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Dehydrogenation Promotion of $\text{LiBH}_4 \cdot \text{NH}_3$ Through Heating in Ammonia or Mixing with Metal Hydrides

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Amminelithium borohydride ($\text{LiBH}_4 \cdot \text{NH}_3$) is one of the most hydrogen-rich inorganic materials, showing potential application for hydrogen storage. In this paper, the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$ was promoted significantly through heating in ammonia atmosphere which demonstrated that the coordinate between NH_3 and LiBH_4 is a crucial factor in inducing the hydrogen release for this system. Meanwhile, several metal hydrides LiH , NaH , and CaH_2 were found to be effective in promoting the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$. Among the studied additives, the effect of LiH , as an example, was discussed in detail. It was found that the promotion of dehydrogenation through LiH is due to the reaction: $3\text{LiH} + 3\text{LiBH}_4 \cdot \text{NH}_3 \rightarrow \text{Li}_4\text{BN}_3\text{H}_{10} + 2\text{LiBH}_4 + 3\text{H}_2$, releasing hydrogen from 60 °C.

Introduction

Solid-state hydrogen storage systems hold great promise for onboard applications. The key criteria for a successful system are high storage capacity, suitable thermodynamics, and fast hydriding and dehydriding kinetics.^{1,2} After decades of intensive work, a series of candidates, including metal hydrides,^{3,4} chemical hydrides,^{5–8} organometallic complexes,⁹ etc., have been investigated and developed. However, no single system has yet been identified that satisfies all the criteria for hydrogen storage in automobile applications.

Recently, ammonia complexes of metal borohydrides, $\text{M}(\text{BH}_4)_m \cdot n\text{NH}_3$, where M is a metal, showed potential as solid hydrogen storage materials.^{10–12} In these compounds, the hydrogen on the nitrogen and boron in their molecules shows protic and hydridic characteristics, respectively, which may allow a facile H_2 elimination pathway, as demonstrated by many previous reports.^{12–24} For instance, $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ has a hydrogen capacity of 16.0 wt % and starts to release hydrogen below 150 °C,¹² which is considered to be competitive with the promising ammonia borane.^{14–16}

Among these ammonia complexes, amminelithium borohydride ($\text{LiBH}_4 \cdot \text{NH}_3$) holds the highest hydrogen capacity of 18.0 wt % and it is also one of the most hydrogen-rich inorganic materials. This material was first reported 50 years ago.¹³ Recently, its crystal structure and decomposition properties have been studied in detail.^{25,26} It has been revealed that $\text{LiBH}_4 \cdot \text{NH}_3$ mainly releases ammonia rather than hydrogen during heating, although the presence of the $\text{N}-\text{H} \cdots \text{H}-\text{B}$ dihydrogen bond ($\text{H} \cdots \text{H} < 2.4 \text{ \AA}$) and relatively close interactions between the BH_4^- anions and NH_3 molecules have been determined in this compound. It has thus been proposed as an effective ammonia storage compound.²⁵ In our recent work, we have demonstrated that $\text{LiBH}_4 \cdot \text{NH}_3$ is able to release a small amount of hydrogen with fast heating rate to around 280 °C in argon, and enhanced hydrogen evolution can be achieved by heating under am-

monia.²⁶ However, the role of an ammonia atmosphere in improving the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$ and its detailed decomposition mechanism were not discussed.

In this paper, the role of ammonia in improving the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$ was studied. In an effort to further promote the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$, mixing it with various metal hydrides has been conducted and several metal hydrides, LiH , NaH , and CaH_2 , were found to be effective in improving the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$.

Experimental Section

The source materials were obtained commercially: LiBH_4 (granule, 95%, Sigma-Aldrich, USA), LiH (98%, –30 mesh powder, Sigma-Aldrich, USA), and NH_3 (Alfa Aesar, USA). LiBH_4 and LiH were used as received. NH_3 was purified by soda lime when used. All handling except for ammonia related procedures was conducted under anaerobic and anhydrous condition by Schlenk techniques and in a glovebox filled with argon.

$\text{LiBH}_4 \cdot \text{NH}_3$ was prepared by exposing LiBH_4 to NH_3 atmosphere at room temperature. Figure S1 (Supporting Information) shows a schematic diagram of the reaction system. A 1.0 g portion of LiBH_4 was loaded into a Schlenk tube and evacuated by a rotary vacuum pump. Subsequently, purified NH_3 at 1 bar pressure was introduced into the tube and kept there for 20 min. The tube was then evacuated for 3 h to yield $\text{LiBH}_4 \cdot \text{NH}_3$.

The mole ratio of NH_3 to LiBH_4 in the product was examined by the following formula: $x = (\text{weight gain}/\text{initial weight of } \text{LiBH}_4) \times 21.8/17.03$. By weighing the products, the mole ratio of NH_3 to LiBH_4 for the prepared sample was determined to be 1.01. The XRD pattern also confirms the formation of $\text{LiBH}_4 \cdot \text{NH}_3$ (Figure S2, Supporting Information).

$\text{LiH}/\text{LiBH}_4 \cdot \text{NH}_3$, $\text{NaH}/\text{LiBH}_4 \cdot \text{NH}_3$, $\text{CaH}_2/\text{LiBH}_4 \cdot \text{NH}_3$, and $\text{MgH}_2/\text{LiBH}_4 \cdot \text{NH}_3$ were prepared by mixing $\text{LiBH}_4 \cdot \text{NH}_3$ with the metal hydride, then the mixture was hand milled for 10 min to get the composites.

Thermal property measurements were performed by thermogravimetry (TGA, STA 409C)/mass spectroscopy (MS, QMS

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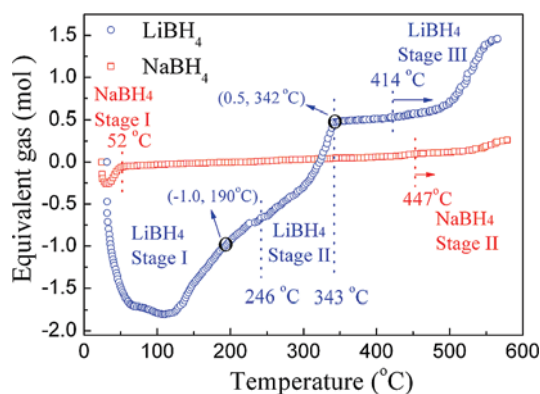


Figure 1. TPD results for LiBH₄ and NaBH₄ in ammonia at heating rates of 5 °C/min.

403) with a heating rate of 10 °C/min under 1 atm of argon. The sample cell was exposed to vacuum and then filled with argon three times before the measurement to avoid oxidation during heating. Desorption properties for some samples were also evaluated using Sievert's volumetric methods with various heating rates under argon at a pressure of 1 bar or ammonia atmosphere with various pressures.

Powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements were conducted to confirm the phase structure. Amorphous polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD measurement. FTIR (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bonds. Samples were pressed with KBr and then loaded into a sealed chamber filled with argon to be measured.

Results and Discussion

1. Dehydrogenation Promotion in Ammonia Atmosphere.

As revealed in our previous study, fast heating rate and the presence of ammonia atmosphere are benefit to increase the hydrogen release content of LiBH₄·NH₃ due to the inhibition of ammonia release at low temperature.²⁶ Herein, the decomposition properties of LiBH₄ under ammonia were investigated in detail in order to get an in-depth understanding of the dehydrogenation mechanism of LiBH₄·NH₃. Figure 1 shows the TPD result of LiBH₄ in 1.5 atm of ammonia, in which three apparent stages can be observed. In the first stage, LiBH₄ quickly absorbed ammonia to form coordination compounds of LiBH₄·xNH₃.²⁶ After heating to about 100 °C, the coordination compounds started to release ammonia and the LiBH₄·NH₃ can be stable until 190 °C, which is much higher than the onset decomposition temperature (~60 °C) of LiBH₄·NH₃ in argon,²⁶ indicating that the presence of ammonia is very effective in stabilizing the ammonia in this compound. In the second stage, gas release proceeded from 120 to 350 °C with an increase gas amount of 0.5 equiv, strongly suggesting that hydrogen release has occurred in this stage. In addition, after the second stage, a weight increase of 10 wt.% was present, which may result from the reaction of LiBH₄ with NH₃, introducing some N into the product. Combined with the results of weight change and gas evolution, the mole ratio of the reacted NH₃ to LiBH₄ is calculated to be 0.23, indicating that the majority of [BH₄]⁻ may still remain. From the XRD patterns for the product heated to 340 °C in ammonia (Figure 2), peaks assigned to LiBH₄ together with other unidentified ones were observed. These unidentified peaks should ascribe to the products of the dehydrogenation reaction. The appearance of LiBH₄ is accordant with the TPD results discussed above. Consequently, the gas evolution in the third stage, starting

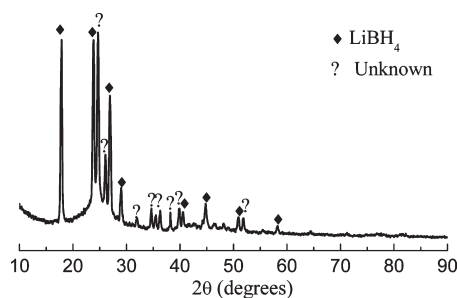


Figure 2. XRD pattern for LiBH₄ heated in 1.5 atm of ammonia to 350 °C.

from above 410 °C should mainly correspond to the dehydrogenation of the regenerated LiBH₄.

As for the above procedure, a seemingly contradictory phenomenon was presented, in which the hydrogen release induced through the combination of [BH₄]⁻ and NH₃ ceased abruptly when temperature rose above 343 °C although a substantial amount of LiBH₄ remained. However, it is not difficult to discover that the temperature contributes a negative effect on the coordination between LiBH₄ and NH₃, namely, higher temperature destroys the Li–N coordinate bond. At lower temperature, NH₃ can bond to LiBH₄ to form LiBH₄·xNH₃, but at a higher temperature (e.g., >343 °C), LiBH₄·xNH₃ will decompose into LiBH₄ and gaseous NH₃. Thus, it is concluded that the formation of a Li–N coordinate bond between LiBH₄ and NH₃ was crucial in inducing the dehydrogenation. To confirm the above assumption, the decomposition properties for an alternative borohydride, NaBH₄, was investigated at the same conditions. TPD results (Figure 1) revealed that the NaBH₄ can also absorb ammonia at low temperature, but the formed coordinate compound was very unstable and decomposed completely at 52 °C, implying its quite weak binding strength compared to LiBH₄·NH₃. Further heating NaBH₄, distinguished from that of LiBH₄, no apparent gas evolution was observed until the sample was heated above the decomposition temperature of NaBH₄. This result clearly demonstrates that formation of a coordinate between NH₃ and borohydrides is benefit to the combination of [BH₄]⁻ and NH₃ to release hydrogen.

Furthermore, it is known that an equilibrium exists between the ammonia complex of LiBH₄ and the ammonia pressure, i.e., a higher pressure resulting in a larger ammonia content in the ammonia complex of LiBH₄ at a certain temperature.¹³ It suggests that an elevated ammonia pressure may be effective in improving the dehydrogenation properties of the ammonia complex. Figure 3a shows the TPD curves for LiBH₄ in ammonia with various pressures. All these processes undergo similar stages: ammonia absorption, ammonia desorption, and hydrogen releasing. But the final gas release content increased with increasing ammonia pressure. On the basis of the gravimetric and volumetric results, the N content in the final product and the hydrogen release amount can be calculated²⁶ as shown in Figure 3b. It revealed that both the N content in the final product and the hydrogen release content increased with the increase of the ammonia pressure. This further confirms that the formation of a coordinate bond between NH₃ and LiBH₄ is crucial for the hydrogen release from this system. Generally, an ammonia atmosphere is a benefit for the stabilization of the coordinate compound of LiBH₄·NH₃ and an elevated ammonia pressure may enable more NH₃ bonding to LiBH₄ at the temperature above the dehydrogenation temperature, resulting in promotion of hydrogen release during heating.

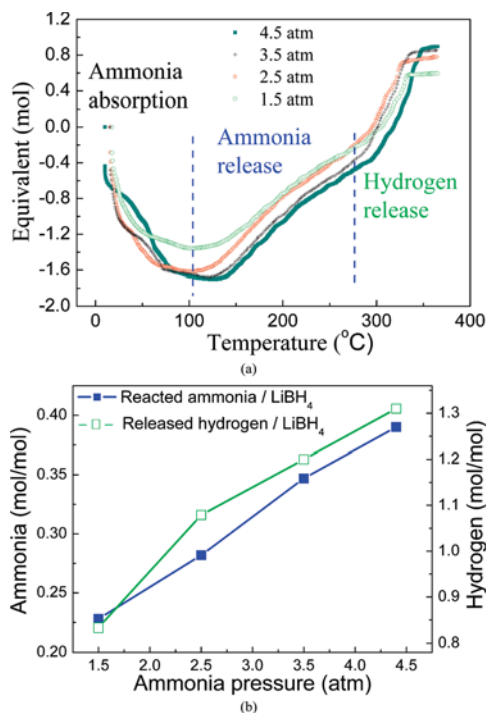


Figure 3. (a) TPD results for LiBH_4 in ammonia with various pressure ranging from 1.5 to 4.7 atm at a heating rate of $5^{\circ}\text{C}/\text{min}$. (b) The N content in the final product and the total hydrogen release amount.

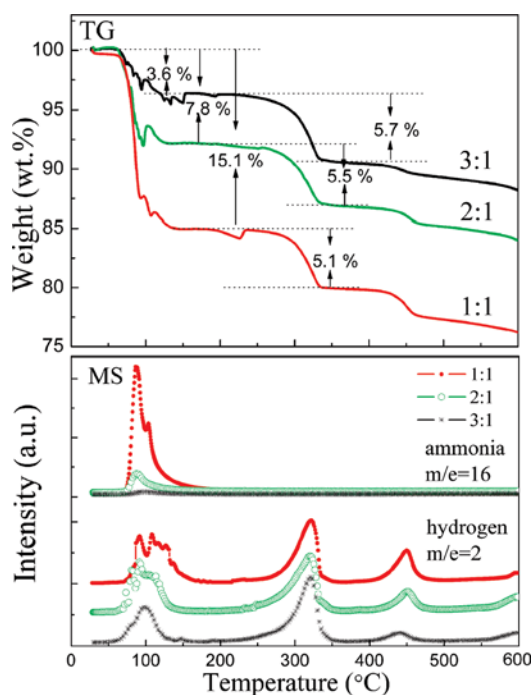


Figure 4. TG/MS results for $\text{LiH}/\text{LiBH}_4 \cdot \text{NH}_3$ with mole ratios of 1:1, 2:1, and 3:1. The heating rate is $10^{\circ}\text{C}/\text{min}$.

2. Dehydrogenation Promotion through Metal Hydrides.

Although full dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$ may be achieved in ammonia with an elevated pressure, the temperature is still high to above 300°C . Furthermore, the presence of ammonia is unlikely to be used with a fuel cell as ammonia is a potent fuel cell catalyst poison. Therefore, seeking new approaches to stabilize the NH group is necessary. Here, our results show that a few metal hydrides are effective additives to realize hydrogen liberation from $\text{LiBH}_4 \cdot \text{NH}_3$.

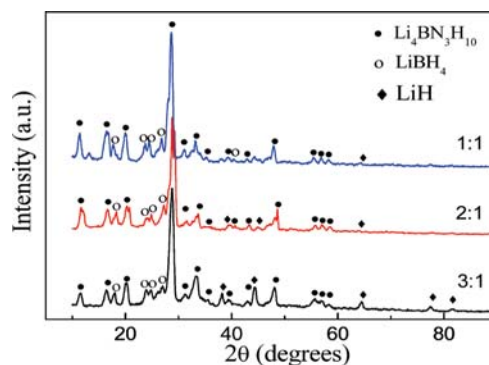


Figure 5. XRD patterns for the products of $\text{LiH}/\text{LiBH}_4 \cdot \text{NH}_3$ (mole ratios: 1:1, 2:1, 3:1) heated to 150°C .

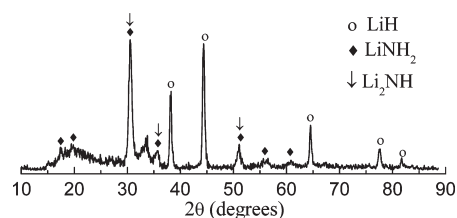


Figure 6. XRD pattern for LiH heated in ammonia at 60°C for 1 h.

Figure 4 shows the TG/MS results for the $\text{LiH}/\text{LiBH}_4 \cdot \text{NH}_3$ system, which exhibits a three-step decomposition. In the first stage (60 – 150°C), emissions of both ammonia and hydrogen were detected, but the emission of ammonia can be suppressed significantly by increasing the LiH content in the mixtures, and total suppression of ammonia emission was achieved when the mole ratio of LiH to $\text{LiBH}_4 \cdot \text{NH}_3$ increased to 3:1. In the second (260 – 350°C) and third (400 – 480°C) stages, no ammonia was detected in the gaseous product. This clearly demonstrates that LiH can improve the hydrogen release from $\text{LiBH}_4 \cdot \text{NH}_3$, as well as suppressing the ammonia release.

To clarify the hydrogen release mechanism for this system, further investigations were conducted on the samples at different stages. For the three mixtures heated to 150°C , X-ray diffraction (XRD) results (Figure 5) apparently indicate the formation of $\text{Li}_4\text{BN}_3\text{H}_{10}$ ^{22,27–30} and LiBH_4 , while the peaks assigned to $\text{LiBH}_4 \cdot \text{NH}_3$ disappeared. Furthermore, peaks for LiH are unidentified in the 1:1 ratio sample but can be observed in the samples with mole ratios of 2:1 and 3:1. These results suggest that LiH can react with $\text{LiBH}_4 \cdot \text{NH}_3$ to form $\text{Li}_4\text{BN}_3\text{H}_{10}$ and LiBH_4 below 150°C , and the stoichiometric LiH to $\text{LiBH}_4 \cdot \text{NH}_3$ mole ratio for the reaction should be less than 2:1. In the Fourier transform infrared (FTIR) spectra of these products (Figure S3 in Supporting Information), the B–H stretching modes were observed at 2220 , 2290 , and 2390 cm^{-1} , and the BH_2 deformation band was observed at 1120 cm^{-1} , indicating that the $[\text{BH}_4]^-$ group did not change much during the reaction. This also suggests that the reaction may be occurring between the LiH and the NH_3 group in the $\text{LiBH}_4 \cdot \text{NH}_3$.

It has been reported that $\text{Li}_4\text{BN}_3\text{H}_{10}$ can be formed through the reaction of two potential hydrogen storage materials, LiBH_4 and LiNH_2 .^{22,27–30} So it is predicted that LiNH_2 forms an intermediate via reactions 1 and 2 below, and then LiNH_2 will further react with LiBH_4 to produce $\text{Li}_4\text{BN}_3\text{H}_{10}$ via reaction 3. It has been reported that the reaction between LiH and NH_3 is ultrafast,³¹ and our attempt to synthesize LiNH_2 by exposing LiH in 1 bar of ammonia atmosphere at 60°C also indicates the feasibility of the reaction of LiH with ammonia to produce LiNH_2 (Figure 6). Thus reaction between LiH and $\text{LiBH}_4 \cdot \text{NH}_3$

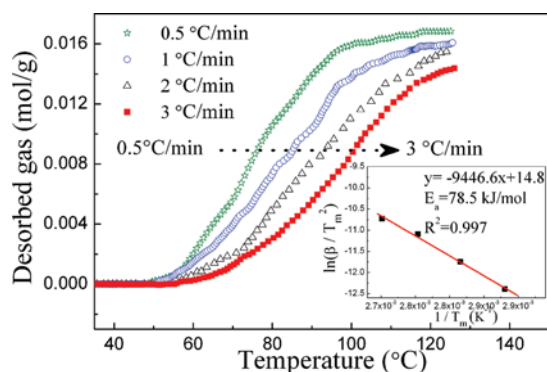
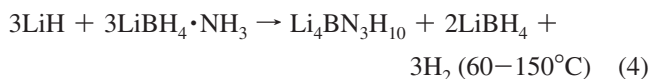
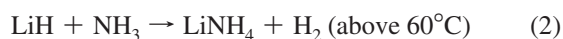


Figure 7. TPD curves of the first-step dehydrogenation of LiH/LiBH₄·NH₃ mixture (mole ratio 3:1) at various heating rates, and Kissinger's plot (insert).

is probably a three-step reaction as predicted above. And the overall reaction in the first step can be speculated as eq 4.



On the basis of eq 4, it is estimated that the theoretical hydrogen release capacity of the first step from the stoichiometric mixture, i.e., the 1:1 ratio, is 4.3 wt %. However, this mixture lost 15.1 wt % of its original weight according to the TG results (Figure 4), much of which was definitely the result of ammonia release. Increasing the LiH amount was shown to be an effective way to suppress ammonia emission. For the LiH/LiBH₄·NH₃ mixture with a mole ratio of 3:1, a weight loss of 3.6 wt %, which is quite close to the theoretical hydrogen capacity (3.2 wt %) for the first step, was observed, indicating the good suppression of ammonia release. The fact that excessive LiH addition is required to depress the ammonia evolution from LiBH₄·NH₃ is related to the reaction kinetics between LiH and NH₃. As shown previously,³² increasing the surface area of LiH particles can effectively suppress escape of NH₃ from the LiNH₂ + LiH system because more surfaces are available for the reaction between LiH and NH₃ (above 60 °C).

Furthermore, the apparent activation energy (E_a) for the first hydrogen release step was determined using Kissinger's method.³³ In the present study, LiH/LiBH₄·NH₃ with a mole ratio of 3:1 was used to obtain mainly hydrogen release from the mixture. T_m was extracted from the temperature-programmed desorption (TPD) curves of the LiH/LiBH₄·NH₃ system at various heating rates, as shown in Figure 7. Results show that the gas desorption curves were shifted to higher temperatures, as expected, with increasing heating rates from 0.5 to 3 °C/min. T_m values were obtained by differentiating the hydrogen desorption curves. They are 74, 82, 90, and 97 °C, corresponding to the heating rates of 0.5, 1, 2, and 3 °C/min, respectively. From the slope of the fitted $\ln(\beta/T_m^2)$ versus $1/T_m$ line, the apparent activation energy E_a was determined to be approximately 78.5 kJ/mol as shown in Figure 7.

In the temperature range of 260–350 °C, more than 5 wt % hydrogen was further released from these mixtures. The hydrogen evolution temperature range was similar to that of Li₄BN₃H₁₀.^{27–29} XRD results for the mixture heated to 350 °C (Figure 8) indicate the disappearance of Li₄BN₃H₁₀ and appear-

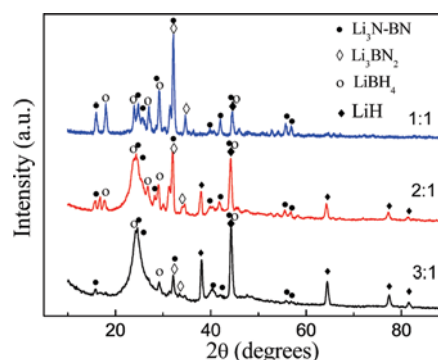


Figure 8. XRD patterns for the products of LiH/LiBH₄·NH₃ (mole ratios 1:1, 2:1, 3:1) heated to 350 °C.

ance of new phases assigned to Li₃N–BN and Li₃BN₂, which have been reported to be the decomposition products of Li₄BN₃H₁₀.^{22,27–29} In addition, peaks for LiBH₄ and LiH were still apparent in the products of the LiH/LiBH₄·NH₃ mixture when its mole ratio exceeded 2:1. Meanwhile, the FTIR results (Figure S4 in Supporting Information) for these products show subdued characteristic frequencies of the [BH₄][−] group between 2200 and 2400 cm^{−1}, indicating the consumption of the [BH₄][−] group in the second hydrogen release stage. On the basis of the above results, it can be concluded that the subsequent hydrogen release is likely due to the decomposition of Li₄BN₃H₁₀, while LiBH₄ and residual LiH do not have obvious effects toward improving its decomposition. For the last hydrogen release step above 400 °C, as LiBH₄ was observed in the products heated to 350 °C (Figure 8) and the onset temperature is similar to that of pure LiBH₄, it is clearly ascribed to the decomposition of LiBH₄.

A differential scanning calorimetry (DSC) curve (Figure S5 in Supporting Information) of LiH/LiBH₄·NH₃ (mole ratio 3:1) shows clear endothermic peaks centered at 58 and 113.7 °C that correspond to the melting of LiBH₄·NH₃ and the phase transformation of LiBH₄, respectively. However, no apparent peak was observed over the temperature range of 60–150 °C, suggesting insignificant thermal effects for reaction 4. But attempts to recharge the decomposition products of LiH/LiBH₄·NH₃ (mole ratio: 3:1) at 130 °C and 8.5 MPa of H₂ for 8 h were unsuccessful.

From the decomposition behavior of the LiH/LiBH₄·NH₃ system, we can deduce that the negatively charged hydrogen in LiH is more reactive than the hydrogen in [BH₄][−] in combining with the negatively charged hydrogen in NH₃. After the reaction between LiH and the NH₃ released from LiBH₄·NH₃ that eventually results in the formation of Li₄BN₃H₁₀, the H⁺ carrier [NH₂][−] group was able to stay stable together with [BH₄][−] in one molecule to higher temperature, enabling the combination of NH^{•••}HB to produce hydrogen without ammonia emission. Moreover, the onset temperature of 260 °C for hydrogen release from Li₄BN₃H₁₀ suggests the difficulty of the combination of NH^{•••}HB in Li₄BN₃H₁₀ and also gives indirect proof of the difficulty for the combination of the NH^{•••}HB dihydrogen bond in LiBH₄·NH₃.

Guided by the above combination mechanism, it is proposed that other metal hydrides, in which the hydrogen is also negatively charged, may have a similar effect as LiH did. Therefore, more metal hydrides, including NaH, CaH₂, and MgH₂ were further investigated. Figure 9 shows their TPD results together with LiH/LiBH₄·NH₃ and LiBH₄·NH₃. Compared with LiH/LiBH₄·NH₃, similar three-step decompositions were observed for NaH/LiBH₄·NH₃ and CaH₂/LiBH₄·NH₃.

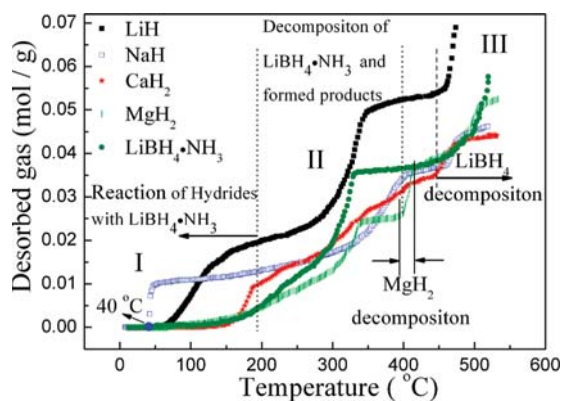


Figure 9. TPD results for LiH/LiBH₄·NH₃ (mole ratio 2:1), NaH/LiBH₄·NH₃ (mole ratio 2:1), CaH₂/LiBH₄·NH₃ (mole ratio 1:1), MgH₂/LiBH₄·NH₃ (mole ratio 1:1), and LiBH₄·NH₃ at a heating rate of 5 °C/min.

Similarly, in the first stage, NaH and CaH₂ were proposed to react with LiBH₄·NH₃, resulting in hydrogen release at about 40 and 150 °C, respectively. Then the formed intermediate products decomposed in the temperature range from 200 to 400 °C. Finally, the regenerated LiBH₄ decomposed at above 440 °C. The above results clearly suggest that NaH and CaH₂ can also promote the dehydrogenation of LiBH₄·NH₃ as LiH did, while the onset hydrogen release temperature, i.e., the reaction temperature of LiBH₄·NH₃ with the metal hydrides, increases in the order of NaH < LiH < CaH₂. However, unlike the above hydrides, no obvious effect was found for MgH₂/LiBH₄·NH₃, which may be due to the slow reaction of MgH₂ with NH₃ as indicated by previous report.³⁴ It is believed that electronegativity of hydrogen atom for the metal hydride plays an important role in promoting the dehydrogenation of LiBH₄·NH₃. As NaH in which the hydrogen atom is more electronegative than that of LiH^{35,36} reacted easier with LiBH₄·NH₃, it is likely that the more electronegative the hydrogen is in the metal hydrides, the easier for it to combine with the positively charged hydrogen in NH₃. Further studies on the factors influencing the combination of metal hydrides with LiBH₄·NH₃ are still in progress.

Conclusions

In summary, two important properties of amminelithium borohydride (LiBH₄·NH₃), the mechanism of dehydrogenation of LiBH₄·NH₃ and dehydrogenation promotion of LiBH₄·NH₃ through metal hydrides, were reported in this paper. The formation of a coordinate bond between NH₃ and LiBH₄ was found to be a crucial factor in inducing hydrogen release from LiBH₄·NH₃, and an elevated ammonia pressure was able to improve the dehydrogenation due to an increased ammonia content bonding to LiBH₄ above its dehydrogenation temperature. Meanwhile, several metal hydrides including LiH, NaH, and CaH₂ were found effective in suppressing the ammonia evolution from LiBH₄·NH₃. In the case of a LiH/LiBH₄·NH₃ system, they can react via $3\text{LiH} + 3\text{LiBH}_4 \cdot \text{NH}_3 \rightarrow \text{Li}_4\text{BN}_3\text{H}_{10} + 2\text{LiBH}_4 + 3\text{H}_2$, releasing hydrogen from 60 °C. Our results will provide help in deep understanding of the decomposition of ammonia complexes of borohydrides as well as an alternative method to promote the dehydrogenation and suppress the ammonia evolution from B–N related hydrogen storage candidates.

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Supporting Information Available: Schematic diagram of the reaction system, XRD pattern for the as-prepared LiBH₄·NH₃ at room temperature, FTIR spectra for the products of LiH/LiBH₄·NH₃ heated to 150 and 350 °C, and DSC curve for LiH/LiBH₄·NH₃ at a heating rate of 2 °C/min. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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