SYNTHESIS AND CHARACTERIZATION OF NOVEL ANIONIC TRANSITION METAL BOROHYDRIDES

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ABSTRACT

Zinc borohydride (Zn(BH₄)₂) has been the focus of much recent research in the field of hydrogen storage. This material has a low decomposition temperature (around 85°C) and a high theoretical hydrogen capacity (8.5% H₂). These studies include mechanochemical synthesis of zinc borohydride and its derivatives at room temperature without solvent following the reaction:

\[ \text{ZnX}_2 + n\text{MBH}_4 \rightarrow M_{n-2}\text{Zn(BH}_4)_n + 2\text{MX} \]

where \( M = \text{Li, Na, or K; } X = \text{Cl; and } n = 1, 2, 3, \text{ or } 4. \)

Product mixtures were characterized by IR, XRD, and CPMAS \(^{11}\text{B}\) NMR spectroscopy. Analysis of material properties was completed by thermal decomposition mass spectrometry (TD-MS) and isothermal dehydrogenation studies.

These fundamental studies confirmed the synthesis of novel borohydride materials. It was found that the milling of zinc chloride with alkali borohydrides reduces the dehydrogenation temperature. However, upon dehydrogenation, both hydrogen and diborane are liberated.
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CHAPTER ONE

INTRODUCTION
Hydrogen Economy

Environmentally safe and cost-effective fuels are of great interest around the world. Hydrogen can provide a clean and economical fuel source for on-board applications in automobiles. It is the most abundant element in the universe and the only byproduct from the combustion of hydrogen is water (H₂O). Ideal materials for on-board applications would be lightweight, solid-state hydrogen storage materials that could reversibly release and absorb hydrogen. These materials should meet the 6.5 weight percent minimum hydrogen capacity required by the U.S. Department of Energy. In addition, the ideal temperature for hydrogen desorption would be around 100 °C.

Researchers have examined many different complex hydride materials for these applications. The advantage for using complex metal hydrides is their high gravimetric hydrogen storage capacity, while their disadvantage is their high dehydrogenation temperatures (Table 1). Alkali borohydrides²,³,⁴ are appealing considering their high hydrogen capacities ranging from 7.4-18.4 weight percent hydrogen. However, these materials have impractical dehydrogenation temperatures of 380 °C for lithium borohydride, 400 °C for sodium borohydride, and 500 °C for potassium borohydride. The same is essentially true for sodium alanate (NaAlH₄), however, the inclusion of titanium additives have been shown to enhance its hydrogen storage properties.⁵

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¹ www.doe.gov
³ Nakamori, Y. and Orimo, S. JALCOM. 2004, 370, 271.
It is interesting to note that, similar to lithium alanate (LiAlH₄), zinc borohydride (Zn(BH₄)₂) has a high hydrogen capacity (8.5%) while maintaining a low decomposition temperature (85 °C) (Table 1).

In addition, the alkali derivatives of zinc borohydride also have high theoretical hydrogen capacities (Table 2).

<table>
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<th>Material</th>
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<tr>
<td>Zn(BH₄)₂</td>
<td>8.50%</td>
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<tr>
<td>Li₂Zn(BH₄)₃</td>
<td>10.30%</td>
</tr>
<tr>
<td>Li₂Zn(BH₄)₄</td>
<td>11.60%</td>
</tr>
<tr>
<td>Na₂Zn(BH₄)₃</td>
<td>9.10%</td>
</tr>
<tr>
<td>Na₂Zn(BH₄)₄</td>
<td>9.40%</td>
</tr>
<tr>
<td>K₂Zn(BH₄)₃</td>
<td>8.10%</td>
</tr>
<tr>
<td>K₂Zn₂(BH₄)₆</td>
<td>7.90%</td>
</tr>
<tr>
<td>K₂Zn₃(BH₄)₆</td>
<td>8.20%</td>
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These transition metal borohydride materials have been studied very little in the context of hydrogen storage. It is possible that these complex borohydrides are the novel approach needed to develop useful hydrogen storage materials.

Transition Metal Borohydrides

There is an increasing curiosity about the nature of transition metal borohydride complexes. The tetrahydroborate anion, BH₄⁻, has a tendency to form unusual covalent
complexes with transition metals. The complexes have been proposed to take the form of bidentate and tridentate coordination through hydrogen bridging atoms (Figure 1).

![Figure 1. Bidentate and tridentate coordination of borohydride anion ligands to transition metal center. Borrowed from Marks, T.J. and Kolb, J.R. Chem. Rev. 1977, 77(2), 263.](image)

While borohydrides have traditionally been used in organic chemistry as synthetic reducing agents, there is more interest in organometallic and inorganic chemistry due to the unusual nature of bonding that takes place and the unique interaction between the metal center and the small, electron rich borohydride ligands. Some of these complexes are thought to be useful as catalysts in hydrogenation and polymerization processes.

Other possible applications for these materials include procedures involving depositing boride layers on surfaces by thermal decomposition of vapor or by electrolysis, the synthesis of new compounds, and isotope separation processes.

The following study begins with an examination of first row late transition metal borohydrides. This includes the borohydride complexes of iron, cobalt, nickel, copper, and zinc. Marks and Kolb completed a review of these and other transition metals. Ferrous tetrahydroborate, Fe(BH$_4$)$_2$, is a colorless solid which decomposes above -10 °C yielding pyrophoric products. Cobalt tetrahydroborate, Co(BH$_4$)$_2$, which has also been studied by Hinzman and Ganem, is reported to be unstable. The result is decomposition.

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to cobalt metal or cobalt boride (Co₂B) and hydrogen when allowed to warm from its -80 °C synthesis temperature. The details of the preparation and properties of nickel borohydride, Ni(BH₄)₂, are not easy to come by. Solid state reactions of nickel chloride and sodium tetrahydroborate have been shown to decompose to nickel boride, Ni₂B, with nickel borohydride as an intermediate. Other research has proposed that nickel(II) is reduced by the borohydride anion to Raney nickel (a mixture of metal and metal hydride). Copper borohydride, Cu(BH₄)₂, has been reported to decompose to copper metal, diborane, and hydrogen at 0 °C. Overall, the borohydrides of iron, cobalt, nickel, and copper are not useful as hydrogen storage materials due to their degree of instability.

Zinc Borohydride Synthesis and Characterization

Unlike the transition metal borohydrides discussed above, zinc borohydride, Zn(BH₄)₂, has unique chemical properties that set it apart from the rest. The complex has been synthesized in two ways:

\[ \text{ZnCl}_2 + 2\text{MBH}_4 \rightarrow \text{Zn(BH}_4\text{)}_2 + 2\text{MCl}, \text{ M = Li, Na, K} \]

\[ \text{B}_2\text{H}_6 + \text{ZnH}_2 \rightarrow \text{Zn(BH}_4\text{)}_2 \]

The products of these reactions are white solids that decompose around 85 °C and are water sensitive.

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13 Wiberg, E. Angew. Chem. 1953, 65, 16.
In further studies, Noeth, Wiberg, and Winter\textsuperscript{20} have reported the synthesis of anionic zinc tetrahydroborates (in ether or tetrahydrofuran) by altering the stoichiometric ratio of alkali borohydride starting material to zinc chloride as shown the following reactions:

\[ \text{ZnCl}_2 + 3\text{LiBH}_4 \rightarrow \text{LiZn(BH}_4\text{)}_3 + 2\text{LiCl} \]
\[ \text{ZnCl}_2 + 4\text{LiBH}_4 \rightarrow \text{Li}_2\text{Zn(BH}_4\text{)}_4 + 2\text{LiCl} \]

Similar reactions were completed with sodium borohydride instead of lithium borohydride. Structures of zinc accommodating three borohydride groups via bidentate coordination have been proposed.\textsuperscript{21,22} However, literature does not demonstrate the accommodation of four borohydride groups. It may be possible that the reaction with a 4:1 LiBH\textsubscript{4}:ZnCl\textsubscript{2} ratio may not give Li\textsubscript{2}Zn(BH\textsubscript{4})\textsubscript{4}, but rather, will result in a mixture of LiZn(BH\textsubscript{4})\textsubscript{3} with other hydride phases.

A unique reaction takes place between zinc chloride and potassium borohydride\textsuperscript{23,24}:

\[ 7\text{ZnCl}_2 + 8\text{KBH}_4 \rightarrow \text{K}_2\text{Zn}_3\text{(BH}_4\text{)}_8 + 2\text{K}_3\text{Zn}_2\text{Cl}_7 \]

This (K\textsubscript{2}Zn\textsubscript{3}(BH\textsubscript{4})\textsubscript{8}) is the only alkali zinc borohydride complex that has been reported as a solid crystalline substance, while all others exist as solutions or complex-solvent adducts. However, these crystals react vigorously with atmospheric oxygen and moisture.\textsuperscript{25}

\textsuperscript{23} Hagenmuller, P. and Rault, M. \textit{Compt. Rend.}, 1959, 248, 2758.
\textsuperscript{25} Mikheeva, V.I.; Mal'tseva, N.N.; Alekseeva, L.S. \textit{Russian J. Inorg. Chem.}, 1968, 13(5), 682.
It is important to note that the above mentioned reactions were all completed in tetrahydrofuran or diethyl ether. These reactions result in solvated products (except the complex $K_2Zn_3(BH_4)_6$). Isolation of the nonsolvated product from solution is difficult because it is often accompanied by the decomposition of the hydride compound or adduct formation. Mikheeva et al. reported that when zinc borohydride was formed in ether, the solvent could not be removed and attempts to remove it resulted in effervescing and decomposition. Further attempts to crystallize the zinc borohydride were completed with dioxane and resulted in adduct formation.

Some recent studies have reported synthesis by solid state methods, mainly mechanochemical activation, and will be discussed later. Mechanical activation causes local changes in pressure and temperature at sites of collisions of solid mixtures and milling ball bearings. These “active states” then result in chemical reactions because of the build up of energy due to point defects or the displacement of atoms from equilibrium. The advantage of mechanical milling is that it would produce a non-solvated borohydride. However, this facile approach causes the problem of a product mixture composed of both the desired product and an alkali chloride byproduct.

Infrared analysis has been a primary method in characterizing various zinc borohydride materials. Solid state synthesis of zinc borohydride reported by

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Mal'tseva et al.\textsuperscript{35,36} showed that completeness of the reaction could be monitored by the infrared spectra. This method is most useful because it provides information about the metal-ligand coordination geometry and bonding. The borohydride anion in alkali metal tetrahydroborates has a characteristic band at 2290 cm\textsuperscript{-1}. In the spectrum for zinc borohydride this band disappears and the appearance of bands corresponding to the vibrations of bridging (\(~2100\) cm\textsuperscript{-1}) and terminal (\(~2450\) cm\textsuperscript{-1}) B-H bonds are observed. The presence of both bridging and terminal bands provides evidence that the borohydride groups are coordinated to the zinc metal center (Appendix A). In addition, the appearance of a band at \(~1410\) cm\textsuperscript{-1} indicates a Zn-H stretching mode that also provides evidence of coordination to the metal center.

Similar bands have been reported for a mechanically activated mixture of sodium borohydride and zinc chloride to form NaZn(BH\textsubscript{4})\textsubscript{3} (B-H bridging at 2060 cm\textsuperscript{-1} and B-H terminal at 2440 cm\textsuperscript{-1}).\textsuperscript{37} This means that the presence of these bands is an indication of the formation of the alkali derivatives of zinc borohydride as well. The B-H bridging band undergoes a greater shift (from 2100 cm\textsuperscript{-1} to 2060 cm\textsuperscript{-1}) because the bridging bonds will have a more intense interaction with the presence of additional borohydride groups when compared to the terminal bonds (which only shift from 2450 cm\textsuperscript{-1} to 2440 cm\textsuperscript{-1}).

Additional studies by Mal’tseva et al.\textsuperscript{38} included the synthesis of various borohydrides, including $K_2Zn_3(BH_4)_8$. The reactions were again monitored by IR and bands were observed in the 2000-2500 cm\textsuperscript{-1} region which is characteristic of covalent tetrahydroborates. The samples were stored in a cryostat cooled with liquid nitrogen. When allowed to warm to room temperature, the samples decomposed. The IR spectra showed the disappearance of bands at around 2100 and 2500 cm\textsuperscript{-1} and only the band around 2300 cm\textsuperscript{-1} remaining. This 2300 cm\textsuperscript{-1} band corresponds to the initial alkali tetrahydroborate. The authors proposed that the complex anionic zinc borohydride decomposes to the alkali borohydride starting material and zinc borohydride (which then undergoes further decomposition) following the reaction:

$$M_n[Zn(BH_4)_{2+n}] \rightarrow MBH_4 + Zn(BH_4)_2$$

In other literature the complex $K_2Zn_3(BH_4)_8$ has been expressed as $2KBH_4\cdot3Zn(BH_4)_2$.\textsuperscript{39}

Powder x-ray diffraction (XRD) is also a versatile, non-destructive technique that reveals detailed information about the chemical composition of the synthesized materials. A crystal lattice is a regular three-dimensional distribution of atoms in space. These are arranged to form a series of parallel planes separated from one another by a distance ($d$), which varies according to the nature of the material. Planes exist in different orientations with specific $d$-spacings. When an X-ray beam is projected onto a material at a given angle, diffraction may occur. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the

\textsuperscript{38} Mal’tseva, N.N.; Kedrova, N.S.; Klinkova, V.V.; Chumarevskii, N.A. Russian J. Inorg. Chem., 1975, 20(3) 339.

sample. Where a mixture of different phases is present, the resulting pattern is formed by the addition of the individual patterns.

For the material $K_2Zn_3(BH_4)_8$, both Mal'tseva$^{40}$ and Mikheeva$^{41}$ reported XRD patterns that confirmed the formation of the complex from the starting materials zinc chloride and potassium borohydride. In addition, Jeon and Cho$^{42}$ monitored the decomposition of $Zn(BH_4)_2(+NaCl)$ by XRD and observed the formation of free Zn metal.

Another useful method of characterization of borohydrides is $^{11}B$ NMR. The $^{11}B$ nucleus has a spin of 3/2 and has a low quadrupole moment making it more sensitive than the $^{10}B$ nucleus.$^{43}$ Coupling to boron is observed only in small, symmetric molecules, such as NaBH$_4$. The only reported $^{11}B$ NMR data has been done in solution with solvated products.$^{44,45}$ These reports examined $Zn(BH_4)_2$, $LiZn(BH_4)_3$, $Li_2Zn(BH_4)_4$, $NaZn(BH_4)_3$, and $NaBH_4$. Chemical shifts ranged from +35 to +47 ppm. No prior studies have been reported using solid-state $^{11}B$ NMR to study zinc borohydride and its alkali derivatives.

**Zinc Borohydride Hydrogen Storage Properties**

As mentioned in the initial analysis of late first-row transition metal borohydrides, zinc borohydride and its derivatives appear to have the material properties (high
hydrogen capacities and low dehydrogenation temperatures) required to make a useful hydrogen storage material.

While the reversibility of these various zinc borohydride materials have not been reported, the reversible storage of lithium borohydride (LiBH₄) is possible with the addition of magnesium hydride (MgH₂). This is because the enthalpy of the reaction is reduced by the destabilizing effects of the magnesium hydride. Perhaps it is possible to have similar effects with transition metal borohydrides.

In addition, the synthesis of zinc borohydride includes a transition from the ionic bonding in lithium borohydride to the covalent bonding of zinc borohydride. This change in the nature of bonding results in a reduced dehydrogenation temperature (LiBH₄ dehydrogenation temperature is 380 °C, while Zn(BH₄)₂ dehydrogenation temperature is 85 °C). This is because less energy is needed to break the B-H bonds in zinc borohydride when compared to the alkali borohydride starting material and, therefore, releases hydrogen at lower temperatures. For this reason, it can be inferred that zinc borohydride derivatives would also more easily release hydrogen. The reaction of alkali borohydride and zinc chloride at different ratios would result in hydrogen storage materials with lower dehydrogenation temperatures.

Synthesis by traditional wet-chemistry methods, as mentioned earlier, resulted in solutions of zinc borohydrides from which pure crystals could not be isolated. Rather, an adduct of the borohydride with large volumes of solvent is formed. These crystals have a reduced hydrogen capacity and are not useful as hydrogen storage materials. Thus, the mechanical activation of the starting materials seems the most favorable method of

synthesis. Furthermore, milling of materials results in nanoscale particles. The high
surface energy alters thermodynamic properties while the increased surface area enhances
kinetic properties of dehydrogenation.\(^48\)

Zinc borohydride has a low decomposition temperature (\(-85^\circ\text{C}\)). Some
decomposition pathways have been proposed as follows\(^49\):

\[
\text{Zn}(\text{BH}_4)_2 \rightarrow \text{Zn} + 2B + 4H_2
\]

\[
\text{Zn}(\text{BH}_4)_2 \rightarrow \text{Zn} + H_2 + B_2H_6
\]

There are serious safety concerns about the desorption of diborane (the second
proposed decomposition pathway shown above), as it is an environmentally harmful and
toxic gas. This issue has been studied by Jeon and Cho\(^50\) who observed the desorption of
12.1\% of gaseous material from a mixture of Zn(BH\(_4\))\(_2\)(+NaCl). If only hydrogen was
being released the expected loss would be 3.8\% when considering the presence of 2 mol
of NaCl (which is present as a byproduct of milling ZnCl\(_2\) and NaBH\(_4\)) rather than the
8.5\% hydrogen from pure Zn(BH\(_4\))\(_2\). However, if one considers the decomposition
pathway to hydrogen and diborane, the expected loss is 14.0\%, which is more
comparable to the observed result (12.1\%). It is important to note that these experiments
were done at a heating rate of 10 \(^\circ\text{C/minute}.\) A slower heating rate (perhaps 1-2
\(^\circ\text{C/minute}) might liberate only hydrogen rather than a mixture of hydrogen and diborane.
The products of the first proposed decomposition reaction (which include zinc metal,
boron, and hydrogen gas) have an enthalpy of formation equal to zero. These products
are more thermodynamically stable when compared to the reaction that gives diborane

2004.


because the enthalpy of formation of diborane is +41.00 kJ/mol.\textsuperscript{51} Perhaps a slower heating rate would target the more thermodynamically stable products and release only hydrogen.

Additional studies by Volkov et. al.\textsuperscript{52} included the examination of diborane liberation from mechanically activated mixtures of zinc chloride, ZnCl\textsubscript{2}, and alkali borohydrides, MBH\textsubscript{4} (where M = Li, Na, or K), when milled for 3.3 hours at 90 °C. Results showed that when using LiBH\textsubscript{4}, 73.8% diborane was released; NaBH\textsubscript{4}, 82.5% diborane; and KBH\textsubscript{4}, 50% diborane. However, these same reactions at room temperature resulted in Zn(BH\textsubscript{4})\textsubscript{2} and the salt byproduct, not diborane.

When the reaction of zinc chloride and lithium borohydride was studied by Differential Thermal Analysis (DTA), gas liberation was observed at 50-60 °C, then a second stage at 140 °C, and finally a third time at 280 °C. It was found the diborane yield depends on the stoichiometric ratio (n) of alkali borohydride to zinc chloride starting material. Diborane yield was 46.2% when n = 1.2; 16.2% when n = 1.9; and 5.4% when n = 2.7. The reaction of sodium borohydride and zinc chloride resulted with emission of hydrogen gas at 215 °C and no diborane evolution. Zinc chloride and potassium borohydride mixtures emitted gas at 200 °C. Diborane yield was 31.0% when n = 1.1 and 0% when n = 3.2. Overall, diborane yield decreased when the stoichiometric ratio of alkali borohydride to zinc chloride increased.

\textsuperscript{51} http://webbook.nist.gov/chemistry/
Myakishev et al.\textsuperscript{53} studied the dependence of diborane yield on temperature when a mixture of zinc chloride and alkali metal borohydride was mechanically activated. It was found that the mixture of zinc chloride and lithium borohydride gave 0% diborane at 25 °C, but released 73.8% at 90 °C. Sodium borohydride with zinc chloride also gave 0% diborane at 25 °C, however 80.8% diborane was released at 90 °C. While the mixture of zinc chloride with potassium borohydride also gave off 0% diborane at 25 °C, it interestingly only released 25% diborane at 90 °C.

It is obvious that there are serious concerns surrounding the release of diborane from these materials. For that reason, these issues are examined in these studies.

Overview

The following studies include fundamental research on the nature of zinc borohydride and its alkali derivatives. The materials (Table 3) were synthesized via solid-state mechanochemical methods at room temperature following the reaction:

\[ \text{ZnCl}_2 + n\text{MBH}_4 \rightarrow M_{n-2}\text{Zn(BH}_4)_n + 2\text{MX} \]

\[ M = \text{Li, Na, or K}; n = 1, 2, 3, \text{ or 4} \]

The product mixtures can be altered by changing the stoichiometric ratio of the alkali borohydride to the zinc halide salt. The only previously reported product mixture produced via mechanochemical methods is Zn(BH\textsubscript{4})\textsubscript{2}(+ MCl)\textsuperscript{54,55}. However, other studies\textsuperscript{56,57} have examined the milling of different molar ratios of alkali borohydride to

zinc chloride (the actual reaction products were not proposed). These included reactions where the ratio of LiBH₄:ZnCl₂ was 1.1, 2.0, 2.9; NaBH₄:ZnCl₂ was 0.9, 2.0, 2.6, 3.0; and KBH₄:ZnCl₂ was 1.1, 2.0, 2.9.

Milling was followed by the analysis of the infrared spectrum and X-ray diffraction of the materials. Compounds were further characterized by ¹¹B NMR spectroscopy. In addition, the thermal decomposition of the zinc compounds were examined by thermal desorption mass spectroscopy and an assessment of the hydrogen storage properties of these materials was conducted.

<table>
<thead>
<tr>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂ + 2LiBH₄ → Zn(BH₄)₂ + 2LiCl</td>
</tr>
<tr>
<td>ZnCl₂ + 3LiBH₄ → Li₂Zn(BH₄)₁ + 2LiCl</td>
</tr>
<tr>
<td>ZnCl₂ + 4LiBH₄ → Li₂Zn(BH₄)₁ + 2LiCl</td>
</tr>
<tr>
<td>ZnCl₂ + 3NaBH₄ → Na₂Zn(BH₄)₁ + 2NaCl</td>
</tr>
<tr>
<td>ZnCl₂ + 4NaBH₄ → Na₂Zn(BH₄)₁ + 2NaCl</td>
</tr>
<tr>
<td>ZnCl₂ + 3KBH₄ → K₂Zn(BH₄)₁ + 2KCl</td>
</tr>
<tr>
<td>ZnCl₂ + 4KBH₄ → K₂Zn(BH₄)₁ + 2KCl</td>
</tr>
<tr>
<td>7ZnCl₂ + 8KBH₄ → K₂Zn₃(BH₄)₁ + 2K₂Zn₃Cl₇</td>
</tr>
</tbody>
</table>

Table 3. Summary of reactions.

CHAPTER TWO

SYNTHESIS AND CHARACTERIZATION OF NOVEL ZINC BOROHYDRIDE MATERIALS
While the proposed reactions (Table 3) have been examined previously (Chapter 1), the only product mixture that have been successfully produced by ball milling is Zn(BH$_4$)$_2$(+ MCl)$_8$. The focus of this section is to complete a fundamental examination of the optimization of the synthesis of these novel zinc borohydride materials and the comprehensive characterization of the product mixtures. For the remainder of the discussion all reactions will be referred to by their expected product mixtures.

**Experimental**

Due to the availability and location of instruments, two separate reaction conditions were used to complete the synthesis of the materials studied in this research. The first set of reaction conditions (Reaction Conditions #1) were monitored by the infrared spectrum (IR) and were then analyzed by boron nuclear magnetic resonance ($^{11}$B NMR spectroscopy) and by the isothermal kinetics of dehydrogenation. The second set of reaction conditions (Reaction Conditions #2) were monitored by powder X-ray diffraction (XRD) and were then analyzed by thermal desorption mass spectrometry (TD-MS).

Reaction Conditions #1 are different from Reaction Conditions #2 mainly in that the milling bowl used in Conditions #1 had a volume of 12 cc as opposed to the milling bowl in Conditions #2 that had a volume of 25 cc. The differences in milling bowl size required the milling time to be changed in order to obtain the same products. The smaller milling bowl required longer milling times while the larger milling bowl required shorter times.

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milling times. In addition, the milling bowls under Conditions #1 were only charged with a total of 1.0 grams of solid material while the milling bowls under Conditions #2 were charged with a total of 1.5 grams of solid material.

**Reaction Conditions #1:**

Lithium borohydride (LiBH₄, 95%), sodium borohydride (NaBH₄, 99%), potassium borohydride (KBH₄, 98%) from Sigma-Aldrich were used as received. Zinc chloride (ZnCl₂, 99.99%) packed in an ampule under argon from Alfa Aesar was used as received. All materials were stored and handled in a nitrogen glove box.

All ball milling was performed by a Fritsch Pulverisette planetary ball mill at room temperature. Samples were stored at room temperature in a nitrogen glove box. All analysis and characterization was completed within 48 hours of synthesis as samples do decompose at room temperature under nitrogen after longer periods of time.

Infrared spectra were determined with a Nicolet Nexus 470 FT-IR with EZ Omnic programming in the range of 400-4000 cm⁻¹. Pellets were made in dry potassium bromide and placed in a nitrogen chamber for use in the instrument.

Solid-state $^{11}$B NMR experiments were performed on a Varian Unity Inova spectrometer operating at a $^1$H resonance frequency of 399.992 MHz using a 3.2 mm CPMAS probe (Varian Chemagnetics, Ft. Collins, CO). For these experiments, samples were packed into a 3.2 mm rotor. The sample spinning rate was 8 kHz (+/- 1 kHz). Chemical shifts
were externally referenced to 1% H$_3$BO$_4$ ($\delta$ ($^{11}$B) = 0.0 ppm). All spectra were recorded using direct polarization (DP). The $^{11}$B frequency was 128.332 MHz and the spectra were recorded using a 2.0 mS pulse (approximately a 30° tip angle) using a spectral width of 350 kHz, acquisition time of 10 mS, and a recycle delay of 10 S. $^1$H broad band decoupling was used during acquisition. Spectra were processed using a 50 Hz line broadening function and zero filled to a final data size of 8 k.

Dehydrogenation curves were determined with a calibrated Sievert’s apparatus from LESC Co., Japan, with a high-precision pressure transducer and a silicon oil bath. Samples were dehydrogenated at 100 °C (except where noted) from vacuum and rehydrogenated at 100 °C at ~10 MPa.

**Synthesis of Zinc Borohydride and Derivatives:** A 1.0 g mixture of alkali borohydride and zinc chloride precursors in different ratios (Table 4) was charged with seven tungsten-carbide balls in a 12 cc tungsten-carbide milling bowl and fitted with a lid and Teflon O-ring inside the glove box. Mixtures were milled at room temperature for 5 hours (reversing milling direction every hour) at 350 rpm.

<table>
<thead>
<tr>
<th>Alkali Borohydride Precursor (MBH$_4$)</th>
<th>Molar Ratio MBH$_4$ : ZnCl$_2$</th>
<th>Target Zinc Borohydride Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH$_4$</td>
<td>2.0 : 1</td>
<td>Zn(BH$_4$)$_2$</td>
</tr>
<tr>
<td></td>
<td>2.9 : 1</td>
<td>LiZn(BH$_4$)$_3$</td>
</tr>
<tr>
<td></td>
<td>4.0 : 1</td>
<td>Li$_2$Zn(BH$_4$)$_4$</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>2.9 : 1</td>
<td>NaZn(BH$_4$)$_3$</td>
</tr>
<tr>
<td></td>
<td>4.0 : 1</td>
<td>Na$_2$Zn(BH$_4$)$_4$</td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>3.0 : 1</td>
<td>KZn(BH$_4$)$_3$</td>
</tr>
<tr>
<td></td>
<td>4.0 : 1</td>
<td>K$_2$Zn(BH$_4$)$_4$</td>
</tr>
<tr>
<td></td>
<td>1.1 : 1</td>
<td>K$_2$Zn$_3$(BH$_4$)$_8$</td>
</tr>
</tbody>
</table>

Table 4. Reaction Conditions #1: Various alkali borohydride precursors with different molar ratios to zinc chloride resulting in zinc borohydride and related derivatives via ball milling methods.
Reaction Conditions #2:

Lithium borohydride (LiBH₄, 93.5%), sodium borohydride (NaBH₄, 98%), potassium borohydride (KBH₄, 98%), and zinc chloride (ZnCl₂, 99.99%) packed in ampule under argon from Sigma-Aldrich were used as received. All materials were stored and handled in a glove box (Innovative Technology) filled with nitrogen.

All ball milling was performed by a Fritsch Pulverisette planetary ball mill at room temperature. Samples were stored at room temperature in a nitrogen glove box. All analysis and characterization was completed within 48 hours of synthesis as samples do decompose at room temperature under nitrogen for longer periods of time.

The product compositions were determined by X-ray diffractometry using a Scintag X1 Advanced Diffraction System with a Cu tube run at 45KV 35ma with a Scintag Peltier Detector equipped with a special isolation chamber attachment made by Scintag.

Thermal desorption mass spectrometric analysis was performed with a Heiden HPR20 Residual Gas Analysis Mass Spectrometer with a heated capillary inlet system fixed with an attachment to accommodate air-sensitive samples which was loaded under nitrogen in the glove box. For study of the starting materials, the heating rate was fixed at 2 °C/min until the sample reached 350 °C. The sample was then held at 350 °C for one hour. For the study of the product mixtures, the heating rate was fixed at 2 °C/min until the sample reached 200 °C. The sample was then held at 200 °C for one hour. The flow rate of nitrogen gas was set at 10 mL/min.
Synthesis of Zinc Borohydride and Derivatives: A 1.5 g mixture of alkali borohydride and zinc chloride precursors in different ratios (Table 5) was charged with seven tungsten-carbide balls in a 25 cc tungsten-carbide milling bowl and fitted with a lid and Teflon O-ring inside the glove box. Mixtures were milled at room temperature at 350 rpm for varying amounts of time.

<table>
<thead>
<tr>
<th>Alkali Borohydride Precursor (MBH₄)</th>
<th>Molar Ratio MBH₄ : ZnCl₂</th>
<th>Target Zinc Borohydride Product</th>
<th>Optimized Ball Milling Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄</td>
<td>2.1 : 1</td>
<td>Zn(BH₄)₂</td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td>3.1 : 1</td>
<td>LiZn(BH₄)₃</td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td>4.1 : 1</td>
<td>Li₂Zn(BH₄)₄</td>
<td>2 h</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>3.0 : 1</td>
<td>NaZn(BH₄)₃</td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td>4.1 : 1</td>
<td>Na₂Zn(BH₄)₄</td>
<td>2 h</td>
</tr>
<tr>
<td>KBH₄</td>
<td>3.0 : 1</td>
<td>KZn(BH₄)₃</td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td>4.0 : 1</td>
<td>K₂Zn(BH₄)₄</td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td>1.1 : 1</td>
<td>K₂Zn₃(BH₄)₈</td>
<td>3 h</td>
</tr>
</tbody>
</table>

Table 5. Reaction Conditions #2: Various alkali borohydride precursors with different molar ratios to zinc chloride resulting in zinc borohydride and related derivatives via ball milling methods.

Results and Discussion

The two sets of reaction conditions (#1 and #2) were monitored for completion by IR and XRD analysis, respectively. The reaction of zinc chloride and lithium borohydride was monitored for five hours with an IR spectra obtained every hour (Figure 2). It was shown that at five hours the borohydride anion band at ~2290 cm⁻¹ (Figure 2: F) had reduced intensity. On the other hand, the bands corresponding to the vibrations of bridging (~2100 cm⁻¹) and terminal (~2450 cm⁻¹) B-H bonds were observed with greater intensity. In addition the appearance of the Zn-H stretching band is observed at 1412 cm⁻¹. These observations indicate the formation of bonds between the borohydride

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ligands and the zinc metal center. This signifies that the nature of the bonding transitioned from the ionic bonding of the lithium borohydride precursor to the covalent bonding of zinc borohydride. (Note: Bands around 1120 cm\(^{-1}\) correspond to BH\(_2\) bending.\(^{61}\))

Figure 2. IR spectra monitoring reaction of ZnCl₂ + 2LiBH₄ → Zn(BH₄)₂ + 2LiCl. (A) 0 hours milling; (B) 1 hour milling; (C) 2 hours milling; (D) 3 hours milling; (E) 4 hours milling; (F) 5 hours milling.
Examination of the IR spectra during the synthesis of zinc borohydride under Reaction Conditions #1 showed evidence of product formation. Therefore, it was assumed that these reaction conditions would be ideal for the remaining syntheses. The following examination of the IR spectra shows compelling evidence that these conditions were ideal for the proposed reactions.

The IR spectra were obtained for all the starting materials and product mixtures (Figures 3, 4, 5; Tables 6 and 7). The spectra indicate that for all the product mixtures a change took place in the nature of bonding because all the spectra show evidence of new and different peaks when compared to the spectra of the starting materials.
Figure 3. IR spectra of (A) pure LiBH₄, (B) Zn(BH₄)₂ + 2LiCl, (C) LiZn(BH₄)₂ + 2LiCl, (D) Li₂Zn(BH₄)₄ + 2LiCl.
Figure 4. IR Spectra of (A) pure NaBH₆, (B) Na₂Zn(BH₄)₂ + 2NaCl, (C) Na₂Zn(BH₄)₄ + 2NaCl.
Figure 5. IR spectra of (A) pure KBH₄, (B) KZn(BH₄)₂ + 2KCl, (C) K₂Zn(BH₄)₄ + 2KCl, (D) K₂Zn₂(BH₄)₆ + 2K₃Zn₂Cl₇.

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>IR Peaks (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄</td>
<td>2290</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>2285</td>
</tr>
<tr>
<td>KBH₄</td>
<td>2288</td>
</tr>
</tbody>
</table>

Table 6. Major band observed in IR spectra of alkali metal borohydride starting materials.
Table 7. Summary of major bands observed in IR spectra of reaction products. Note: While only the assumed products are noted in the table, bands corresponding to the starting materials are present after milling.

Milling was not continued past five hours due to the start of discoloration of the product (an off-white color rather than a white color). This color change is an indication of the start of decomposition. Further milling resulted in gray colored samples which indicated the presence of zinc metal (and, therefore, a more advanced state of decomposition). In spite of this, the spectral data indicates that the reaction was mostly complete since there are bands corresponding to the stretching modes of the reaction product in addition to bands indicating the starting material.

Certain reactions studied in this research have the same starting materials which were used in different stoichiometric amounts. For example, the synthesis of Zn(BH₄)₂, LiZn(BH₄)₃, and Li₂Zn(BH₄)₄ began with ZnCl₂ and LiBH₄. The molar ratios of LiBH₄ to ZnCl₂ were approximately 2:1, 3:1, and 4:1, respectively. This was done in order to obtain different products. It is reasonable to suggest that different products were formed in each of these reactions as they have been proposed as the products of previously studies via wet chemistry methods.

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Examination of the IR spectra also gives reason to suggest that each reaction gave unique products. Upon comparison of the IR spectra of Zn(BH$_4$)$_2$, LiZn(BH$_4$)$_3$, and Li$_2$Zn(BH$_4$)$_4$ (Figure 3: B, C, D), it can be seen that the spectrum for Li$_2$Zn(BH$_4$)$_4$ clearly has broader bands than those of Zn(BH$_4$)$_2$ and LiZn(BH$_4$)$_3$, even though all the major bands are at about the same wavenumbers. In addition, these spectra obviously vary from the IR spectrum of the LiBH$_4$ starting material (Figure 3: A) which has an intense band at 2290 cm$^{-1}$.

Upon examination of the sodium complexes with the sodium borohydride precursor (Figure 4:A) it is clear that a chemical reaction took place. Sodium borohydride exhibits a broad band at 2295 cm$^{-1}$, while the spectra of the compounds NaZn(BH$_4$)$_3$ and Na$_2$Zn(BH$_4$)$_4$ (Figure 4: B, C) have new and unique bands. These two product mixtures clearly differ in that the spectrum in that NaZn(BH$_4$)$_3$ has broader bands and the starting material band (usually around 2290 cm$^{-1}$) is not detected. The starting material band is clearly observed for Na$_2$Zn(BH$_4$)$_4$ at 2295 cm$^{-1}$. Also, a major band for NaZn(BH$_4$)$_3$ exists at 2223 cm$^{-1}$, meaning that there are differences in the two complexes.

It was attempted to make zinc borohydride from the sodium borohydride precursor (IR spectrum not shown) as well as the lithium borohydride precursor. Results of both of these syntheses were similar in that the product mixture Zn(BH$_4$)$_2$(+ 2LiCl) gave B-H stretching bands at 2449 cm$^{-1}$ and 2086 cm$^{-1}$ and a Zn-H stretching band at 1412 cm$^{-1}$ while the mixture Zn(BH$_4$)$_2$(+ 2NaCl) gave B-H stretching bands at 2451 cm$^{-1}$.
and 2089 cm$^{-1}$ and a Zn-H stretching band at 1408 cm$^{-1}$. It is evident that both reactions gave zinc borohydride product. The focus of these studies was to obtain the maximum hydrogen capacity for the product mixtures, therefore, further studies examine only the zinc borohydride synthesized from lithium borohydride as the lithium chloride byproduct is lighter in weight.

Similar evidence is provided in the case of the potassium compounds. The spectrum for potassium borohydride exhibits a broad band at 2288 cm$^{-1}$ (Figure 5:A), while the product mixtures KZn(BH$_4$)$_3$, K$_2$Zn(BH$_4$)$_4$, and K$_2$Zn$_3$(BH$_4$)$_6$ (Figure 5: B, C, D) clearly have distinctive bands. However, discrepancies to the expected bands for zinc borohydride complexes exist for the products of KZn(BH$_4$)$_3$ and K$_2$Zn(BH$_4$)$_4$ (Figure 5: B, C). For the product KZn(BH$_4$)$_3$, the band thought to correspond to the B-H terminal bond (usually at ~2450 cm$^{-1}$) is found at 2365 cm$^{-1}$. In addition, the band corresponding to the B-H bridging bond (usually at ~2100 cm$^{-1}$) is observed at 2216 cm$^{-1}$. This means that the product mixture may not have the expected bonding structure. Also, the band at 2289 cm$^{-1}$ is more intense than the others. This provides evidence that starting material still remains in the product mixture (KBH$_4$ has a main IR peak at 2288 cm$^{-1}$). However, some product exists as the peaks around 1410 cm$^{-1}$ indicate Zn-H stretching and, therefore, coordination of the borohydride ligands to the zinc metal center.

The product K$_2$Zn(BH$_4$)$_4$, resulted in a broad band at 2280 cm$^{-1}$. There was no clearly defined band at ~2450 cm$^{-1}$, however, there was a band at 2088 cm$^{-1}$, which corresponds to the B-H bridging bond. Perhaps this reaction resulted in a bonding pattern that is different from the expected.
When comparing these complexes (KZn(BH₄)₃ and K₂Zn(BH₄)₄) with the derivative K₂Zn₃(BH₄)₈ (Figure 5: D) the spectrum for K₂Zn(BH₄)₄ clearly has the broadest bands and the spectrum for KZn(BH₄)₃ has the narrowest bands. In addition the wavenumbers of the major bands for K₂Zn₃(BH₄)₈ are clearly different from the other potassium complexes (Table 7). The differences in all of the IR spectra for the different product mixtures provide evidence that the product mixtures are in fact different. More evidence of this will be seen upon further characterization of the products.

Overall the IR spectra support the argument of the bidentate coordination of the borohydride ligands to the zinc metal center (Chapter 1, Figure 1). While unidentate and tridentate coordination seem possible, analysis of the B-H bridging and terminal stretches (Appendix A) provide evidence for the bidentate coordination.

X-ray diffraction patterns for the materials synthesized by Reaction Conditions #2 also show product formation (Figures 6, 7, 8). While the diffraction patterns of the desired compounds are currently unknown (except K₂Zn₃(BH₄)₈)⁷²,⁷³, the patterns indicate successful synthesis upon the identification of the lithium-, sodium-, or potassium-chloride byproducts. The formation of the respective alkali chloride byproducts is evident in the X-ray patterns of Zn(BH₄)₂, LiZn(BH₄)₃, Li₂Zn(BH₄)₄, NaZn(BH₄)₃, and Na₂Zn(BH₄)₄ (Figures 6 and 7). However, this evidence is not obvious in the X-ray patterns of KZn(BH₄)₃ and K₂Zn(BH₄)₄ (Figure 8: A, B) where the diffraction peaks corresponding to the potassium chloride byproduct are not as obvious. For these patterns, the major peaks correspond to the potassium borohydride precursor.

For the XRD pattern of the K$_2$Zn$_3$(BH$_4$)$_8$ product mixture (Figure 8: C), peaks clearly matched X-ray patterns already obtained for the crystalline material. In this case, it is also not obvious if KCl is part of the product mixture or if the proposed K$_3$Zn$_2$Cl$_7$ byproduct is present.
Figure 6. Powder X-ray diffraction patterns of (A) Zn(BH₄)₂ + 2LiCl, (B) LiZn(BH₄)₃ + 2LiCl, (C) Li₂Zn(BH₄)₄ + 2LiCl.
Figure 7. Powder X-ray diffraction patterns of (A) NaZn(BH₃)₃ + 2NaCl, (B) Na₂Zn(BH₄)₄ + 2NaCl.
Figure 8. Powder X-ray diffraction patterns of (A) KZn(BH₄)₃ + 2KCl, (B) K₂Zn(BH₄)₄ + 2KCl, (C) K₂Zn₃(BH₄)₈ + 2K₂ZnCl₇.
In addition to the formation of the alkali chloride byproducts for the compounds Zn(BH₄)₂, LiZn(BH₄)₃, Li₂Zn(BH₄)₆, NaZn(BH₄)₃, and Na₂Zn(BH₄)₄, the XRD patterns for these compounds also show unidentified major peaks between 15-25 two-theta degrees. These new peaks are evidence of product formation. For the products KZn(BH₄)₃ and K₂Zn(BH₄)₄, the XRD patterns do not show any major unidentified peaks. The major peaks in these diffraction patterns correspond to the potassium borohydride precursor. However, there are some minor peaks that are unidentified and may imply that the actual product formed is amorphous. This is a reasonable explanation because ball milling processes often result in the formation of small particles.

While product formation is evident, there still exists elemental peaks for the alkali borohydride and zinc chloride starting materials. However, further milling of the reaction mixture having a LiBH₄:ZnCl₂ ratio of 2.0 resulted in discoloration indicating the start of decomposition (discussed earlier). Therefore, samples were milled only for the amount of time specified in Reaction Conditions #2 and then used for further analysis by TD-MS (discussed later).

It is important to note that attempts were made to synthesize zinc borohydride (Zn(BH₄)₂) with all three alkali borohydride precursors (LiBH₄, NaBH₄, and KBH₄). According to XRD analysis (not shown for the precursors NaBH₄ and KBH₄), the syntheses beginning with LiBH₄ and NaBH₄ both resulted in the formation of the alkali chloride byproducts LiCl and NaCl, respectively (Product formation was also confirmed by IR analysis). In additions, new peaks were observed in the XRD patterns for these product mixtures. However, the synthesis beginning with KBH₄ did not result in the formation of KCl and only starting material was detected in the XRD pattern. These
studies focused on utilizing the zinc borohydride product mixture that employed the precursor LiBH₄. This is because the LiCl byproduct has the lightest molecular weight when compared to NaCl and KCl. Later, when hydrogen capacity of the materials is examined, it will be obvious that the lighter molecular weight of the byproduct will be most advantageous in obtaining optimal hydrogen storage properties.

The compound $K_2Zn_3(BH_4)_8$ was successfully synthesized and matched with an identical pattern for the compound in our database. (This compound has been previously synthesized in non-aqueous solutions, but synthesis has not been reported via mechanochemical activation methods). This complex $K_2Zn_3(BH_4)_8$ was also the model for a side study in which it was attempted to synthesize the complex $Li_2Zn_3(BH_4)_8$ (XRD pattern not shown) which would also have beneficial hydrogen capacity properties due to its lighter weight and high hydrogen content. The reaction mixture had a LiBH₄:ZnCl₂ ratio of 1.1. Unfortunately, the major peaks of the XRD pattern for this product mixture were associated with LiCl and the precursors LiBH₄ and ZnCl₂. Nevertheless, there were some peaks that were unaccounted for between 15-25 two-theta degrees. Perhaps this indicates the formation of some $Zn(BH_4)_2$. For further studies, including TD-MS and dehydrogenation properties of these materials, the focus is $K_2Zn_3(BH_4)_8$ as opposed to the product mixture labeled as “$Li_2Zn_3(BH_4)_8$” because the product $K_2Zn_3(BH_4)_8$ was confirmed by XRD and has been previously studied.

It should be discussed that the milling time for the synthesis of $K_2Zn_3(BH_4)_8$ was three hours as opposed to the two hours of milling for the other samples. When comparing this sample milled for one hour to the sample milled for three hours, the X-ray pattern matching the product was more intense at three hours.
An additional potassium zinc hydride phase (K$_2$ZnH$_4$) was also identified in the diffraction pattern K$_2$Zn$_3$(BH$_4$)$_8$ (not shown). However, the peaks corresponding to this phase are very small in comparison to the product peaks for K$_2$Zn$_3$(BH$_4$)$_8$ and perhaps the identification of this phase may be imprecise due to overlap of other peaks due to the reaction precursors. Also, this hydride has been synthesized previously by a solid state reaction between potassium hydride and zinc metal at 650 K and 80 bar H$_2$. This indicates that perhaps this alternative hydride phases could not actually have been produced under Reaction Conditions #2 due to its comparatively mild conditions.

Finally, it is difficult to determine from XRD alone whether the product mixtures of Zn(BH$_4$)$_2$, LiZn(BH$_4$)$_3$, Li$_2$Zn(BH$_4$)$_4$, NaZn(BH$_4$)$_3$, and Na$_2$Zn(BH$_4$)$_4$ do, in fact, actually have different identities. With the major unidentified peaks all in the same region of the diffraction patterns it is not easy to determine if changes in molar ratio really change the identity of the product. However, the combination of evidence from all characterization techniques (including IR and $^{11}$B NMR) will prove that these individual complexes have different chemical and material properties.

Further analysis of these product mixtures were conducted with $^{11}$B NMR spectroscopy. These preliminary studies were conducted at varying spinning speeds, however, this dissimilarity in method does not cause changes in the shift of the central peak. These variances do cause dissimilarities in satellite peak locations and the spacing between satellite peaks.

No prior studies concerning the materials studied here have been analyzed using solid-state $^{11}$B NMR spectroscopy. The only reported $^{11}$B NMR data has been done in

---

solution with solvated products. These reports examined $\text{Zn(BH}_4\text{)}_2$, $\text{LiZn(BH}_4\text{)}_3$, $\text{Li}_2\text{Zn(BH}_4\text{)}_4$, $\text{NaZn(BH}_4\text{)}_3$, and $\text{NaBH}_4$. Chemical shifts ranged from +42.0 to +48.0 ppm (Table 8). This data provides evidence that each of these complexes have unique identities. Each complex exhibits relatively small differences in chemical shifts when compared to the others, therefore, we expect similar results in the following studies.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$ $^{11}$B (ppm)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Zn(BH}_4\text{)}_2\cdot\text{2OC}_2\text{H}_5$</td>
<td>46.8</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>$\text{Zn(BH}_4\text{)}_2\cdot\text{2NC}_2\text{H}_5$</td>
<td>45.5</td>
<td>Pyridine</td>
</tr>
<tr>
<td>$\text{LiZn(BH}_4\text{)}_2$</td>
<td>42.3</td>
<td>Ether</td>
</tr>
<tr>
<td>$\text{Li}_2\text{Zn(BH}_4\text{)}_4$</td>
<td>42.6</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>$\text{NaZn(BH}_4\text{)}_3$</td>
<td>42.0</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>$\text{NaBH}_4$</td>
<td>43.2</td>
<td>Ether</td>
</tr>
<tr>
<td></td>
<td>43.5</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td></td>
<td>48.0</td>
<td>Water</td>
</tr>
</tbody>
</table>


All the chemical shifts for the central peaks of the materials studied in these experiments were observed in the range of -57 to -66 ppm. These observed chemical shifts differ from previous studies because the reference chemical is different in these experiments. It should be mentioned that some NMR spectra include the presence of satellite peaks (Figures 9, 10, 11; Note: The $^{11}$B NMR spectra shown here are displayed on varied scales.) In solution NMR, satellite peaks are not observed because samples are homogeneous and result in only a single, central peak. However, in solid-state NMR the lattice of boron nuclei are not homogeneous. Due to these anisotropic effects, satellite peaks are observed. At faster spinning speed the detection of differences in each lattice direction is more difficult, therefore, resulting in fewer satellite peaks. Slower spinning speeds produce more apparent satellite peaks.

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Figure 9. $^{11}$B NMR spectra of (A) pure LiBH$_4$, (B) Zn(BH$_4$)$_2$ + 2LiCl, (C) LiZn(BH$_4$)$_3$ + 2LiCl, (D) Li$_2$Zn(BH$_4$)$_4$ + 2LiCl.
Figure 10. $^{11}$B NMR spectra of (A) pure NaBH$_4$, (B) NaZn(BH$_4$)$_2$ + 2NaCl, (C) Na$_2$Zn(BH$_4$)$_3$ + 2NaCl.
Figure 11. $^{11}$B NMR spectra of (A) pure KBH$_4$, (B) KZn(BH$_4$)$_3$ + 2KCl, (C) K$_2$Zn(BH$_4$)$_4$ + 2KCl, (D) K$_2$Zn$_3$(BH$_4$)$_6$ + 2K$_2$Zn$_2$Cl$_7$. 
Upon comparison of the shifts of the central peaks of the starting materials (Table 9) and the product mixtures (Table 10), interesting conclusions can be drawn. While the shifts are seemingly insignificant, they are in fact evidence of the formation of new complexes as the subtle differences were seen in previous studies by solution NMR.

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Central $^{11}$B NMR Peak Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH$_4$</td>
<td>-60.887</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>-61.589</td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>-57.819</td>
</tr>
</tbody>
</table>

Table 9. Chemical shifts of central $^{11}$B NMR peak for starting materials.

<table>
<thead>
<tr>
<th>Products</th>
<th>Central $^{11}$B NMR Peak Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(BH$_4$)$_2$ + 2LiCl</td>
<td>-63.860</td>
</tr>
<tr>
<td>LiZn(BH$_4$)$_3$ + 2LiCl</td>
<td>-65.282</td>
</tr>
<tr>
<td>Li$_2$Zn(BH$_4$)$_3$ + 2LiCl</td>
<td>-61.215</td>
</tr>
<tr>
<td>NaZn(BH$_4$)$_3$ + 2NaCl</td>
<td>-64.617</td>
</tr>
<tr>
<td>Na$_2$Zn(BH$_4$)$_4$ + 2NaCl</td>
<td>-81.806</td>
</tr>
<tr>
<td>KZn(BH$_4$)$_3$ + 2KCl</td>
<td>-57.819</td>
</tr>
<tr>
<td>K$_2$Zn(BH$_4$)$_4$ + 2KCl</td>
<td>-57.819</td>
</tr>
<tr>
<td>K$_2$Zn$_3$(BH$_4$)$_6$ + 2K$_2$Zn$_5$Cl$_7$</td>
<td>-62.471</td>
</tr>
</tbody>
</table>

Table 10. Chemical shifts of central $^{11}$B NMR peak for product mixtures.

Examination of the central peak shifts show the trend that the peaks for the starting materials of lithium borohydride and sodium borohydride shift upfield upon reaction with zinc chloride (Figures 9 and 10, Tables 9 and 10). However, some shifts are more extreme than others. For example, those reaction mixtures synthesized from lithium borohydride starting material (-60.887 ppm) resulted in the following shifts: Zn(BH$_4$)$_2$, -63.860 ppm; LiZn(BH$_4$)$_3$, -65.282 ppm; and Li$_2$Zn(BH$_4$)$_4$, -61.215 ppm (Figure 9). Since a change in the chemical shift took place, it is safe to presume that the ball milling of the starting materials resulted in the formation of new complexes. Furthermore, because the chemical shifts of these three complexes are all different, it can be assumed that the three complexes have unique identities.
In addition, inspection of the reaction mixtures originating from sodium borohydride (-61.589 ppm) follow a similar trend whereas the formation of NaZn(BH₄)₃ (-64.617 ppm) shows a greater upfield shift when compared to Na₂Zn(BH₄)₄ (-61.806 ppm) (Figure 10). Again, this indicates the formation of unique complexes.

For the reactions concerning the lithium and sodium borohydride starting materials, the zinc centers coordinated with three borohydride groups (LiZn(BH₄)₃ and NaZn(BH₄)₃) show a greater change in chemical shift than the zinc centers with four borohydride ligands (Li₂Zn(BH₄)₄ and Na₂Zn(BH₄)₄). This indicates that the boron environments for the complexes LiZn(BH₄)₃ and NaZn(BH₄)₃ may be similar and the environments for the complexes Li₂Zn(BH₄)₄ and Na₂Zn(BH₄)₄ may be similar. The steric around the zinc metal center are different if three or four borohydride groups surround it and, thus, will effect the electronic environments of each borohydride ligand.

Discrepancies occur upon examination of the shift for potassium borohydride (-57.819 ppm) and the product mixtures KZn(BH₄)₃ and K₂Zn(BH₄)₄ (Figure 11: A, B, C) which have identical shifts (-57.819 ppm). This probably means that the chemical environments of boron in the two complex zinc borohydrides are similar to that of KBH₄. Another explanation is that in the product mixtures of the two complex borohydrides, the molar ratio of the desired product to the remaining starting material is small which results in a major signal due to the starting material. This is supported by the shoulder observed for K₂Zn(BH₄)₄ at -62.471 ppm which indicates the presence of some product even though the peak indicating remaining starting material is more intense. This is also supported by the IR spectra of the product mixtures which confirmed some product formation.
The shift for $K_2Zn_3(BH_4)_8$ at -62.471 ppm (Figure 11:D) is drastically different from the other potassium zinc complexes even though it was also synthesized from potassium borohydride. It is likely that this shift upfield indicates a change in the boron environment and, thus, that B-H bridging bonds were formed to the zinc metal center.

The combination of IR, XRD, and $^{11}$B NMR data exhibit convincing evidence of the proposed product formation via mechanochemical methods (with the exception of $KZn(BH_4)_3$ and $K_2Zn(BH_4)_4$). While these methods have been used previously for the synthesis of $Zn(BH_4)_2(\text{+MCl})$; this is the first report confirming the product formation of the remaining reaction mixtures by these synthesis methods.
CHAPTER THREE

THERMAL DESORPTION MASS SPECTROMETRY ANALYSIS
As noted earlier, several decomposition pathways have been proposed for the thermal decomposition of zinc borohydride. These pathways include:

\[
Zn(BH_4)_2 \rightarrow Zn + 2B + 4H_2
\]

\[
Zn(BH_4)_2 \rightarrow Zn + H_2 + B_2H_6
\]

in which the release of hydrogen is the thermodynamically favored reaction (the first reaction), while the release of hydrogen and diborane is the kinetically favored reaction (the second reaction). For the product mixtures formed, thermal desorption mass spectrometry (TD-MS) analysis was performed to determine the actual decomposition pathway.

For the study of the starting materials, heating began at room temperature and increased to 350 °C at a rate of 2 °C/min. The samples were then held at 350 °C for one hour. The data shows (Figure 12) that no diborane gas was released from the starting materials.
Figure 12. TD-MS curves of reaction starting materials. (A) LiBH₄; (B) NaN₃; (C) KBH₄. Hydrogen shown by pink line, diborane shown by yellow line, and heating ramp shown by brown line.
Upon examination of the hydrogen desorption from the starting materials, it is found that the decomposition temperatures for these materials are reported at higher temperatures (Table 1) than observed in these studies. Lithium borohydride has a decomposition temperature of 380 °C. While the maximum hydrogen release was observed at 325 °C, the hydrogen release took place over the time period of about an hour (Figure 12: A). This indicates that at lower temperatures hydrogen is released, but slowly. The decomposition temperatures for sodium borohydride and potassium borohydride are 400 °C and 500 °C, respectively. The spectra indicate the maximum release of hydrogen at around 350 °C for both materials (Figure 12: B, C). Interestingly, the spectrum for sodium borohydride shows a prior minor release of hydrogen around 240 °C. For both sodium borohydride and potassium borohydride the pressure of hydrogen is relatively low and the spectra show a broad release which was not completed by the end of the one hour hold at 350 °C. This signifies that the materials decompose slowly at lower temperatures.

For the study of the product mixtures, heating began at room temperature and increased to 200 °C at a rate of 2 °C/min. The samples were then held at 200 °C for one hour. This heating rate is much slower than the 10 °C/min used in prior experiments. The slower heating rate was used in an attempt to prevent the kinetic decomposition reaction and, thus, release only hydrogen rather than a hydrogen and diborane mixture.

The result of the TDMS data (Table 11; Figures 13, 14, 15) shows that, upon heating, these compounds (including the alkali chloride byproduct) release diborane and hydrogen simultaneously. This provides evidence that the second decomposition

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pathway (noted earlier) is most probable, even under the conditions of a reduced heating rate. However, the amount of hydrogen released is greater than the amount of diborane released (Table 12) because the hydrogen to diborane ratio is greater than one for all the complexes.

<table>
<thead>
<tr>
<th>Product Mixture</th>
<th>Appx. Temp. of Max H₂ peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(BH₄)₂ + 2LiCl</td>
<td>140 °C</td>
</tr>
<tr>
<td>Li₂Zn(BH₄)₃ + 2LiCl</td>
<td>140 °C</td>
</tr>
<tr>
<td>Li₂Zn(BH₄)₄ + 2LiCl</td>
<td>140 °C</td>
</tr>
<tr>
<td>Na₂Zn(BH₄)₃ + 2NaCl</td>
<td>140 °C</td>
</tr>
<tr>
<td>Na₂Zn(BH₄)₄ + 2NaCl</td>
<td>115 °C</td>
</tr>
<tr>
<td>KZn(BH₄)₃ + 2KCl</td>
<td>145 °C</td>
</tr>
<tr>
<td>K₂Zn(BH₄)₄ + 2KCl</td>
<td>145 °C</td>
</tr>
<tr>
<td>K₂Zn₃(BH₄)₈ + 2K₂Zn₂Cl₇</td>
<td>155 °C</td>
</tr>
</tbody>
</table>

Table 11. Approximate temperature of maximum hydrogen peak for product mixtures found by TD-MS.
Figure 13. TD-MS analysis of (A) Zn(BH₄)₂ + 2LiCl, (B) LiZn(BH₄)₂ + 2LiCl, (C) Li₂Zn(BH₄)₄ + 2LiCl. Hydrogen shown by pink line, diborane shown by yellow line, and heating ramp shown by brown line.
Figure 14. TD-MS analysis of (A) NaZn(BH₄)₃ + 2NaCl, (B) Na₂Zn(BH₄)₄ + 2NaCl. Hydrogen shown by pink line, diborane shown by yellow line, and heating ramp shown by brown line.
Figure 15. TD-MS analysis of (A) KZn(BH₄)₂ + 2KCl, (B) K₂Zn(BH₄)₂ + 2KCl, (C) K₂Zn₂(BH₄)₃ + 2K₂Zn₂Cl₃. Hydrogen shown by pink line, diborane shown by yellow line, and heating ramp shown by brown line.
<table>
<thead>
<tr>
<th>Product</th>
<th>Ratio (H₂/B₂H₆)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH₄</td>
<td>0.00</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>0.00</td>
</tr>
<tr>
<td>KBH₄</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn(BH₄)₂</td>
<td>4.66</td>
</tr>
<tr>
<td>LiZnBH₄</td>
<td>4.46</td>
</tr>
<tr>
<td>Li₂Zn(BH₄)₄</td>
<td>2.99</td>
</tr>
<tr>
<td>NaZn(BH₄)₂</td>
<td>3.84</td>
</tr>
<tr>
<td>Na₂Zn(BH₄)₄</td>
<td>2.20</td>
</tr>
<tr>
<td>KZn(BH₄)₂</td>
<td>9.40</td>
</tr>
<tr>
<td>K₂Zn(BH₄)₄</td>
<td>7.25</td>
</tr>
<tr>
<td>K₂Zn₃(BH₄)₈</td>
<td>5.97</td>
</tr>
</tbody>
</table>

Table 12. Summary of the ratio of hydrogen to diborane calculated from the maximum hydrogen peak in TD-MS data.

The product mixtures released the maximum amount of hydrogen at various temperatures ranging from 115 to 155 °C (Table 11). The compound with the lowest hydrogen release temperature was Na₂Zn(BH₄)₄ (at 115 °C) (Figure 14: B). This temperature is close to the target 100 ºC dehydrogenation temperature desired for practical hydrogen storage materials.

Hydrogen and diborane were released symmetrically for the compounds Zn(BH₄)₂, LiZn(BH₄)₃, Li₂Zn(BH₄)₄, and Na₂Zn(BH₄)₄ (Figure 13: A, B, C; Figure 14: B).

Hydrogen and diborane were released asymmetrically for the compounds NaZn(BH₄)₃ and K₂Zn₃(BH₄)₈ (Figure 14: A; Figure 15: C). For NaZn(BH₄)₃ a sharp jump is observed. This phenomenon may correspond to the melting of the material. For K₂Zn₃(BH₄)₈, a broad, rounded peak is observed. This may indicate that a multiple-step dehydrogenation takes place for this material.

In addition, the compound K₂Zn₃(BH₄)₈ had the highest temperature at its maximum hydrogen release (155 °C). This could mean that this compound is the most
stable of the product mixtures studied. This is supported by the fact that it is the only compound studied here that has been previously isolated by researchers.

For the compounds KZn(BH₄)₃ and K₂Zn(BH₄)₄ (Figure 15: A, B) there were two releases, one at around 145 °C and the other at 200 °C. This provides evidence for a multi-step dehydrogenation pathway. There may also be starting material present in the product mixtures. Although, potassium borohydride is reported to decompose at 500 °C, it was shown earlier that it can release hydrogen at lower temperatures over longer periods of time. However, these releases of hydrogen at 145 °C and 200 °C are lower than the 350 °C observed earlier. Perhaps the presence of the zinc transition metal promotes desorption of hydrogen at lower temperatures by destabilizing potassium borohydride.

Upon examination of the hydrogen to diborane ratios (Table 12) it can be seen that as the stoichiometric ratio of alkali borohydride to zinc chloride increases, the hydrogen to diborane ratio decreases. For example, Zn(BH₄)₂ (LiBH₄/ZnCl₂ = 2.0; H₂/B₂H₆ = 4.66), LiZn(BH₄)₃ (LiBH₄/ZnCl₂ = 3.0; H₂/B₂H₆ = 4.46), and Li₂Zn(BH₄)₄ (LiBH₄/ZnCl₂ = 4.0; H₂/B₂H₆ = 2.99). This indicates that diborane liberation increases as the alkali borohydride to zinc chloride ratio increases.

The hydrogen to diborane ratio is highest for the potassium zinc complexes. This includes KZn(BH₄)₃ (H₂/B₂H₆ = 9.40), K₂Zn(BH₄)₄ (H₂/B₂H₆ = 7.25), and K₂Zn₃(BH₄)₈ (H₂/B₂H₆ = 5.97). This means, when compared to the lithium and sodium complexes, the potassium complexes release more hydrogen than diborane. This would make sense if potassium borohydride precursor was remaining in the product mixture because it was shown earlier that the reaction precursors did not release diborane.
Overall, the product mixtures have lower hydrogen desorption temperature than their corresponding precursors. However, the product mixtures exhibit the release of diborane in addition to hydrogen gas that is not seen in the analysis of the starting materials. When considering these dehydrogenation properties in addition to the analysis examined in Chapter 2, it is clear that each product mixture has a distinct identity and they are not all simply mixtures resulting in the same products with differing amounts of remaining starting material.
CHAPTER FOUR

HYDROGEN STORAGE PROPERTIES
Some previous research has focused on the use of borohydrides as hydrogen storage materials.\textsuperscript{78, 79} While the focus of these studies was the synthesis and characterization of new materials, it is interesting to examine the storage properties in order to determine whether they are useful as hydrogen storage materials.

The dehydrogenation curves shown (Figures 16, 17, 18) only exhibit the dehydrogenation of the first and second cycles. The rehydrogenation curves are not shown as no hydrogen uptake took place. All dehydrogenation curves were obtained at 100 °C in an attempt to target only the release of hydrogen and prevent the release of a hydrogen and diborane mixture (as supported by TD-MS data in Chapter 3). In addition, calculations of hydrogen capacity are based on the assumption that only hydrogen is liberated from the product mixtures.


Figure 16. Dehydrogenation profiles at 100 °C for product mixtures (A) Zn(BH₄)₂ + 2LiCl, (B) Li₂Zn(BH₄)₄ + 2LiCl, (C) Li₂Zn(BH₄)₄ + 2LiCl. Blue line corresponds to first dehydrogenation while yellow line corresponds to second dehydrogenation.
Figure 17. Dehydrogenation profiles at 100 °C for product mixtures (A) NaZn(BH₄)₃ + 2NaCl, (B) Na₂Zn(BH₄)₄ + 2NaCl. Blue line corresponds to first dehydrogenation while yellow line corresponds to second dehydrogenation.
Figure 18. Dehydrogenation profiles at 100 °C for product mixtures (A) KZn(BH₄)₃ + 2KCl, (B) K₂Zn(BH₄)₃ + 2KCl, (C) K₂Zn₃(BH₄)₈ + 2K₂Zn₂Cl₇. Blue line corresponds to first dehydrogenation while yellow line corresponds to second dehydrogenation.
Most of the complexes exhibited quick dehydrogenation kinetics. This property is observed for the complexes Zn(BH$_4$)$_2$, NaZn(BH$_4$)$_3$, Na$_2$Zn(BH$_4$)$_4$, and K$_2$Zn$_3$(BH$_4$)$_8$ (Figure 16: A; Figure 17: A, B; Figure 18: C).

It is interesting to note the behavior of LiZn(BH$_4$)$_3$, Li$_2$Zn(BH$_4$)$_4$, KZn(BH$_4$)$_3$, and K$_2$Zn(BH$_4$)$_4$ (Figure 16: B, C; Figure 18: A, B). The curves show a gradual release of hydrogen during the dehydrogenation of the first cycle. However, the maximum hydrogen weight percent (Table 13) only reaches 1.10%, 0.90%, 0.50%, and 0.45%, respectively. These are some of the lowest hydrogen weight percents observed out of all the materials tested. Since no hydrogen uptake occurred during rehydrogenation, the second dehydrogenation shows the continuing release of hydrogen that was not given off during the first cycle. A reasonable explanation for this observation is that these complexes both have slow dehydrogenation kinetics at 100 °C (K$_2$Zn(BH$_4$)$_4$ having the slowest kinetics and LiZn(BH$_4$)$_3$ having the fastest kinetics).

<table>
<thead>
<tr>
<th>Product Mixture</th>
<th>Appx. H$_2$ Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(BH$_4$)$_2$ + 2LiCl</td>
<td>2.25</td>
</tr>
<tr>
<td>LiZn(BH$_4$)$_3$ + 2LiCl</td>
<td>1.10</td>
</tr>
<tr>
<td>Li$_2$Zn(BH$_4$)$_4$ + 2LiCl</td>
<td>0.90</td>
</tr>
<tr>
<td>Na$_2$Zn(BH$_4$)$_4$ + 2NaCl</td>
<td>1.60</td>
</tr>
<tr>
<td>Na$_2$Zn(BH$_4$)$_4$ + 2NaCl</td>
<td>1.40</td>
</tr>
<tr>
<td>KZn(BH$_4$)$_3$ + 2KCl</td>
<td>0.50</td>
</tr>
<tr>
<td>K$_2$Zn(BH$_4$)$_4$ + 2KCl</td>
<td>0.45</td>
</tr>
<tr>
<td>K$_2$Zn$_3$(BH$_4$)$_8$ + 2K$_2$Zn$_2$Cl$_7$</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 13. Approximate H$_2$ wt% released from product mixtures upon first dehydrogenation.

All the other materials (Zn(BH$_4$)$_2$, NaZn(BH$_4$)$_3$, Na$_2$Zn(BH$_4$)$_4$, K$_2$Zn$_3$(BH$_4$)$_8$) show no hydrogen release during the dehydrogenation in the second cycle (Figure 16: A; Figure 17: A, B; Figure 18: C). This indicates that the dehydrogenation reactions of these materials are not reversible; they cannot be “recharged” with hydrogen for multiple cycles. Of these materials, the highest weight percent was observed from Zn(BH$_4$)$_2$ (2.25
wt%), followed by NaZn(BH₄)₃ (1.60 wt%), then Na₂Zn(BH₄)₄ (1.40 wt%) and K₂Zn₃(BH₄)₈ (1.00 wt%). The reverse reaction may not be possible if diborane was released during dehydrogenation. This would require recharging the samples with both hydrogen and diborane in an effort to reform the decomposition reaction precursors.

According to Table 2 (Chapter 1), the expected hydrogen capacities for these materials are much higher. There are many reasons for the lower observed capacities. First, the product mixtures contain the alkali chloride salt byproducts. By taking this into consideration, the hydrogen weight percent for Zn(BH₄)₂(+ 2LiCl) becomes 4.48 wt% rather than the expected 8.50 wt%. (An attempt was made to separate K₂Zn₃(BH₄)₈ from its byproduct with THF, however characterization by XRD (not shown) proved this effort unsuccessful.)

Another reason for the discrepancy between the expected and actual results is due to the release of diborane. The TD-MS studies (Chapter 3) showed that diborane is released from the product mixtures. However, the calculations performed in the determination of hydrogen capacity assume the release of hydrogen only. This is because the exact ratio of hydrogen to diborane released from the materials is unknown. (The TD-MS data was obtained under conditions different from those used to obtain the dehydrogenation curves).

The experimental hydrogen capacities may also be lower due to decomposition during ball milling. This observation (discussed in detail in Chapter 2) was made during the synthesis when after five hours of milling some discoloration of the product mixture began to occur. The mixture changed from a bright white color to an off-white color. This discoloration is the first indication of decomposition. (Further decomposition
changes the color to gray and then black due to the presence of zinc metal). If decomposition was actually occurring during ball milling, then hydrogen may have been released during synthesis. This means that the observed hydrogen capacity would be much lower for these materials.

A final reason for the lower observed hydrogen capacities is the low temperature used in these studies. All dehydrogenation curves were obtained at 100 °C. This is well below the maximum hydrogen release observed in the TD-MS data. The low temperature was used in an attempt to target a temperature at which the materials might only release hydrogen and not a hydrogen and diborane mixture (as the release of diborane would deem the materials impractical as hydrogen storage materials). This means that the maximum amount of hydrogen contained in these materials may not have been released.

The zinc borohydride product mixture was also studied under the conditions of dehydrogenation at 120 °C (not shown). However, this gave the same result as observed at 100 °C. The hydrogen capacity was observed at a maximum of 2.25 wt% and no hydrogen was released during the second dehydrogenation.

Some researchers propose that the theoretical capacity of 8.5 wt% of Zn(BH₄)₂ can be achieved. Goswami and Stefanakos⁶⁰ reported that this could be achieved after 15-30 minutes of milling (no other conditions were given making reproducibility complicated). It was also reported that further milling reduced the capacity of their material. In addition, they showed that hydrogen storage within Zn(BH₄)₂ was reversible at 100 °C. Their results conflict in many ways with the results reported here. They claimed that XRD showed no elemental peaks of NaBH₄ and ZnCl₂ starting material. However, after two hours of milling, our XRD scans showed some starting material.

Also, they did not mention the separation of \( \text{Zn(BH}_4\text{)}_2 \) from the sodium chloride byproduct, meaning the theoretical capacity of 8.5% could not be fully achieved.

Overall, these materials do not exhibit ideal storage properties to meet today's standards for on-board applications. They exhibit low hydrogen storage capacities and are not reversible. In addition, the release of diborane is dangerous and toxic. Nevertheless, the presence of the transition metal chloride proved advantageous in that the overall dehydrogenation temperature of the alkali borohydride starting materials were lowered upon milling with zinc chloride.
CHAPTER FIVE

CONCLUSIONS
These studies have shown fundamental research involving the synthesis of novel zinc borohydride materials by mechanochemical method. Based on characterization by IR, powder XRD, and $^{11}$B NMR; the synthesis reactions resulted in the expected product formation (except those product mixtures of $\text{KZn(BH}_4\text{)}_3$ and $\text{K}_2\text{Zn(BH}_4\text{)}_4$).

In the mechanochemical synthesis of zinc borohydride and its derivatives, it turned out that KBH$_4$ as the borohydride precursor gave different types of complex borohydride compared to those from LiBH$_4$ and NaBH$_4$ precursors. In addition, the molar ratio between borohydride precursor and zinc chloride is important to the final zinc borohydride product. These indicate that it is possible to obtain novel zinc borohydride complexes by optimizing borohydride precursors and the ratio of starting materials.

Further studies demonstrated interesting material properties. Mass spectroscopy showed dehydrogenation temperature of zinc borohydride and its derivatives are much lower than those of alkali borohydrides, probably due to the different bonding between metals and borohydrides (covalent bonding in the former and ionic bonding in the latter). This indicates that synthesis of covalent transition-metal borohydrides is a promising strategy to decrease the dehydrogenation temperature of borohydrides.

Mass spectroscopy also showed the decomposition of the zinc borohydride product mixtures release not only hydrogen, but diborane gas. Nevertheless, the gas mixture had higher hydrogen content than diborane (Chapter 3, Table 12).

Dehydrogenation of the resulting zinc borohydrides gives about 0.45–2.25 weight percent hydrogen (Chapter 4, Table 13; Note: Calculations do not consider the presence of diborane gas). The much lower hydrogen capacity than the theoretical values (7.9–11.6 weight percent hydrogen; Chapter 1, Table 2) might be due to the decomposition during
the ball-milling process, the presence of the alkali chloride byproduct in the product mixture, or the low dehydrogenation temperature (100 °C). In addition, cycling experiments exhibited that the materials are not reversible under our rehydrogenation conditions (10 MPa, 100 °C).

When considering the characterization data and analysis of material properties of each complex together, it is obvious that each product mixture exhibits unique chemical and material properties which confirms their individual, exclusive identities.

Overall, these studies have exhibited a promising future for the development of novel transition metal borohydrides for the application of solid-state hydrogen storage materials.
APPENDIX A

The result of the reaction of zinc chloride and an alkali metal borohydride can be monitored by IR analysis. It has been predicted that the borohydride anion in alkali metal tetrahydroborates has a characteristic band at $\sim 2290 \text{ cm}^{-1}$. In the spectrum for zinc borohydride this band disappears and the appearance of bands corresponding to the vibrations of bridging ($\sim 2100 \text{ cm}^{-1}$) and terminal ($\sim 2450 \text{ cm}^{-1}$) B-H bonds are observed.

In the complex zinc borohydride it is assumed that each borohydride group coordinates to the zinc metal center via two bridging hydrogen bonds (bidentate coordination) as this is the most accepted model of this complex. These bonds could result in planar coordination ($D_{2h}$ symmetry) with respect to the metal center (Figure 19) or tetrahedral coordination ($C_{2v}$ symmetry) (Figure 20).

![Figure 19. Structure of zinc borohydride with planar coordination with respect to the bonding between the zinc metal center and the hydrogen bridging atoms.](image-url)
For the following analysis the focus will be on the planar coordination to the metal center for ease of interpretation (Figure 21 depicts this structure labeled for the following analysis). However, the results of the B-H stretching modes should be similar for each proposed structure.

Bridging B-H stretches are found at lower wavenumbers than terminal B-H stretches. Analysis of these stretches shows that both symmetric and asymmetric stretching takes place at the bridging and terminal B-H bonds. Tables 14 and 15 show the different possible combinations of symmetric and asymmetric stretching. The German words gerade and ungerade literally mean even and odd. Here, gerade refers to
a representation that is symmetric with respect to inversion while ungerade is a representation that is antisymmetric to inversion. According to the D<sub>2h</sub> character table, those stretches which are antisymmetric to inversion are IR active while the stretches which are symmetric to inversion are not IR active.

<table>
<thead>
<tr>
<th>Terminal B-H Stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁→B₁  B₂←H₇</td>
</tr>
<tr>
<td>H₂→B₁  B₃←H₉</td>
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<table>
<thead>
<tr>
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<th>gerade</th>
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<tbody>
<tr>
<td>H₁→B₁</td>
<td>B₂←H₇</td>
<td>H₁→B₁</td>
<td>B₂→H₇</td>
</tr>
<tr>
<td>H₂←B₁</td>
<td>B₃→H₉</td>
<td>H₂←B₁</td>
<td>B₃→H₈</td>
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<tr>
<td>H₁→B₁</td>
<td>B₂←H₇</td>
<td>H₁→B₁</td>
<td>B₂→H₇</td>
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<tr>
<td>H₂←B₁</td>
<td>B₃→H₉</td>
<td>H₂←B₁</td>
<td>B₃→H₈</td>
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Table 14. Predicted symmetric and asymmetric terminal B-H stretches for zinc borohydride.

<table>
<thead>
<tr>
<th>Bridging B-H Stretching</th>
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<tbody>
<tr>
<td>B₁→H₃  H₄←B₂</td>
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<tr>
<td>B₁→H₄  H₅←B₂</td>
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<tbody>
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<td>B₁→H₃</td>
<td>H₄←B₂</td>
<td>B₁→H₃</td>
<td>H₆→B₂</td>
</tr>
<tr>
<td>B₁←H₄</td>
<td>H₅→B₂</td>
<td>B₁←H₄</td>
<td>H₆→B₂</td>
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<tbody>
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<td>B₁→H₃</td>
<td>H₄←B₂</td>
<td>B₁→H₃</td>
<td>H₆→B₂</td>
</tr>
<tr>
<td>B₁←H₄</td>
<td>H₅→B₂</td>
<td>B₁←H₄</td>
<td>H₆→B₂</td>
</tr>
</tbody>
</table>

Table 15. Predicted symmetric and asymmetric bridging B-H stretches for zinc borohydride.

The results of this analysis show that there are two IR active terminal B-H stretches and two IR active bridging B-H stretches for zinc borohydride. However, in solid state IR (used to analyze the product mixtures in these studies), only one IR band is observed for each terminal and bridging. This is probably due to the overlapping of these bands, as they are likely very close in energy. Solid state IR usually results in broad bands while solution IR may allow these bands to be resolved into two. Also, upon the

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addition of more borohydride groups (as in the cases of LiZn(BH₄)₃ and Li₂Zn(BH₄)₄) these bands may shift (especially the bridging B-H bands) due to more intense interactions between borohydride groups.

Regardless of whether or not these bands can be resolved, the presence of bands corresponding to the bridging and terminal B-H stretches and the disappearance of bands corresponding to the borohydride anion is an indication that a chemical reaction occurred and that bonds have been formed between the zinc metal center and the borohydride ligands. This analysis also provides evidence that the borohydride groups do, in fact, coordinate via bidentate coordination rather than unidentate or tridentate coordination since an alternative coordination would not have the same expected bands.
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