect might be common to other complex hydrides.

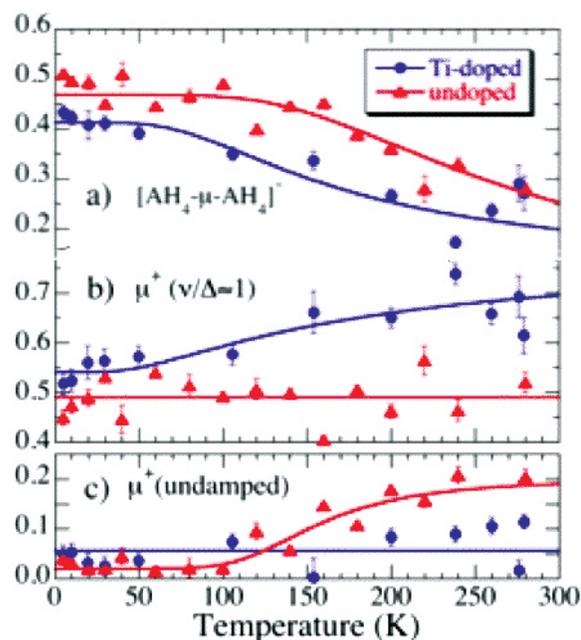


FIGURE 4. Temperature dependence of the fractional yield for a) muon bialanate state (f), b) muons at the O-site (g), and c) undamped state (h), where $f + g + h \equiv 1$ (color online). Solid curves represent the best fits to a simple activation model.

Our future work will focus on the following points:

- Development of additional neutral and anionic transition metal borohydrides.
- Reversibility of transition metal borohydride materials. (Re-hydrogenation has not been achieved for any of member of this class of materials under pressures of up to 100 atm of H_2 .)

- Determination of ΔH_{dehyd} through deferential thermal analysis.
- Attempting rehydrogenation at high pressures in collaboration with Dr. Ronnebro at Sandia National Laboratories.
- Study of alane as a hydrogen storage material.

Special Recognitions & Awards/Patents Issued

1. Co-chair, International Symposium on Metal Hydride Systems, October 2006.
2. Co-Chair, Gordon research Conference on Hydrogen Metal Systems, July 2007.

FY 2007 Publications/Presentations

Publications

1. S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen, "Intrinsic and Mechanically Modified Thermal Stabilities of α -, β - and γ -Aluminum Trihydride, AlH_3 ," *Appl. Phys. A*, 2006, 117, 27.
2. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Martin Sulic, and Craig M. Jensen, "Fast H-vacancy Dynamics During Alanate Decomposition by Anelastic Spectroscopy: Model for Ti-induced Defect Transport," *Phys. Rev. B*, 2006, 110, 9105.
3. H.W. Brinks, C. Brown, C.M. Jensen, J. Graetz, J.J. Reilly, B.C. Hauback, "Crystal Structure of γ - AlD_3 ," *J. Alloys and Compd.*, 2007, in press.
4. H.W. Brinks, W. Langley, C.M. Jensen, J. Graetz, J.J. Reilly, B.C. Hauback, "Synthesis and Crystal structure of β - AlD_3 ," *J. Alloys and Compd.*, 2007, in press.
5. R.S. Kumar, A.I. Cornelius, O. Tshauner, M.P. Sulic, C.M. Jensen "Pressure Induced Structural Phase Transition in NaAlH_4 ," *J. Phys. Chem. B*, 2007, in press.
6. T. Kato, S. Orimo, Y. Nakamori, T. Komuro, C. Brown, C. M. Jensen, "Thermal Properties of AlH_3 -etherate and its De-solvation Reaction into AlH_3 ," *J. Alloys and Compd.*, 2007, in press.
7. "L. Cullane, D. Wilson, I. Robertson, C. Jensen," "Electron Microscopy Studies of NaAlH_4 Doped with TiF_3 : Hydrogen Cycling Effects," *J. Alloys and Compd.*, 2007, in press.
8. R. Cantelli, O. Palumbo, A. Paolone, C.M. Jensen, M.T. Kuba, R. Ayabe, "Dynamics of Defects in Alanates," *J. Alloys and Compd.*, 2007, in press.
9. S.-J. Hwang, R.C. Bowman, J. Graetz, J.J. Reilly, W. Langley, and C.M. Jensen, "NMR Studies of the Aluminum Hydride Phases and their Stabilities," *J. Alloys and Compd.*, 2007, in press.
10. G.J. Lewis, J.W.A. Sachtler, J.J. Low, D.A. Lesh, S.A. Faheem, P.M. Dosek, L.M. Knight, C.M. Jensen, J. Yung, A. Sudik, D.J. Sigel, D. Halliday, A. Drews, R. Carter, C. Wolverton, V. Ozolins, S. Zhang, "High Throughput Screening of the Ternary LiNH_3 - MgH_2 - LiBH_4 Phase Diagram," *J. Alloys and Compd.*, 2007, in press.
11. R. Kadono, K. Shimomura, K.H. Satoh, S. Takashita, A. Koda, K. Nishiyama, E. Akiba, R.M. Ayabe, M. Kuba, C.M. Jensen, "The Role of Hydrogen Bonding in the Dehydrogenation Kinetics of Sodium Alanate," submitted to *Phys. Rev. Lett.*

Presentations

1. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, California; August 20, 2006.
2. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," Joint NEDO Los Alamos National Laboratory Workshop on Hydrogen Storage, Santa Fe, New Mexico, August 26, 2006.
3. "Development of Transition Metal Borohydride Complexes as Hydrogen Storage Materials," Materials Research Society Fall Meeting, Symposium on Hydrogen Storage Materials, Boston, Massachusetts; November 28, 2006.
4. "Hydrogenation of Aluminum in a Supercritical Fluid System," Focus Session of Hydrogen Storage Materials, Annual meeting of the American Physical Society, Denver, Colorado, March 6, 2007.
5. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," Hawaii Natural Energy Institute, University of Hawaii, April 10, 2007.
6. "Development of Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials," Symposium on Hydrogen Storage Materials, Studies of Matter at Extreme Conditions, 2007 meeting; Miami Beach, Florida, April 17, 2007.
7. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," ANL User Week 2007, Argonne National Laboratory, Illinois; May 08, 2007.
8. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," Griffith University, Brisbane, Australia, June 19, 2007.
9. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," Australian Nuclear Science and Technology Organization, Sydney, Australia, June 20, 2007.
10. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials," University of Sydney, Australia, June 21, 2007.