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Improved dehydrogenation properties of the combined $\text{Mg}(\text{BH}_4)$ $2 \cdot 6\text{NH}_3\text{-nNH}_3\text{BH}_3$ system

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Improved dehydrogenation properties of the combined $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ - nNH_3BH_3 system

Abstract

A combined strategy via mixing $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ with ammonia borane (AB) is employed to improve the dehydrogenation properties of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. The combined system shows a mutual dehydrogenation improvement in terms of dehydrogenation temperature and hydrogen purity compared to the individual components. A further improved hydrogen liberation from the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB is achieved with the assistance of ZnCl_2 , which plays a crucial role in stabilizing the NH_3 groups and promoting the recombination of $\text{NH}_3 + \text{BH}_3 \rightarrow \text{H}_2 + \text{B-NH}_2$. Specifically, the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 (with a mole ratio of 1:0.5) composite is shown to release over 7 wt.% high-pure hydrogen (>99 mol%) at 95 °C within 10 min, thereby making the combined system a promising candidate for solid hydrogen storage.

Keywords

$\text{Mg}(\text{BH}_4)_2$, dehydrogenation, nNH_3BH_3 , improved, system, BH_4 , mg, combined, properties, 2

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Structure and Dehydrogenation Improvement of Hexaammine Magnesium Borohydride

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Abstract

In this paper, the crystal structure and dehydrogenation improvement of a H-enriched complex, hexaammine magnesium borohydride ($\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$), are reported. Structural analysis revealed that this compound crystallizes in a cubic lattice with the lattice constant of $a = 10.7806 \text{ \AA}$, in which the Mg atom coordinates to six NH_3 groups, while the BH_4 groups occupy the $(1/4, 1/4, 1/4)$ tetrahedral sites. As $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ tends to release large amounts of ammonia upon decomposition, a combined strategy *via* mixing $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ with AB was employed to advance its dehydrogenation properties. The combined system showed a significant mutual dehydrogenation improvement in terms of dehydrogenation temperature and hydrogen purity. A further improved hydrogen liberation from the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB was achieved with the assistance of ZnCl_2 , which plays an crucial role in stabilizing the NH_3 groups and promoting the recombination of $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$. Specifically, the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 (mole ratio of 1 : 0.5) composite was shown to release over 7 wt.% fairly pure hydrogen at $95 \text{ }^\circ\text{C}$ within 10 min, thereby demonstrating the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ /AB combined system to be a promising candidate for solid hydrogen storage.

Key words: hydrogen storage; ammine metal borohydrides; crystal structure; ammonia borane

1 Introduction

The lack of safe and efficient technique for hydrogen storage is one of the key challenges in developing hydrogen-based energy substructure for mobile application.¹⁻³ Various methodologies to store hydrogen including physical means (high pressure tanks),³ sorbents (nano-porous materials),^{4,5} metal hydrides,⁶ and chemical hydrides^{7,8} are currently under examination. Among these candidates, hydrides based on lightweight elements are considered the most feasible solution to meet the established long-term goals with respect to gravimetric and volumetric hydrogen capacities.^{9,10} Metal borohydrides have recently received great attentions owing to their high theoretical hydrogen capacities.¹¹⁻¹³ However, due to the thermodynamic and kinetic limitations, most of these compounds release hydrogen at high temperature, which make them unfavorable in a practical application. For example, $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ start to release H_2 at about 300 °C, and a complete dehydrogenation from them requires a temperature higher than 500 °C.¹⁴⁻¹⁶ Although literature protocols showed that the thermodynamics of hydrogen storage in metal borohydrides can be improved using catalysts,^{17,18} dopants,^{19,20} or nanostructural templates,^{21,22} almost all of these materials still exhibit poorer hydrogen release kinetics/thermodynamics than would be desirable.

Recently, tremendous efforts have been devoted to the B–N–H composites as chemical hydrogen storage resources, where the corresponding protic and hydridic characters of the hydrogens on the nitrogen ($\text{H}^{\delta+}$) and boron ($\text{H}^{\delta-}$), respectively, allow a facile hydrogen release via a dihydrogen combination.^{7,9,10} Up to now, a series of B–N–H materials, such as ammonia borane (AB),⁷ metal amidoboranes (LiAB , NaAB)¹⁰ and ammine metal borohydrides (AMBs)²³⁻²⁵ have been developed. Particularly, the research on the AMBs has been intensified to become a highly active

and exciting area today owing to their high theoretical hydrogen capacities and favorable dehydrogenation performances.²³⁻³⁵ Among them, the hexaammine complex of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, with a theoretical H_2 capacity of 16.6 wt.% seems also a promising and safe high-density chemical hydrogen storage source.²⁵ However, due to the excessive NH_3 groups in this compound, a significant release of ammonia occurs upon heating along with the hydrogen evolution, which is fatal for fuel cell operation. Thus, seeking effective approaches to depress the evolution of ammonia from $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ are necessary before any potential application of this compound as hydrogen storage material. A previous study has demonstrated that reducing the number of coordinating NH_3 groups in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ is a feasible means of suppressing ammonia evolution, for example, the diammoniate complex of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ was shown to release high purity of hydrogen upon decomposition.²⁵ Alternatively, introduction of a suitable substance that can either stabilize the NH_3 groups or provide fresh BH groups to consume the excessive NH_3 may be another route to depress the release of ammonia in the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. Our recent report has demonstrated that $\text{LiBH}_4 \cdot \text{NH}_3 - n\text{NH}_3\text{BH}_3$ eutectic system showed significantly improved dehydrogenation properties compared to the neat AB and $\text{LiBH}_4 \cdot \text{NH}_3$ alone, resulting from an interaction of AB and NH_3 groups in the $\text{LiBH}_4 \cdot \text{NH}_3$,³⁶ suggesting that AB may be an effective additive to improve the dehydrogenation of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$.

In this paper, we report our results on the successful identification of the structure of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, and then a binary compounds strategy via combining $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ with AB was employed to advance its dehydrogenation properties. Our results demonstrated that the combined system exhibited a significant mutual dehydrogenation improvement in terms of dehydrogenation temperature and hydrogen purity. Furthermore, ZnCl_2 was added to further

improve the dehydrogenation properties of the combined system and the improved mechanism was clarified.

2 Experimental sections

2.1 Reagents and synthesis

$\text{Mg}(\text{BH}_4)_2$ was synthesized from MgCl_2 (99.9% purity, Sigma) and NaBH_4 (95% purity, Sigma) in dried diethyl ether as described in reference.³⁷ $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ was prepared by solid-gas reaction between $\text{Mg}(\text{BH}_4)_2$ and anhydrous ammonia as described in reference.²⁵ Ammonia borane (NH_3BH_3 , AB) (97% purity) and ZnCl_2 (98% purity) were purchased from Sigma-Aldrich and used in as-received form without further treatment.

For the preparation of the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -*n*AB composites, approximately 0.3 g of mixtures of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ /AB with mole ratios of 1 : 1, 1 : 2, 1 : 5 and 1 : 6 were mixed and ball milled using a QM-3SP2 planetary ball mill at 260 rpm for 4 h in a 100 ml hardened steel bowl. The mass ratio of the sample to steel balls is 1 : 30. For the preparation of the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 composite, approximately 0.3 g mixtures of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB and ZnCl_2 with a molar ratio of 2 : 1, 4 : 1 and 8 : 1 were mechanically milled at 260 rpm for 4 h in argon using stainless steel spheres with a ball-to-powder ratio of 30 : 1. The $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ / ZnCl_2 (mole ratio of 1 : 0.25) and AB/ ZnCl_2 (mole ratio of 6 : 0.25) mixtures were prepared using the same procedure. All sample handling was done in an argon-filled glove box equipped with a recirculation system to keep the H_2O and O_2 levels below 1 ppm.

2.2 Instrumentation and analyses

Hydrogen release property measurements were performed by thermogravimetry thermal analysis (TG, STA 449 C) connected to a mass spectrometer (MS, QMS 403) using a heating rate of 5

$^{\circ}\text{C}/\text{min}$ under a 1 atm N_2 atmosphere. Typical sample quantities were 5–10 mg, which is sufficient for getting accurate results due to the high sensitivity of the employed equipment. Temperature-programmed desorption (TPD) was also performed to determine the decomposition behavior of the sample on a semi-automatic Sievert's apparatus, connected with a reactor filled with sample (~ 0.1 g) under an argon atmosphere (1 bar) at a heating rate of $5^{\circ}\text{C}/\text{min}$.

The H_2 and NH_3 contents were determined using gravimetric and volumetric results based on the fact that the emission gas mainly consisted of H_2 and NH_3 . Firstly, the mole per gram (M_p) data of gas released from the sample was obtained by the Sievert's type apparatus as a volumetric result, while the mass percent (W_p) of gas released from the sample was calculated from the weight change of the sample, and then the mole proportion of H_2 (C_{H_2}) and NH_3 (C_{NH_3}) from gas released could be calculated from the following two equations:

$$C_{\text{H}_2} + C_{\text{NH}_3} = 1 \quad (1)$$

$$(C_{\text{H}_2} \times 2.02 + C_{\text{NH}_3} \times 17.03) \times M_p = W_p \quad (2)$$

High-resolution synchrotron X-ray powder diffraction data were collected on the Powder Diffraction Beamline, Australian Synchrotron by using a Mythen-II detector. For phase identification, samples were loaded into pre-dried 0.7 mm glass capillary tubes inside the argon atmosphere glove box and sealed with vacuum grease for X-ray diffraction measurements. The wavelength for all these measurements was $0.8264 \text{ \AA}$. For in situ high temperature measurements, the sample was heated from 20°C to 240°C at temperature intervals of 20°C . The heating rate was $5^{\circ}\text{C min}^{-1}$, and data were collected for 8 min at each point. The phase composition of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}/\text{ZnCl}_2$ was analyzed by X-ray diffraction (D8 Advance, Bruker AXS) with Cu K α radiation. Amorphous tape was used to prevent any possible reactions between the sample and

air during the XRD measurements.

Fourier transform infrared (FT-IR) (Magna-IR 550 II, Nicolet) analyses were conducted to confirm the chemical bonds in the sample. Products were pressed with KBr and then loaded in a sealed chamber for the measurement.

The solid-state nuclear magnetic resonance (NMR) spectra were measured using a Bruker Avance 300 MHz spectrometer, using a Doty CP-MAS probe with no probe background. The powder samples collected after the decomposition reaction were spun at 5 kHz using 4 mm ZrO₂ rotors filled up in purified argon atmosphere glove boxes. A 0.55 ms single-pulse excitation was employed, with repetition times of 1.5 s.

2.3 Computational Details

First-principles calculations based on density-functional theory (DFT) were performed by using Vienna ab initio simulation package (VASP)³⁸ with the projector-augmented wave scheme³⁹ and the generalized-gradient approximation of Perdew-Burke-Ernzerhof^{40,41} for the electronic exchange-correlation functional. The energy cut-off for the plane wave expansion was set to 400 eV to ensure sufficient convergence (less than 1 meV/cell). In the k-point sampling routine, a 2×2×2 Monkhorst-Pack mesh⁴² is used for unit cell of Mg(BH₄)₂·6NH₃. Tests showed that our choice of k points yielded energies that converged within 0.01 eV/(f.u.). The geometric optimization was performed using fixed lattice constants, while atomic positions in the unit cell were allowed to fully relax until the residual forces were less than 0.03 eV·Å⁻¹.

3 Results and discussion

3.1 Crystal structure and electronic structure of Mg(BH₄)₂·6NH₃

Mg(BH₄)₂·6NH₃ was indexed from the high-resolution synchrotron radiation powder diffraction

pattern (Figure 1) as having a cubic lattice (space group $Fm-3$) with the lattice constant of $a = 10.7806 \text{ \AA}$, which is consistent with previous report.²⁵ The crystal structure was then identified using the direct space method in which the BH_4 and NH_3 groups were input as rigid bodies with common bond lengths and bond angles. Rietveld structural refinement for this compound was then conducted using this structure model as shown in Figure 1, where the Rietveld fit is excellent and consistent with the experimental X-ray profile, yielding the agreement factors of $R_{\text{wp}} = 2.9\%$, $R_{\text{B}} = 2.1\%$ and $\text{GoF} = 2.57$. The details of the structural information are given in Table 1 and S1. Note that the powder X-ray data cannot provide highly accurate atomic coordinates, especially for H, so it is necessary to optimize the atomic positions by adopting first-principles calculations, which were then performed to identify the most stable structure and favorable hydrogen positions. The refined structure obtained from first-principles calculations is in good agreement with the indexing results.

The crystal structure of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ is illustrated in Figure 2, in which the Mg atom centrally resides in a slightly distorted octahedral environment and coordinates with six NH_3 groups, while the BH_4 groups occupy the $(1/4, 1/4, 1/4)$ tetrahedral sites. The observed average Mg-N distance is $2.25 \text{ \AA}$ in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, which is slightly longer than that in $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ of $2.15 \text{ \AA}$.²⁵ The shortest $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$ distance between the neighboring NH_3 and BH_4 groups is $1.909 \text{ \AA}$, shorter than that in NH_3BH_3 ($2.02 \text{ \AA}$),⁷ suggesting the formation of dihydrogen bonding as addressed in other AMBs.^{24,29} As shown in Figure 2(b), $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ comprises $\text{H}^{\delta+}$ from NH_3 groups and $\text{H}^{\delta-}$ from BH_4 groups, indicating the high possibility to possess strongly hybridized valence electrons or closed shell bonds between B-H and between N-H, which can be primarily responsible for stability of this structure at room temperature.

In order to understand the bonding nature of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, the charge density states and the electron localization function were investigated. The calculated total and partial electronic density of states (DOS) for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ is shown in Figure 3(a), which exhibits a large energy gap of about 5 eV, indicating that $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ is a wide-gap insulator. However, the band gaps of semiconductors and insulators are usually underestimated since density functional theory has difficulties in treating the excited states. The actual band gaps of the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ composites could be even larger. The valence band of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ is split into three groups. The energy region located at -7~-5 eV is dominated by B 2s, N 2p and H 1s states; the next band is primarily composed of N 2p and Mg 2s states; the top of the valence band is mainly composed of B 2p, N 2p and (B)H 1s hybridized states. The above analysis indicates that the covalent interactions of B-H bonds are contributed by B 2s, 2p and H 1s states; the N-H covalent bonds are composed of N 2p and H 1s states. This interpretation is supported by an analysis of the electron localization function (ELF) as shown in Figure 3(b). As can be seen from the connected ELF isosurface, NH_3 and BH_4 are covalently bound while Mg is forming ionic bonds with adjacent NH_3 molecular entities.

3.2 Dehydrogenation properties of the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ ($n = 1, 2, 5$ and 6) composites

The thermal decomposition behaviours of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ ($n = 1, 2, 5$ and 6) composites were evaluated using synchronous TG-MS analysis and TPD measurement as compared with the neat $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and AB, and the corresponding results are shown in Figure 4 and Figure S1. As shown in Figure 4(a), a two-step decomposition is observed for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, with a total weight loss of 52.8 wt.% by 300 °C. Unlike the $\text{Ca}(\text{BH}_4)_2 \cdot n\text{NH}_3$ ($n=1, 2, 4$ and 6), which was

shown to release NH_3 at low temperature and finally produced $\text{Ca}(\text{BH}_4)_2$ alone to decompose at high temperature,^{35,43} the first step decomposition of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ is a mixing evolution of H_2 and NH_3 in the temperature range of RT to 170 °C, and the second step decomposition from 170 to 300 °C is mainly ascribed to the evolution of H_2 , accompanied with a small amount of diborane. This might be related to their electronic structural characteristics. In the case of $\text{Ca}(\text{BH}_4)_2 \cdot n\text{NH}_3$, Ca cations have hardly any projection in the valence band, indicating that they play the role of electron donors.³⁰ However, for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, as discussed above, the NH_3 groups are coordinated with Mg cations, whereas the Mg 2s orbitals overlap with N 2p orbitals. Thus, the evolution of H_2 via the combination of $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$ may occur before a complete escaping of NH_3 from the structure of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$.

Compared with the dehydrogenation of neat $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and AB, multiple hydrogen release peaks were observed for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ ($n = 1, 2, 5$ and 6) composites upon decomposition (Figure 4(a)). The first and second peaks of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ composites centered at around 115 °C and 134 °C, respectively, much lower than that for neat AB. In addition, the relative intensity of these two peaks increased along with the increasing AB content, suggesting that these two desorption steps may mainly contribute to the decomposition of AB in the composites. Our previous results have demonstrated that, with exposition of AB to anhydrous ammonia, a chemical reaction between AB and ammonia could occur at 90 °C resulting in the release of hydrogen.³⁶ Hence, it is possible that the NH_3 groups in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ may also act as an acid activity for the dehydrogenation of AB, whereas $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ serves as a solid carrier of ammonia. The TG results in Figure 4(b) show that the weight loss of the combined $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ composites are significantly lower than that of the neat AB and

$\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, indicating an effective suppression on the evolution of toxic gases, i.e., diborane, borozine and ammonia. More interestingly, the weight loss of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ composites decreased with the increased mole ratio of AB, suggesting that an enhanced dehydrogenation purity can be obtained by increasing the AB content in the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ composites. This is supported by our above analysis that the initial dehydrogenation of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ composites may mainly arise from the interaction between AB and NH_3 group, by which the increased AB content will consume more NH_3 units in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, and thus lowering the coordination number of NH_3 on Mg cations.

To clarify the reaction mechanism in detail and to obtain information about the decomposition products during the dehydrogenation process, in situ high-resolution XRD, IR and NMR measurements were conducted on the studied composites. The XRD patterns for the as-prepared $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{AB}$ composites revealed that no chemical reaction had occurred between $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and AB during the preparation (Figure S2). Upon heating from 40 to 100 °C, the intensity of AB diffraction peaks reduced gradually and only $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ phase can be observed at 100 °C, indicating this step is mainly attributed to the decomposition of AB, in good agreement with the above MS analysis. Upon further heating to 140 °C, the peaks belonging to the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ disappeared, and only amorphous state was presented at higher temperatures.

The FTIR and ^{11}B NMR spectra of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3-6\text{AB}$ measured at different temperatures are presented in Figure 6. At room temperature (Figure 6(a)), typical features of B-H, N-H and N-B bonds can be identified for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3-6\text{AB}$, i.e., (i) the stretching and bending of B-H bands in the regions between 2215 and 2520 cm^{-1} and between 1070 and 1200, respectively; (ii) the stretching and bending of N-H bands in the regions between 3250 and 3330 cm^{-1} and between

1376 and 1620 cm^{-1} , respectively; (iii) two weak adsorption peak located at 722 and 793 cm^{-1} corresponds to stretching of B-N bands. Upon heating to 150 $^{\circ}\text{C}$, the peaks assigned to both B-H and N-H vibrations are all diminished, along with the appearance of new B-N stretching band located at 900 cm^{-1} , suggesting the consumption of B-H and N-H in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$ and the formation of BN-like residue during dehydrogenation. On further heating to 400 $^{\circ}\text{C}$, after which the dehydrogenation reaction is accomplished, vibrations associated with BH groups disappear, while vibrations assigned to NH groups are still remained, suggesting the excessive supplement of NH during the decomposition, which is in consistent with the unbalanced numbers of NH and BH groups in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$. At the same time, the intensity of the B-N stretching bands is increased, indicating that the final solid residue is BN-like amorphous compound. The formation of the B-N polymer upon dehydrogenation was further confirmed by ^{11}B NMR measurement as shown in Figure 6(b). For the as-synthesized $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$, an asymmetric resonance peak centered at -38.6 ppm, accompanied with two small peaks around at -25 and -28.5 ppm, are observed. The slight downfield shift of the ^{11}B resonance in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$ (-38.1 ppm) compared with that in $\text{Mg}(\text{BH}_4)_2$ (-42.1 ppm) ⁴⁴ indicates the definite difference in the chemical environment of boron in these two compounds. The two weak resonance peaks at -25 and -28.5 ppm, corresponding to another boron site (BH_3) were derived from AB. ⁴⁵ After treatment at 400 $^{\circ}\text{C}$, two kinds of B nuclei peaks around 16 and -6 ppm appeared, indicating the generation of tetravalent B-N based substances. ⁴⁶

Based on the results above, although the amorphous intermediate phases upon decomposition are not very clear currently, it is concluded that dehydrogenation of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot n\text{AB}$ is based on the combination of $\text{H}^{\delta+}$ and $\text{H}^{\delta-}$. The initial two-step dehydrogenation of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot n\text{AB}$ are

resulted from the interaction of BH groups in AB and NH groups in the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, whereas $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ serves as a solid carrier of ammonia. As a result, an increased consumption of NH_3 group has been occurring with the enhancement of AB content in the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/n\text{AB}$ composites, leading to the decreased dehydrogenation temperature and enhanced dehydrogenation purity in this combined system.

3.3 Dehydrogenation properties of ZnCl_2 -modified $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB composites

A recent study about the electronic structure of AMBs indicated that Zn cations are strongly associated with NH_3 groups due to the distribution of Zn $4s$ and $3d$ states in valence bands, resulting in the destabilization of N–H and B–H bonds and then accelerating the recombination between the positively charged H and the negatively charged H within the $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$ bonds.³⁰ In an attempt to further improve the dehydrogenation properties of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB composite, ZnCl_2 with various content was added to this compound. A comparison of TG-MS traces and TPD results for ZnCl_2 -modified $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB recorded under ramping temperature conditions is presented in Figure 7 and S3, respectively. It shows that the adduct ZnCl_2 in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB has two significant advantages: (1) suppress the release of toxic gas, e.g., diborane, borazine and ammonia and (2) decrease the dehydrogenation temperature. After the introduction of 0.125 mole ZnCl_2 to this system, the decomposition pathway changed to two steps in the temperature range of 75-200 °C with two peaks located at 100 and 115 °C, respectively. TG results gave a total mass loss of 15.38 wt.%, which is 19.1 wt.% lower than that of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB, suggesting the effective suppression of the toxic gas emission. On further increasing the ratio of ZnCl_2 to 0.25 moles, the peak temperatures of the first and second

decomposition were decreased to 93 and 112 °C, which is about 22 °C lower than that of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$. Furthermore, the introduction of 0.5 moles ZnCl_2 was shown to further improve the dehydrogenation of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$ composite, in which the hydrogen is released via three steps with peaks at 85, 102 and 131 °C, respectively, with a total weight loss of 9.79 wt.%. Table S2 lists a summary of dehydrogenation properties of all the ZnCl_2 -modified $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$ composites in the temperature range of 30-200 °C. Clearly, the hydrogen purity increased with the increasing ZnCl_2 content. For example, a high purity of hydrogen (99.04 mol %) can be released from $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}/\text{ZnCl}_2$ (mole ratio of 1 : 0.5) sample, whereas the hydrogen purity is 94.6 mol % for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}/\text{ZnCl}_2$ (mole ratio of 1 : 0.125) at the same decomposition conditions.

As $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}/\text{ZnCl}_2$ (mole ratio of 1 : 0.5) composite showed the most favorable dehydrogenation properties, the isothermal desorption kinetics measurement was conducted to obtain more detailed decomposition information on this mixture at different temperatures. The isothermal TPD results in Figure 8 show that favorable dehydrogenation kinetics can be obtained at temperatures above 75 °C, from which hydrogen capacities of 3.34 wt.%, 4.24 wt.% were released within 30 min at 75 °C and 85 °C, respectively. Further elevated temperature resulted in enhanced dehydrogenation capacities and accelerated kinetics, i.e., over 7 wt.% H_2 were released within 10 min and 5 min at 95 °C and 105 °C, respectively. The fact that the hydrogen capacity is temperature dependent could be ascribed to its stepwise decomposition, as shown in Figure S3, in which 3.5 wt.%, 6.3 wt.%, and 9 wt.% of H_2 were released from the three dehydrogenation stages. Clearly, the dehydrogenation properties of ZnCl_2 assisted $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$ are greatly improved compared to the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$.

FTIR results in Figure S4 reveal that the intensity of both B–H and N–H bonds are greatly reduced upon heating the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 (mole ratio of 1 : 0.5) composite to 150 °C, which implies that both BH and NH groups contribute to the hydrogen release. The XRD patterns of the as-prepared $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 (Figure 9(a)) composite show the formation of a new phase assigned to $\text{ZnCl}_2(\text{NH}_3)_2$, indicating that an ammonia transfer between metal halides and $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ has occurred during the preparation. Our previous report has demonstrated that besides the central metal cations, the coordination number of ammonia, which will affect the crystal and electronic structure of AMBs, is another crucial factor in tuning the dehydrogenation properties of AMBs.²⁷ For instances, the main dehydrogenation peaks of ammine aluminum borohydrides ($\text{Al}(\text{BH}_4)_3 \cdot n\text{NH}_3$, $n = 5, 4, 3, 2$) decreased gradually with decreasing coordination number of ammonia.²⁷ As NH_3 transferred from Mg^{2+} to Zn^{2+} , the increased ionic character of the Metal–N bond and the decreased coordination number of ammonia on Mg cations not only stabilize the ammonia from emission, but also lead to more positively charged H on N than in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, and thus accelerating the recombination between the positively charged H and the negatively charged H to release hydrogen at low temperature. After dehydrogenation by 150 °C, zinc was formed in the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB system, which is similar to the decomposition product of $\text{Zn}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ and $\text{NaZn}(\text{BH}_4)_3 \cdot 2\text{NH}_3$.^{29,34} This result suggests that the $\text{ZnCl}_2(\text{NH}_3)_2$ which exists in the as-milled sample (Figure 9) may further react with $\text{Mg}(\text{BH}_4)_2 \cdot n\text{NH}_3$ ($n \leq 6$) during the decomposition of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB composite, to reproduce newly single (Zn-based) or double cation (ZnMg-based) ammine borohydrides, hence triggering the subsequent $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$ recombination. Interestingly, our results showed that the ZnCl_2 added sample did not release the borazine as $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB did, suggesting that the presence of $\text{ZnCl}_2(\text{NH}_3)_2$ in

the composite is also effective in restraining the formation of borazine during the decomposition.

To further understand the role of ZnCl_2 on the decomposition of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB composite, the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{ZnCl}_2$ (mole ratio of 1 : 0.25) and AB/ ZnCl_2 (mole ratio of 6 : 0.25) samples were prepared and the corresponding decomposition properties are shown in Figure 10. Compared with the dehydrogenation of neat $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, multiple hydrogen release peaks appear for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{ZnCl}_2$ composite during decomposition. The first and second hydrogen evolution peaks are centered at 99 and 120 °C, respectively, much lower than that for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. Therefore, similar to the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -AB/ ZnCl_2 composites, the introduction of ZnCl_2 in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ may also result in the formation of $\text{ZnCl}_2(\text{NH}_3)_2$ and $\text{Mg}(\text{BH}_4)_2 \cdot n\text{NH}_3$ ($n \leq 6$), and then further reproducing single (Zn-based) or double cation (ZnMg-based) ammine borohydrides upon heating, thus accelerating the $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$ recombination to release hydrogen at low temperature. Furthermore, the AB/ ZnCl_2 mixture starts to release hydrogen at around 96 °C, with a two-step dehydrogenation process with peaks at 120 °C and 160 °C, respectively, comparable to that of neat AB. TG results gave a total mass loss of 26.5 wt.% and 24.3 wt.% for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{ZnCl}_2$ and AB/ ZnCl_2 , respectively. Although the decomposition of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{ZnCl}_2$ and AB/ ZnCl_2 composites cannot depress the emission of toxic gases totally, the weight loss of the combined $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{ZnCl}_2$ and AB/ ZnCl_2 composites are significantly lower than that of the neat AB and $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, demonstrating that the addition of ZnCl_2 is effective in improving the dehydrogenation either $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ or AB alone. However, it can be seen that the dehydrogenation properties of the ZnCl_2 assisted $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB are much advanced compared to the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3/\text{ZnCl}_2$ and AB/ ZnCl_2 composites, indicating the importance of the synergic function between $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and AB

on advancing the dehydrogenation properties of the combined system.

Conclusion

In summary, the crystal structure of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and its dehydrogenation properties by combined with AB were investigated in detail. The $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot n\text{AB}$ ($n=1, 2, 5$ and 6) composites showed a significant mutual dehydrogenation improvement, i.e. reduction of dehydrogenation temperature and suppression of toxic gas formation, compared with the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and AB alone. The improved hydrogen release of the new system is attributed to the initial interaction of AB and NH_3 group in the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. Further improved hydrogen liberation from the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$ was realized with the assistance of ZnCl_2 *via* stabilizing the NH_3 and promoting the recombination of $\text{NH}^{\delta+} \cdots \text{HB}^{\delta-}$. The $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB} / \text{ZnCl}_2$ (mole ratio of 1 : 0.5) composite showed the most favorable dehydrogenation properties, which not only significantly suppress the emission of ammonia and borazine from $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3 \cdot 6\text{AB}$, but also lead to lower dehydrogenation temperatures, for example, at 95 °C over 7 wt.% fairly pure hydrogen can be released within 10 min, thereby enabling this system a promising hydrogen storage candidate.

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Supporting Information Available: XRD, TPD, and FTIR results, including Figure S1–S4 and Tables S1–S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Figure captions

Figure 1. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) synchrotron XRD profiles for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. Vertical bars indicate the calculated positions of Bragg peaks for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ ($\lambda=0.8264 \text{ \AA}$).

Figure 2. 3D network of the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ crystal structure.

Figure 3. (a) The electronic density of states for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$. The Fermi level is set to 0 eV and marked by the vertical dashed line. (b) The electron localization function for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ plotted as yellow-colored transparent isosurfaces at a level of 0.9.

Figure 4. (a) MS spectra and (b) TGA results of the AB, $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ and $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ - n AB ($n = 1$ and 6) composites with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ under 1 atm dynamic N_2 atmosphere.

Figure 5. Selected parts of in situ synchrotron high-resolution X-ray diffraction patterns for the $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB composite heated from 30 to $240 \text{ }^\circ\text{C}$ with a constant heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ in a closed capillary tube under Ar atmosphere ($\lambda=0.8264 \text{ \AA}$). $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ (∇), NH_3BH_3 (*).

Figure 6. (a) FTIR and (b) ^{11}B NMR spectra for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB acquired at different temperatures.

Figure 7. (a) MS spectra and (b) TGA results of the as prepared $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -AB/ ZnCl_2 composites with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ under 1 atm dynamic N_2 atmosphere.

Figure 8. Isothermal TPD curves for the decomposition of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 (mole ratio of 1 : 0.5) sample at various temperatures.

Figure 9. XRD results for (a) as-prepared $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ -6AB/ ZnCl_2 with a mole ratio of 1:0.5

and (b) the mixture after heating to 150 °C.

Figure 10. (a) MS spectra and (b) TGA results of the as prepared $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ - ZnCl_2 and AB- ZnCl_2 composites with a heating rate of 5 °C/min under 1 atm dynamic N_2 atmosphere.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Table 1 Crystallographic and experimental details for $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$

Chemical formula	$\text{Mg}_4\text{B}_8\text{H}_{104}\text{N}_{24}$
Formula weight	624.69 g/mol
Crystal system	cubic
Space group	$Fm\bar{3}$ (No. 202)
Unit cell dimensions	$a = 10.7806(3) \text{ \AA}, \alpha = 90^\circ$ $b = 10.7806(3) \text{ \AA}, \beta = 90^\circ$ $c = 10.7806(3) \text{ \AA}, \gamma = 90^\circ$
Z	4
Density (calculated)	$0.823 \text{ g}\cdot\text{cm}^{-3}$
Volume	$1254.28(2) \text{ \AA}^3$
R_B	2.1 %
R_{wp}	2.9 %
GoF	2.57