Decomposition mechanisms in metal borohydrides and their ammoniates

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Ammoniation in metal borohydrides (MBs) with the form \(\text{MBH}_x\) has been shown to lower their decomposition temperatures with \(\chi\) of low electronegativity (\(\chi_p \lesssim 1.6\)), but raise it for high-\(\chi_p\) MBs (\(\chi_p \gtrsim 1.6\)). Although this behavior is just as desired, an understanding of the mechanisms that cause it is still lacking. Using \textit{ab initio} methods, we elucidate those mechanisms and find that ammoniation always causes thermodynamic destabilization, explaining the observed lower decomposition temperatures for low-\(\chi_p\) MBs. For high-\(\chi_p\) MBs, we find that ammoniation blocks \(\text{B}_2\text{H}_6\) formation—the preferred decomposition mechanism in these MBs—and thus kinetically stabilizes those phases. The shift in decomposition pathway that causes the distinct change from destabilization to stabilization around \(\chi_p = 1.6\) thus coincides with the onset of \(\text{B}_2\text{H}_6\) formation in MBs. Furthermore, with our analysis we are also able to explain why these materials release either \(\text{H}_2\) or \(\text{NH}_3\) gas upon decomposition. We find that \(\text{NH}_3\) is much more strongly coordinated with higher-\(\chi_p\) metals and direct \(\text{H}_2\) formation/release becomes more favorable in these materials. Our findings are of importance for unraveling the hydrogen release mechanisms in an important new and promising class of hydrogen storage materials, allowing for a guided tuning of their chemistry to further improve their properties.

1 Introduction

Hydrogen is an ideal energy carrier in a clean energy system\cite{1,2} but there is no known material to economically and safely store hydrogen in a package sufficiently small and hydrogen-dense for use in mobile applications. In the search for a material that meets the US Department of Energy’s targets for a practical hydrogen storage material,\cite{3,4} metal borohydrides (MBs) have seen a surge of interest\cite{5,6} and remain one of the most promising classes of hydrogen storage materials.\cite{7} In recent years, various studies have found that these metal borohydrides typically demonstrate improved hydrogen storage properties when complexed with ammonia, forming a new class of materials called metal borohydride ammoniates (MBAs).\cite{10,11} Generally, MBAs tend to release hydrogen gas at more practical temperatures and greater purity than their plain MB counterparts.\cite{12} Furthermore, recent experiments have mixed various MBAs with MBs or ammonia borane (\(\text{NH}_3\text{BH}_3\)) to tune the \(\text{H}_2\) release temperature and purity.\cite{13,14}

Looking at the available experimental data for a large number of MBAs, a clear pattern emerges between the Pauling electronegativity \(\chi_p\) of the metal \(\chi\) in \(\text{MBH}_x\), and the material’s decomposition temperature.\cite{15} As can be seen in Fig. \ref{fig:1} ammoniating a MB lowers the decomposition temperature of an MBA based on a metal with electronegativity \(\chi_p \lesssim 1.6\), but stabilizes an MBA based on a high-electronegativity metal with \(\chi_p \gtrsim 1.6\). While this experimental observation constitutes significant progress towards improved hydrogen storage materials, the underlying mechanism causing it is not understood. As such, further systematic improvements beyond simple trial-and-error attempts are challenging. In this paper, we present possible solutions and describe mechanisms that cause the ammoniation to “magically” destabilize just those MBs that need it, while stabilizing those that benefit from a higher decomposition temperature.

Focusing on decomposition temperature alone, however, over-simplifies the understanding of how these materials decompose. There are competing decomposition mechanisms for each of these materials, resulting in different gaseous products—mostly either \(\text{NH}_3\) or \(\text{H}_2\). These products have been included in Fig. \ref{fig:2} and split the destabilized set of materials into two distinct groups: those with low electronegativity (\(\chi_p \lesssim 1.2\)) that release mostly \(\text{NH}_3\) in open systems and those with medium electronegativity (\(1.2 \lesssim \chi_p \lesssim 1.6\)) that may release \(\text{NH}_3\) at lower temperatures and then transition to releasing mostly \(\text{H}_2\) at higher temperatures.

In the decomposition pathway releasing ammonia, the thermodynamics are such that releasing ammonia gas is more favorable than remaining in the MBA structure.\cite{22} As we will discuss in detail below, our data indicates that the ammonia is more weakly bound to the metal in MBAs where \(\chi\) has lower electronegativity. At the temperature where this process occurs, the remaining MBA (or plain MB) is below its decomposition temperature, and
and stabilization observed in Fig. 1. Next, we analyze the thermodynamical stability and find that ammoniation always leads to a lowering of stability. While that explains the lowering of materials with $\chi_p \lesssim 1.6$ in Fig. 1, it does not explain the stabilization for $\chi_p \gtrsim 1.6$. Finally, directly simulating the hydrogen release process, we find that those high-$\chi_p$ materials get kinetically stabilized in that ammoniation blocks the usual decomposition pathway. The exact mechanism is material dependent and we will explain it on a case-by-case basis.

2 Computational Details

We performed calculations using density-functional theory (DFT) as implemented in VASP using the included projector augmented wave (PAW) pseudopotentials and a plane wave energy cutoff of 500 eV. We converged self-consistent energies to at least $10^{-5}$ eV and relaxed all atomic positions until all forces dropped below 10 meV/Å. Because of different unit cell sizes, k-point meshes varied, but all used Γ centered Monkhorst-Pack meshes automatically generated in VASP with at least 20k points in each direction, where $b$ is the length of the reciprocal lattice vector in Å$^{-1}$. We used the vdW-DF1 density-functional to properly account for the van der Waals interactions in the dihydrogen bond networks in these materials.

We performed transition-state searches in VASP using the climbing image nudged elastic band (NEB) method implemented in the VST package. In the case of B$_2$H$_6$ formation, we generated end-point structures for these calculations by bringing together nearby BH$_4$ molecules in the ground-state structures in a directed perturbation of the system to form a stable B$_2$H$_6$ molecule in the structure. This was done through an automated process that first moved the BH$_4$ molecules away from the metal cation or cations to which they were coordinated and then formed a B$_2$H$_6$ molecule along the axis between the moved BH$_4$ molecules. The remaining two H atoms were moved to the original locations of the BH$_4$ molecules. These structures were then allowed to relax until all ionic forces dropped below 10 meV/Å.

In most cases, crystal structures are taken from experiment, but in some cases we drew from theoretical work. Corresponding references are given in Table 1. For transition-state searches, we expanded any structures containing only one formula unit into a $2\times2\times2$ supercell in order to avoid too much distortion in the crystal structure.

3 Results and Discussion

3.1 Examining the dihydrogen bond network

A first attempt to explain the peculiar effect that ammoniation has on the decomposition in Fig. 1 is to study the dihydrogen bond networks in these materials. All MBA materials contain networks of heteropolar dihydrogen bonds (H$^\delta^-$...H$^\delta^+$) and it has been suggested that the proximity of the protic N–H and hydridic B–H allows H$_2$ creation through the simple combination of H$^\delta^+$ and H$^\delta^-$. In low-$\chi_p$ materials, this combination process is suspected to be a possible hydrogen production mechanism and it was proposed that stabilization of high-$\chi_p$ materials may be due to shielding of the metal. The dihydrogen bonds clearly play
some role in determining the stability of these materials, as well as their decomposition, and further investigation is warranted.

We start by analyzing these interactions through a charge partitioning scheme and study how charge is distributed between the H atoms and the small molecules in which they reside. Figures 2 and 3 show the Bader charge of BH4 and NH3 molecules in all MBAs from Table 1 relative to neutral molecules of the same composition. The plots show that the metal's electronegativity weakly affects the charge distribution in these molecules. Higher electronegativity results in weaker BH4− and NH3 anions and NH3 molecules that begin to share charge with other constituents of the material.

On the level of individual H atoms, Fig. 2 shows that some materials demonstrate relatively large variations in the charge held by H atoms in the same molecule. This variation is likely due to how the molecules stack to form a crystal structure; the structure of Al(BH4)3 is built from Al(BH4)3 units where each BH4 coordinates to only one Al atom, but the BH4 units in Zn(BH4)2 act as bridges between multiple Zn atoms. Consequently, the charge on a BH4 anion in Al(BH4)3 is more concentrated on one side of the molecule, giving the H atoms in Al(BH4)3 a larger variation in charge than those in Zn(BH4)2.

We also investigated the effect of the H···H bond length on how much charge builds up on the H atoms in these materials; one might expect that shorter bond lengths would draw stronger relative charges for H5+ and H1−. Figure 4 shows that H3+ in NH3 on average does draw more charge when involved in shorter dihydrogen bonds, but the relationship is weak and H3− shows no relationship at all. To demonstrate the strength of this relationship, we modeled the dihydrogen bond as a Coulomb interaction (q1q2/r2) with calculated Bader charges of H3+ and H1− as q1 and q2. Figure 5 shows that the data points fall almost perfectly along a fit generated by using the average H3+ and H1− charges that we calculated from all MBAs included in Table 1. Thus, bond length has a weak effect on charge buildup on H3+ atoms, and the corresponding increase in the electrostatic force across the bond is very small. This means that there is almost no additional charge polarization across the NH3 and [BH4]− molecules due to short dihydrogen bond lengths and any significant effects are localized to the electron clouds around the H atoms.

To summarize, χp and the specific geometry of the structure are more important for determining the charge distribution in the material than bond lengths. These results indicate that the dihydrogen bond network is very similar between different MBAs. While the dihydrogen bond network may play an important role in the decomposition process, that role does not appear to be linked in an obvious way with χp. It follows that variations (by themselves) in the dihydrogen bond network from one MBA to another cannot explain the distinct destabilizing/stabilizing effect of ammoniation observable in Fig. 1.

### 3.2 Examining thermodynamic stability

Moving beyond the dihydrogen bond network, we next examine the thermodynamics of the ammoniation process by calculating the energy of formation for both MB and MBA materials relative to their constituents in their natural states (i.e., the appropriate, separate amounts of solid Al and B, and gaseous N2 and H2). The results are given in Table 2 and shown graphically in Fig. 6.

The primary result from these data is that all MBAs are thermodynamically destabilized relative to their plain MB counterparts. Furthermore, sequential events of NH3 release from the same structure typically results in a MBA with lower energy of formation per atom. For instance, Sr(BH4)2·4NH3 may decompose by releasing 2NH3, leaving Sr(BH4)2·2NH3, which has a lower energy of formation per atom.

Note that NH3 release in these materials is frequently accompanied by an endothermic event, whereas lowering energy per
3.3 Examining decomposition processes

The processes by which these MBAs decompose have not been clearly determined experimentally. The possible pathways range from simple direct formation of H$_2$ from H$_2^+$ and H$_2^-$ to very complex interactions forming boron nitrides similar to those found in the decomposition of NH$_3$BH$_3$. The observed final products are typically amorphous and poorly characterized. This uncertainty makes the decomposition process difficult to model; without good guidelines from experiment the possible search space is vast.

One recent theoretical study simulated the decomposition of LiBH$_4$-NH$_3$ and Mg(BH$_4$)$_2$-2NH$_3$ and suggests that the decomposition process begins with the NH$_3$ drifting away from the $\mathcal{M}$(BH$_4$)$_3$, allowing the $\mathcal{M}$(BH$_4$)$_3$ to polymerize with its neighbors. Then H$_2^+$ in NH$_3$ attacks H$_2^-$ from [BH$_4$]$^-$. While those findings are valuable, it is unclear whether they can be generalized to materials with $\mathcal{M}$ of very different electronegativities. As mentioned in Section 3.1, the direct combination of H$_2^+$ and H$_2^-$ has been suggested to be a possible hydrogen production mechanism in low-$\chi_p$ materials, and simulated in a few MBAs, but in high-$\chi_p$ materials, the direct H$_2$ creation pathway would compete with the B$_2$H$_6$ creation pathway from the plain MB. B$_2$H$_6$ release is always suppressed in the ammoniated materials, but it is not immediately obvious whether this is because the diborane production pathway has been circumvented or because the produced B$_2$H$_6$ react immediately with the NH$_3$. To elucidate these issues, we simulate each of the broad categories mentioned above—NH$_3$ release, direct H$_2$ formation, and B$_2$H$_6$ formation—and find that each of them becomes the dominating pathway for low-, mid-, and high-$\chi_p$ values, respectively.

3.3.1 NH$_3$ release

Low-$\chi_p$ materials release NH$_3$ preferentially to H$_2$ or B$_2$H$_6$, and some mid-$\chi_p$ materials release NH$_3$ as they are heated before switching to H$_2$ release—see Fig. 1. In order for an MBA to release NH$_3$, the NH$_3$ must escape the metal to which it is coordinated and then escape as a gas.

We quantitatively studied the behavior of the $\mathcal{M}$-NH$_3$ bond by

\[ \mathcal{M}(\text{BH}_4)_3 + \chi_p \cdot \text{NH}_3 \rightarrow \mathcal{M}(\text{BH}_4)_3 \cdot (\chi_p - \chi)\text{NH}_3 + \chi_p \text{NH}_3 \]
approximating it as a spring. For small displacements of NH$_3$ with respect to $\chi_p$, we calculated the total energy of the system and based the increase in energy relative to the ground state we extracted a spring constant from Hooke’s law. The results (depicted in Fig. 7) show that the NH$_3$ molecules face much steeper potential surfaces in high-$\chi_p$ materials, agreeing with the conventional wisdom.$^{13,35}$ This means that NH$_3$ in low-$\chi_p$ MBAs can escape more easily, explaining why these materials can decompose at lower temperatures compared to plain MBs by releasing NH$_3$, whereas the high-$\chi_p$ MBAs do not—see Fig. 1. Going from low-$\chi_p$ values to higher ones, we also see in Fig. 7 that the NH$_3$ release becomes energetically more and more expensive, suggesting that eventually there will be a change in decomposition mechanism once an energetically more favorable pathway becomes available.

In addition to NH$_3$ formation, we must also consider how the NH$_3$ escapes the material before it can be released as a gas. This kind of process may first occur near the surface of the material, creating vacancy defects in the material. Similarly to how Li$^+$ diffuses through LiBH$_4$ as it decomposes by hopping between vacancy defects,$^{29}$ we suggest that NH$_3$ may be able to migrate to the surface through such vacancies.

### 3.3.2 Direct H$_2$ formation

Direct H$_2$ formation has been suggested as dehydrogenation pathway,$^{13,35}$ and can become a more energetically favorable alternative to NH$_3$ release. We modeled direct H$_2$ formation from the H$_2^+$ and H$^-$ pairs that make up the dihydrogen bond network by generating structures that would be similar to transition states for the reaction. We did this by moving H$_2^+$ and H$^-$ from one dihydrogen bond to a separation of 0.74 Å along the axis between them and holding their positions fixed while optimizing the rest of the structure. We did this relaxation for each dihydrogen bond under 2.5 Å; the lowest resulting energies are shown in Fig 8. NEB calculations revealed that there is no kinetic barrier between the ground state structures and the ones that we generated, so we use these energies to approximate the cost of direct H$_2$ production.

Typically, this procedure resulted in the BH$_3$ shifting to capture the H$_2^+$ and the remaining NH$_3$ shortening its distance to the metal cation, with the net result of a BH$_3$H$_2$ and the H$_2$ would only need to break away from the [BH$_3$]$^-$ and diffuse out of the material. This result suggests that in an MBA, H is easier to liberate from NH$_3$ than from [BH$_3$]$^-$ regardless of the metal’s $\chi_p$.

Interestingly, Fig. 6 shows a negative relationship between $\chi_p$ and the barrier to direct H$_2$ creation; while direct H$_2$ release is very expensive in low-$\chi_p$ MBAs, it becomes significantly more favorable for higher-$\chi_p$ materials. One important note that may not be evident in the plot is that structures where the metal is directly bound only to NH$_3$ (e.g. Zr(BH$_4$)$_3$·8NH$_3$ or Al(BH$_4$)$_3$·6NH$_3$) tend to have lower-energy transition states than the structures where the $\text{M}(\text{BH}_4)_3$ units are maintained. This may have to do with

| Formula   | $\chi_p$ | $\Delta E_{\text{atom}}$ | $T_{\text{dec}}$ |
|-----------|----------|--------------------------|-----------------|
| Sr(BH$_4$)$_2$·4NH$_3$ | 0.95     | -0.130                   | 14              |
| Sr(BH$_4$)$_2$·2NH$_3$ | 0.95     | -0.298                   | 130             |
| Sr(BH$_4$)$_2$·NH$_3$  | 0.95     | -0.432                   | 150             |
| Sr(BH$_4$)$_2$         | 0.95     | -0.643                   | 400             |
| Ca(BH$_4$)$_2$·4NH$_3$ | 1.00     | -0.309                   | 85              |
| Ca(BH$_4$)$_2$·2NH$_3$ | 1.00     | -0.286                   | 160             |
| Ca(BH$_4$)$_2$·NH$_3$  | 1.00     | -0.414                   | 225             |
| Ca(BH$_4$)$_2$         | 1.00     | -0.622                   | 380             |
| Y(BH$_4$)$_2$·7NH$_3$  | 1.22     | -0.069                   | 70              |
| Y(BH$_4$)$_2$·6NH$_3$  | 1.22     | -0.066                   | 80              |
| Y(BH$_4$)$_2$·5NH$_3$  | 1.22     | -0.097                   | 110             |
| Mn(BH$_4$)$_2$·3NH$_3$ | 1.55     | -0.016                   | 80              |
| Y(BH$_4$)$_2$·4NH$_3$  | 1.22     | -0.171                   | 165             |
| Y(BH$_4$)$_2$·2NH$_3$  | 1.22     | -0.316                   | 190             |
| Y(BH$_4$)$_2$·NH$_3$   | 1.22     | -0.409                   | 195             |
| Y(BH$_4$)$_2$          | 1.22     | -0.680                   | 200             |
| Mg(BH$_4$)$_2$·2NH$_3$ | 1.31     | -0.131                   | 205             |
| Mg(BH$_4$)$_2$         | 1.31     | -0.339                   | 260             |
| Zr(BH$_4$)$_2$·8NH$_3$ | 1.33     | -0.024                   | 60              |
| Zr(BH$_4$)$_2$         | 1.33     | -0.423                   | 250             |
| Mn(BH$_4$)$_2$·2NH$_3$ | 1.55     | -0.074                   | 135             |
| Mn(BH$_4$)$_2$         | 1.55     | -0.238                   | 155             |
| Al(BH$_4$)$_2$·6NH$_3$ | 1.61     | -0.057                   | 167             |
| Al(BH$_4$)$_2$         | 1.61     | -0.345                   | 15              |
| Zn(BH$_4$)$_2$·2NH$_3$ | 1.65     | -0.087                   | 131             |
| Zn(BH$_4$)$_2$         | 1.65     | -0.249                   | -35             |
| Na$_2$Zn(BH$_4$)$_3$·2NH$_3$ | 0.93, 1.65 | -0.190                  | 133             |
| Li$_2$Mg(BH$_4$)$_3$·6NH$_3$ | 0.98, 1.31 | -0.140                  | 80              |
| Li$_2$Al(BH$_4$)$_3$·6NH$_3$ | 0.98, 1.61 | -0.180                  | 138             |
3.3 Examining decomposition processes

3 RESULTS AND DISCUSSION

BH₄ units being less restricted in their movements when they are not coordinated with any particular metal.

In combination with the previous section we conclude that for low-χₚ MBAs the direct H₂ release is energetically expensive (Fig. 8) whereas NH₃ release is favorable (Fig. 7). Going to higher χₚ values, there is a crossover in those two behaviors and for high-χₚ we find that NH₃ release is now energetically very expensive, while direct H₂ release has become more favorable. This crossover nicely explains the shift from NH₃ release to H₂ observed in Fig. 7. However, it does not explain higher decomposition temperatures for ammonia for high-χₚ materials, which we will further explore in the last section.

3.3.3 B₂H₆ production followed by H₂ release

Up to this point we have found that ammoniation thermodynamically destabilizes all MBs. In addition, the previous two sections help understand the shift in release product as a function of χₚ. But, why do high-χₚ MBs with Al and Zn get stabilized upon ammoniation? As we will show, the ammoniation blocks the standard decomposition pathway that these materials prefer, thus kinetically stabilizing those MBs. We know from the last section that direct H₂ release becomes favorable at mid-χₚ values, but it remains energetically quite expensive. Another pathway for MBs to decompose is through the formation of B₂H₆. Previous studies show a strong correlation between χₚ [31] and decomposition via B₂H₆ formation over B₂H₄ and the reaction for MBs. They also show that this pathway opens up for χₚ ≳ 1.6, where it becomes—as we will show below—an energetically favorable alternative to direct H₂ formation.

Jepsen and coworkers note that B₂H₆ release is always suppressed in the presence of NH₃, where the two react to form ammine metal borohydrides, suggesting that B₂H₆ may be an intermediate in the H₂ release pathway. These materials have a higher decomposition temperature after the ammoniation process, but at the higher temperature where the MBA begins to decompose, the same B₂H₆ formation process may occur. A very low kinetic barrier of only ~ 0.7 eV was found for the reaction:

\[ \text{B}_2\text{H}_6 + \text{NH}_3 \rightarrow \text{NH}_2\text{BH}_2 + \text{BH}_3 + \text{H}_2 \]  (2)

making B₂H₆ formation followed by H₂ release energetically favorable over direct H₂ formation.

If the kinetic barrier to reaction (2) remains small in the MBA environment, then the only other possible bottleneck in MBA decomposition through the B₂H₆ release pathway is the formation of the B₂H₆ intermediate itself. We performed a transition state search using the NEB method to find the kinetic barriers to B₂H₆ production in selected MBAs, as well as the materials’ plain MB counterparts. To find realistic endpoints, we simulated perturbing the system in configuration space by pulling nearby BH₄ units together and allowing the system to relax to a local energy minimum. We performed this process over 250 times and while the relaxations sometimes yielded the desired B₂H₆, it more often resulted in the creation of B₂H₄—a structure that has been observed experimentally [32] and considered as a potential metastable intermediate in Mg(BH₄)₂ decomposition. [32] While B₂H₆ can lead to hydrogen release via reaction (2) with a barrier of ~ 0.7 eV, we found no such reaction with B₂H₇. Instead, using NEB calculation we found that the reaction

\[ [\text{B}_2\text{H}_7]^- + \text{NH}_3 \rightarrow \text{NH}_2\text{BH}_3 + [\text{BH}_4]^- \]  (3)

has a barrier of only 0.75 eV relative to the NH₃ and [B₂H₇]⁻ molecules by themselves in the gas phase—and is thus equally favorable as reaction (2). After this reaction, the NH₃BH₃ is free to decompose on its own (pure NH₃BH₃ decomposes to NH₃BH₂, releasing H₂ at around 100 °C, facing a kinetic barrier of about
In addition to the low reaction barrier, any produced borane must diffuse to the surface in order to escape the system. While we have not performed diffusion simulations in these materials, we argue that the kinetic barrier for this diffusion should increase in MBAs because the dihydrogen bond network creates a steeper potential surface that the molecules would need to traverse, potentially trapping the molecules in the material until they react with NH$_3$.

So, both B$_2$H$_6$ and B$_2$H$_7$ can eventually produce molecular hydrogen via reactions (2) and (3) with barriers of only $\sim$0.7 eV and the formation of B$_2$H$_6$ and B$_2$H$_7$ themselves might now be the rate-limiting step. We thus calculated and report kinetic barriers to the creation of both B$_2$H$_6$ and B$_2$H$_7$ in Fig. 9. We did not calculate kinetic barriers to endpoints that we found were $\geq$ 3 eV above the ground state structure. We find that the kinetic barriers decrease in higher $\chi_p$ materials, making this pathway viable for $\chi_p \gtrsim 1.6$, as suggested previously. In particular, for these high-$\chi_p$ values, this pathway becomes more favorable than direct H$_2$ release (compare Figs. 8 and 9). It only remains to investigate the effect of ammoniation on this pathway and we analyze the two cases $\mathcal{M} = \text{Al}$ and Zn separately.

In Al(BH$_4$)$_3$-6NH$_3$, the ammoniation drastically increases the barrier for B$_2$H$_7$ formation and we could not even find a pathway for B$_2$H$_6$ formation. Ammoniation has thus made this decomposition pathway practically inaccessible below the material’s decomposition temperature, kinetically stabilizing the Al case. B$_2$H$_6$ formation in Zn(BH$_4$)$_2$-2NH$_3$ faces only a slightly increased barrier upon ammoniation, but a significantly decreased barrier for B$_2$H$_7$ formation, pushing the system towards reaction (3). The decomposition is then governed by the hydrogen release from NH$_3$BH$_3$, which occurs around 100 °C and explains the stabilization seen for Zn in Fig. 1.

The difference between Al and Zn may be due to whether the [BH$_4$]$^-$ anions are able to transfer H$^+$ as they form B$_2$H$_6$. In Zn(BH$_4$)$_2$-2NH$_3$, the BH$_4$ are still coordinated with the metal, making the electron transfer simple, but in Al(BH$_4$)$_3$-6NH$_3$, the NH$_3$ molecules may act as neutral ligands, preventing reduction of the metal. Roedern and Jensen made a similar assertion in the case of transition-metal MBA$_3$.

The reasons differ for Al and Zn, but in both cases, the B$_2$H$_6$ formation pathway that dominates decomposition in the plain MB becomes unavailable after ammoniation, leading to a higher decomposition temperature observed in Fig. 1.

### 4 Conclusions

We have examined the decomposition processes of MBAs in order to explain why the ammoniation process results in lower decomposition temperatures in materials with low-$\chi_p$ metals and higher ones for those with high-$\chi_p$ metals.

We found that the dihydrogen bond networks remain very similar between low and high-$\chi_p$ materials and cannot explain the sharp distinction between them in terms of the effect of ammoniation. We also found that the ammoniation process always thermodynamically destabilizes MBs, while—at the same time—a few low-$\chi_p$ materials get kinetically stabilized through a shift in decomposition mechanism. We examined three possible decomposition mechanisms: NH$_3$ release, direct H$_2$ release, and B$_2$H$_6$ or B$_2$H$_7$ formation followed by H$_2$ release. At low-$\chi_p$, NH$_3$ is weakly bound to the metal and the material decomposes by releasing it. Going to mid-$\chi_p$ values, the release of NH$_3$ becomes less favorable and the materials switch to direct H$_2$ release, which becomes more favorable with higher $\chi_p$. Finally, for $\chi_p \gtrsim 1.6$, the production of B$_2$H$_6$ or B$_2$H$_7$ formation becomes more favorable than direct H$_2$ release, resulting in indirect H$_2$ release via case-by-case mechanisms. For the special cases of Al and Zn MBs, we further found that this pathway becomes inaccessible upon ammoniation and those phases get kinetically stabilized. In Al(BH$_4$)$_3$-6NH$_3$, NH$_3$ shields the metal from being reduced, preventing the electron transfer that occurs in B$_2$H$_6$ formation, leaving direct H$_2$ formation as the only available decomposition pathway. In Zn(BH$_4$)$_2$-2NH$_3$, B$_2$H$_7$ formation becomes more favorable, leading to the formation of NH$_3$BH$_3$ rather than B$_2$H$_6$. We can thus explain the peculiar stabilization effect of ammoniation in MBs and link it to the exact onset of diborane production.

These insights into how ammoniation affects decomposition processes in MBs can be used to design new mixed-metal MBA materials that decompose in a more desirable fashion or suggest better catalysts for decomposition, perhaps resulting in more reversible hydrogen storage materials.

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