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:

$$
\text{MCl}_x + (X+Y) \text{M'}\text{BH}_4 \rightarrow \text{M'}\text{M(BH}_4\text{)}_{x+y} + x \text{MCl} \quad (\text{Eq 1})
$$

M = transition metal (Zn, Zr, Mn), M' = Group I metal

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).

$$
\text{M(BH}_4\text{)}_x + Y \text{M'}\text{BH}_4 \rightarrow \text{M'}\text{M(BH}_4\text{)}_{x+y} \quad (\text{Eq 2})
$$
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 M'Mn(BH$_4$)$_3$ at low temperatures with little or no diborane production. For example, gases eliminated from NaMn(BH$_4$)$_3$ exhibited a 50:1 H$_2$/B$_2$H$_6$ molar ratio. Furthermore, no diborane was observed with hydrogen evolved from anionic zirconium borohydrides. These studies also showed that the M$_2$Zr(BH$_4$)$_4$ compounds are much less volatile than Zr(BH$_4$)$_4$. Anionic Zr complexes eliminated 2-7 weight percent hydrogen at around 100°C. In addition, complexes like LiMn(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 example, the exchange of Li with Na in the complex M$_2$Zn(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 LiMn(BH$_4$)$_3$ undergo rapid dehydrogenation kinetics at 100°C.
formation of local atomic cluster consisting of $^3$u and small number of atoms.

$\chi^2$-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 ($\sim 100^\circ$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.

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 $\Delta H_{\text{dehyd}}$ 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


FY 2007 Publications/Presentations

Publications


Presentations