

2010

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### Recommended Citation

Dou, S X.; Guo, Zaiping; Liu, Hua-Kun; Ranjbar, Abbas; Yu, Xuebin; Yang, Zunxian; Sun, D. L.; and Guo, Y H.: A combined hydrogen storage system of Mg(BH<sub>4</sub>)(<sub>2</sub>)-LiNH<sub>2</sub> with favorable dehydrogenation 2010, 4733-4737.

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# A Combined Hydrogen Storage System of Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> with Favorable Dehydrogenation

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*Received: November 4, 2009; Revised Manuscript Received: February 12, 2010*

The decomposition properties of Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> mixtures were investigated. Apparent NH<sub>3</sub> release appeared from 50 to 300 °C for the Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> mixtures with mole ratios of 1:1.5, 1:2, and 1:3, while only hydrogen release was detected for the mixture with a mole ratio of 1:1. In the case of the Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> (1:1) sample, the onset of the first-step dehydrogenation starts at 160 °C, with a weight loss of 7.2 wt % at ~300 °C, which is improved significantly compared to the pure Mg(BH<sub>4</sub>)<sub>2</sub> alone. From Kissinger's method, the activation energy,  $E_a$ , for the first and second step dehydrogenation in Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> (1:1) was estimated to be about 121.7 and 236.6 kJ mol<sup>-1</sup>, respectively. The improved dehydrogenation in the combined system may be ascribed to a combination reaction between [BH<sub>4</sub>] and [NH<sub>2</sub>], resulting in the formation of Li–Mg alloy and amorphous B–N compound.

## 1. Introduction

Safe and efficient storage is one of the major technical obstacles to the implementation of hydrogen as a fuel for mobile transport.<sup>1,2</sup> Current molecule storage technologies using compressed or liquid hydrogen require intensive energy and carry associated safety risks. Conventional metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and a reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty.<sup>3</sup> Recently, great attention has been paid to complex hydrides based on boron (borohydrides), which exhibit the highest weight capacity for hydrogen and are therefore obvious candidates to meet the capacity requirements.<sup>4–9</sup> Among the borohydrides, LiBH<sub>4</sub>, with a gravimetric capacity of 18.3%, is the most extensively studied.<sup>10–13</sup> However, this compound is too stable to be used in hydrogen storage applications. More recently, Mg(BH<sub>4</sub>)<sub>2</sub>, which has more favorable thermodynamics than LiBH<sub>4</sub>, while maintaining attractive hydrogen capacity (14.9 wt%), has been acknowledged as one of the potential candidates for hydrogen storage materials.<sup>14–23</sup>

It was observed that  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>, heated under an inert or hydrogen atmosphere, was first transformed to the  $\beta$ -phase of Mg(BH<sub>4</sub>)<sub>2</sub> at around 190 °C. Hydrogen release started around 300–400 °C in several endothermic steps, and 13 wt % weight loss was detected up to 500 °C. The decomposition of Mg(BH<sub>4</sub>)<sub>2</sub> was assumed to be the following: Mg(BH<sub>4</sub>)<sub>2</sub> → MgH<sub>2</sub> + 2B + 3H<sub>2</sub>.<sup>21</sup> However, Chlopek et al. found that the product spectrum may vary, depending on the conditions under which the temperature treatment was performed. Heating rapidly to 390 °C under a vacuum, maintaining that temperature for 30 min, and then quenching to room temperature gave a product mixture that consisted of MgH<sub>2</sub>, Mg, and MgB<sub>4</sub>.<sup>16</sup> Recently, Soloveichik

et al.<sup>22</sup> reported that hydrogen release from Mg(BH<sub>4</sub>)<sub>2</sub> occurs in at least four steps, with formation of intermediate magnesium polyboranes that are eventually transformed to the most stable magnesium dodecaborate. The process ultimately ends with the formation of MgB<sub>2</sub>. To further improve the dehydrogenation of Mg(BH<sub>4</sub>)<sub>2</sub>, Li et al. recently investigated the effects of ball milling and additives on the dehydriding behavior of Mg(BH<sub>4</sub>)<sub>2</sub><sup>17</sup> and found that the initial dehydrogenation temperature of Mg(BH<sub>4</sub>)<sub>2</sub> is significantly reduced by the addition of TiCl<sub>3</sub>. Furthermore, improved dehydrogenation of Mg(BH<sub>4</sub>)<sub>2</sub> can be achieved by reaction with NH<sub>3</sub> to form an ammoniate magnesium borohydride complex: Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>, which contains one bidentate BH<sub>4</sub> group and one tridentate BH<sub>4</sub> group. These are packed into a layered crystal structure mediated by N–H···H–B dihydrogen bonds, leading to hydrogen release starting at 150 °C and reaching a maximum hydrogen release rate at 205 °C.<sup>20</sup> More recently, Fichtner et al. showed that infiltrating Mg(BH<sub>4</sub>)<sub>2</sub> into the voids of pretreated activated carbon with a pore diameter of <2 nm results in a shift of the decomposition of Mg(BH<sub>4</sub>)<sub>2</sub> to lower temperature.<sup>23</sup> However, except for the above reports, little further improvement has been reported for the Mg(BH<sub>4</sub>)<sub>2</sub> system, e.g., combined with other hydrides. Herein, we report a reactive binary mixture, Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub>, that presents a significant decrease in the dehydrogenation temperature as compared to the constituent compounds.

## 2. Experimental Section

The source materials of LiNH<sub>2</sub> (95%) were obtained commercially. Mg(BH<sub>4</sub>)<sub>2</sub> was synthesized by reaction of magnesium hydride with triethylamine borane complex under an argon atmosphere according to a previous report in the literature.<sup>16</sup> The X-ray diffraction (XRD) pattern revealed synthesized Mg(BH<sub>4</sub>)<sub>2</sub> with good crystallinity, in accordance with ref 16, indicating the formation of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>. First 0.5 g mixtures of Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> with various mole ratios were ball milled using a QM-3SP2 planetary ball mill at 470 rpm for 30 min

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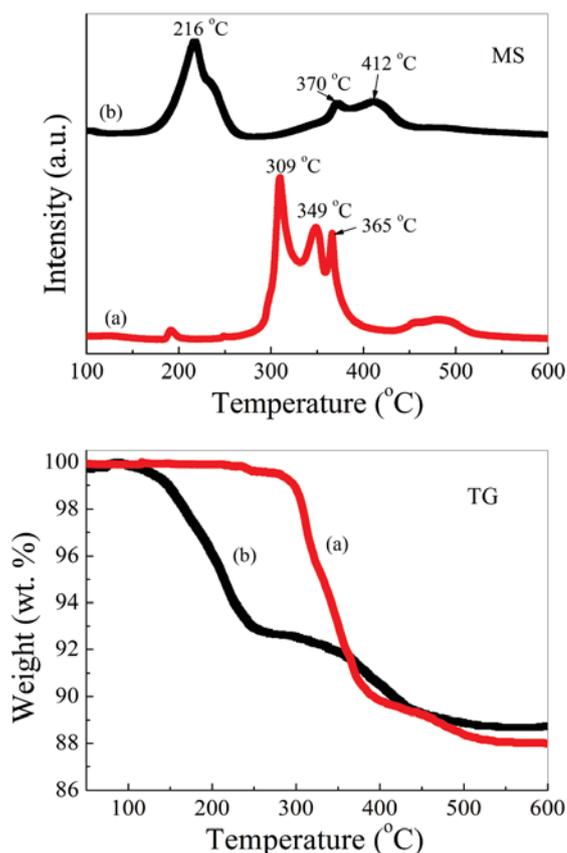
under an inert gas (Ar). For comparison,  $\text{Mg}(\text{BH}_4)_2$  was also ball milled under the above conditions. The mass ratio of the sample to the steel balls was 1:30. All sample handling was done in an argon-filled glovebox equipped with a recirculation system to keep the  $\text{H}_2\text{O}$  and  $\text{O}_2$  levels below 1 ppm.

Hydrogen release measurements were performed by thermogravimetric analysis (TG, STA 409C), with the TG equipment connected to a mass spectrometer (MS, QMS 403), using various heating rates under 1 atm of argon and a carrier flow rate of  $200 \text{ cm}^3 \text{ min}^{-1}$ . Typical sample quantities were 5–10 mg. Moreover, temperature-programmed desorption (TPD) was performed on a Sievert's apparatus, namely, a gas reaction controller (GRC, Advanced Materials Corp., USA) connected to a reactor filled with sample under hydrogen atmosphere (1 bar). The reactor, which was connected to a chamber of known volume, was heated from room temperature to  $400 \text{ }^\circ\text{C}$  at a  $5 \text{ deg min}^{-1}$  heating rate. Powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements were conducted to confirm the crystalline phase. Samples were mounted in a glovebox, and a polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD measurement.

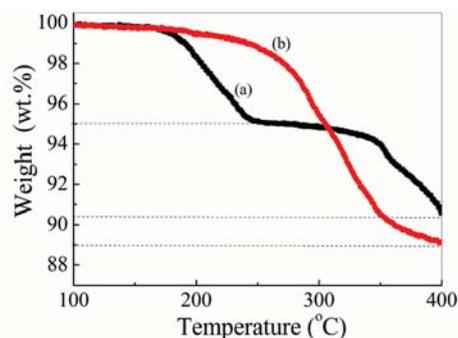
The decomposed  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  products were characterized by  $^{11}\text{B}$  nuclear magnetic resonance (NMR) performed with a Doty charge polarized magic angle spinning (CP-MAS, DSX 300) probe with no probe background. All of those solid samples were spun at  $12 \text{ kHz}$  with use of  $4 \text{ mm ZrO}_2$  rotors filled up in a purified argon atmosphere glovebox. The NMR shifts are reported in parts per million (ppm), externally referenced to  $\text{BF}_3\text{OEt}_2$  at 0 ppm for  $^{11}\text{B}$  nuclei. A  $0.55 \mu\text{s}$  single-pulse excitation was employed, with repetition times of 1.5 s.  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{LiNH}_2$ , and  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  before and after dehydrogenation at various temperatures were characterized by Fourier transform infrared absorption spectroscopy (FT-IR, Nicolet Nexus 470), using KBr pellets. Due to the high reactivity of these compounds with moisture and oxygen, all of the samples were loaded into one tube with  $\text{CaF}_2$  windows.

### 3. Results and Discussion

Figure 1 shows the MS-TG results for  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  (mole ratio 1:1) compared with pure  $\text{Mg}(\text{BH}_4)_2$ . For  $\text{Mg}(\text{BH}_4)_2$ , three main peaks of hydrogen evolution located at  $309$ ,  $349$ , and  $365 \text{ }^\circ\text{C}$  are observed in the MS data, with a total weight loss of 10 wt %. On further heating, there is an additional hydrogen desorption between  $410$  to  $580 \text{ }^\circ\text{C}$  with a weight loss of 1.9 wt %. The above results are comparable with a previous report for  $\text{Mg}(\text{BH}_4)_2$  decomposed under argon.<sup>14</sup> In the case of the  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  (mole ratio 1:1) mixture, two distinct hydrogen release events were observed (peak temperatures at  $216$  and  $412 \text{ }^\circ\text{C}$  with a shoulder at  $370 \text{ }^\circ\text{C}$ , respectively), with onset dehydrogenation at  $160 \text{ }^\circ\text{C}$ , which is about  $100 \text{ }^\circ\text{C}$  lower than that for the pure  $\text{Mg}(\text{BH}_4)_2$ , indicating significant improvement in the dehydrogenation temperature. To further clarify the different decomposition properties, TPD measurements were conducted for the two samples, as shown in Figure 2. The TPD results for  $\text{Mg}(\text{BH}_4)_2$  are comparable to the TG result in Figure 1, releasing about 9.6 wt % hydrogen by  $400 \text{ }^\circ\text{C}$ . For the  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  (mole ratio 1:1) sample, an apparent two-step decomposition was also observed, with a total dehydrogenation capacity of 9.3 wt %, which is in agreement with the TG observations up to  $400 \text{ }^\circ\text{C}$ . However, the hydrogen capacity for the first step is 5 wt %, lower by 2.2 wt % than that in the TG curve. Furthermore, the onset decomposition temperature in the TPD is slightly higher than that in the TG. These differences may be because the decomposition reaction was run



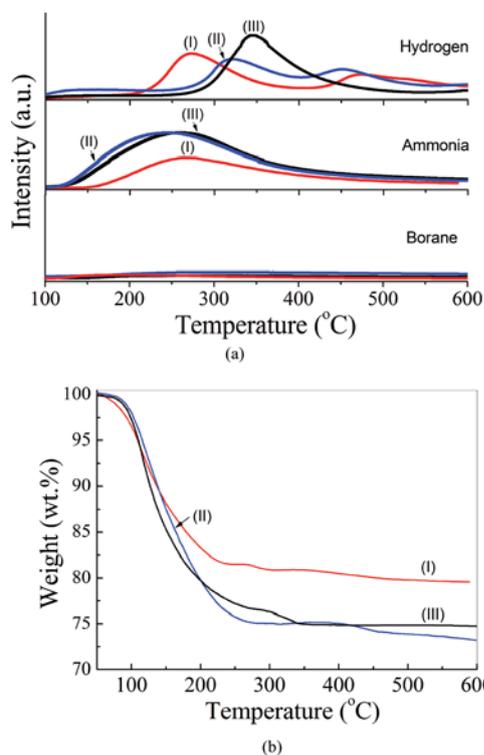
**Figure 1.** MS (top panel) and TG (bottom panel) results for (a)  $\text{Mg}(\text{BH}_4)_2$  and (b)  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  (mole ratio of 1:1), with a heating rate of  $5 \text{ deg min}^{-1}$ .



**Figure 2.** TPD results for  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  (mole ratio of 1:1) compared with pure  $\text{Mg}(\text{BH}_4)_2$  with a heating rate of  $5 \text{ deg min}^{-1}$ .

under different hydrogen partial pressures in these two cases. The TG measurement was conducted under argon, while the TPD was run under 1 bar of hydrogen. Clearly, the hydrogen atmosphere was unfavorable for the hydrogen release reaction, resulting in the increased decomposition temperature, as well as the variation in weight loss.

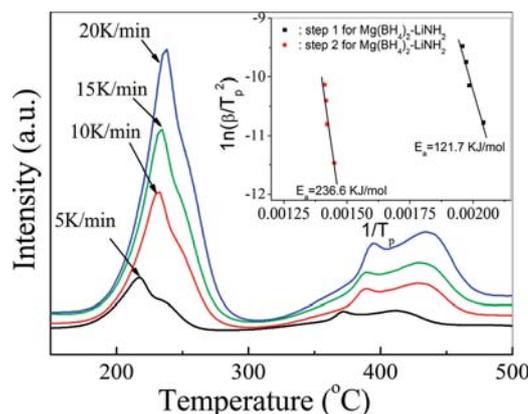
As no potential byproduct of ammonia, such as diborane, borane, or borazine, was detected throughout the desorption process (Figure S1, Supporting Information), the gas evolution in  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  (mole ratio 1:1) was basically attributed to hydrogen release. The TG results yielded the corresponding weight losses for the two steps, 7.2 and 4.2 wt %. The total weight loss of 11.4 wt % for the binary mixture is lower than its theoretical hydrogen capacity (12.98 wt %), suggesting that H still remains in the final products, which was confirmed by the NMR results (see the discussion below). Further investigation of  $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$  with mole ratios of 1:1.5, 1:2, and



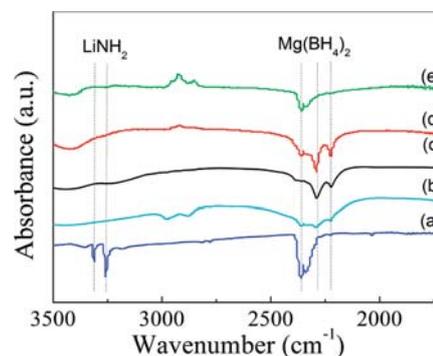
**Figure 3.** (a) MS and (b) TG results for Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> with mole ratios of (I) 1:1.5, (II) 1:2, and (III) 1:3.

1:3 revealed that the hydrogen desorption temperature shifted to higher temperature with increased LiNH<sub>2</sub> content, although it was still lower than that for the pure Mg(BH<sub>4</sub>)<sub>2</sub>. Furthermore, an apparent NH<sub>3</sub> release appeared from 50–300 °C for the samples with a high content of LiNH<sub>2</sub> (Figure 3a), which resulted in an increased weight loss (Figure 3b). The TG results yielded a weight loss of 20.5 wt % for the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (1:1.5), while weight losses of 26.7 and 25.3 wt % were observed for the samples with mole ratios of 1:2 and 1:3, respectively. This indicates that an increased LiNH<sub>2</sub> content in the mixture will lead to more release of ammonia. However, it cannot explain the observations for the 1:2 and 1:3 mol ratio samples, in which almost the same amount of ammonia was released, indicating that, when the ratio of LiNH<sub>2</sub> to Mg(BH<sub>4</sub>)<sub>2</sub> is >2, the destabilized ammonia release does not depend on the content of LiNH<sub>2</sub>. Compared with the pure LiNH<sub>2</sub> (Figure S2, Supporting Information), the NH<sub>3</sub> release temperature from the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> mixtures was decreased significantly, suggesting that, probably due to the formation of Mg–N bonds between the two hydrides, the Mg(BH<sub>4</sub>)<sub>2</sub> may weaken the Li–N bonds in LiNH<sub>2</sub>, causing them to break at lower temperature. This suggests that Mg ions in Mg(BH<sub>4</sub>)<sub>2</sub> may play a crucial role in determining the amount of ammonia release. The above results clearly indicate that the dehydrogenation of Mg(BH<sub>4</sub>)<sub>2</sub> can be improved significantly when it is combined with LiNH<sub>2</sub> and that the sample with a mole ratio of 1:1 showed the most favorable dehydrogenation.

The activation energy,  $E_a$ , during the dehydrogenation for the two steps was estimated by Kissinger's method.<sup>24</sup> The MS profiles at heating rates of 5, 10, 15, and 20 deg min<sup>-1</sup> as a function of temperature were measured for the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio 1:1), as shown in Figure 4. From the peak temperature,  $T_p$ , observed at the heating rate,  $\beta$ , the Kissinger plots, i.e.,  $\ln[\beta/T_p^2]$  as a function of the inverse of  $T_p$ , are given in the inset of the figure. From the slope of the straight line, the activation energy  $E_a$  for the first and second step dehydro-



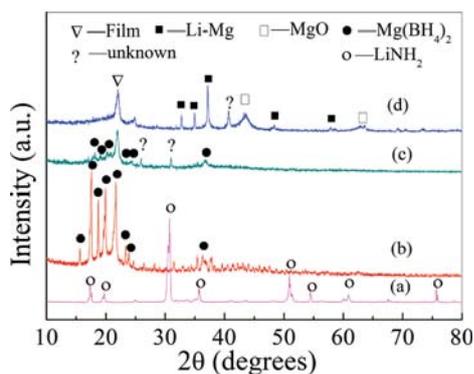
**Figure 4.** MS results for Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio of 1:1) at various heating rates. The inset contains the Kissinger plots for the mixture.



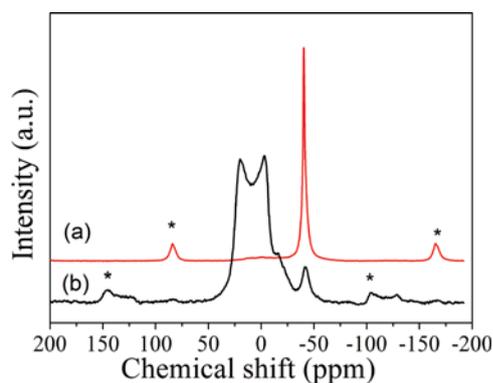
**Figure 5.** FT-IR spectra before dehydrogenation of (a) LiNH<sub>2</sub>, (b) Mg(BH<sub>4</sub>)<sub>2</sub>, and (c) as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio of 1:1); (d and e) the FT-IR spectra of the sample in spectra c after heating to 300 and 500 °C, respectively.

genation was estimated to be about 121.7 and 236.6 kJ mol<sup>-1</sup>, respectively.

To clarify the chemical reactions occurring before and after dehydrogenation, FT-IR, XRD, and NMR measurements were carried out. Figure 5 shows the FT-IR spectra of the sample before and after dehydrogenation. Typical features of the [BH<sub>4</sub>] group can be observed in the spectrum for the as-prepared sample. The B–H absorption band is split into three contributions at 2387, 2296, and 2230 cm<sup>-1</sup>. However, surprisingly, the features for the N–H bond that can be ascribed to LiNH<sub>2</sub>, with its characteristic bands at 3260 and 3315 cm<sup>-1</sup> have almost disappeared, even though no hydrogen or ammonia was released from the mixture during preparation. Moreover, only very weak characteristic bands at 3260 and 3315 cm<sup>-1</sup> can be identified for the mixture even after hand-milling for a few minutes (Figure S3, Supporting Information). This suggests that Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> is not a simple physical mixture, but rather that new phases may be formed during the preparation. The weakening of NH bonds in Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> may result from its complexation with BH bonds, to which similar results have been found in other NH/BH system.<sup>25</sup> The B–H bands at 2296 and 2230 cm<sup>-1</sup> remain present after heating to 300 °C, while disappearing after heating to 500 °C, indicating the progressive decomposition of [BH<sub>4</sub>] with the increasing temperature. The XRD patterns in Figure 6 also give evidence for the formation of new phases. The as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> sample consists of Mg(BH<sub>4</sub>)<sub>2</sub> and two strong new peaks at  $2\theta = 26^\circ$  and  $31^\circ$ , while no LiNH<sub>2</sub> phase was observed. After dehydrogenation to 500 °C, the XRD patterns correspond to MgO and Li–Mg alloy, which appears similar to Mg, but with the peak



**Figure 6.** XRD results for (a) LiNH<sub>2</sub>, (b) Mg(BH<sub>4</sub>)<sub>2</sub>, (c) as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio of 1:1), and (d) the mixture after heating to 500 °C.

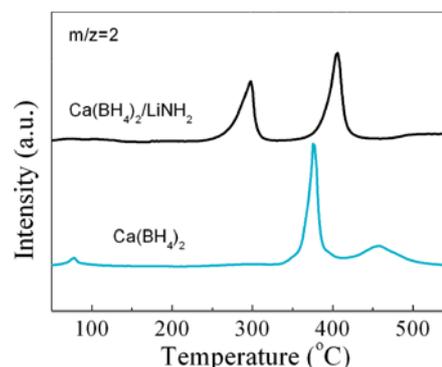


**Figure 7.** <sup>11</sup>B NMR spectra of Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio of 1:1): (a) before and (b) after heating to 500 °C. NMR was performed at 7.1 T (96.3 MHz). The spinning side bands are marked with an asterisk.

positions shifted to higher  $2\theta$  values,<sup>12</sup> except for an unidentified peak at  $2\theta = 40.76^\circ$ , which could be due to an impurity in the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub> sample (Figure S4, Supporting Information). The peaks of MgO, which are broad and partly overlap with the MgB<sub>2</sub>, could come from the reaction between the sample and oxygen or water in the analysis chamber during the dehydrogenation.<sup>16</sup> The <sup>11</sup>B NMR spectra for Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> before and after heating to 500 °C are shown in Figure 7. The sharp line at -40.95 ppm for the as-prepared sample is assigned to the boron nucleus in the tetrahedral BH<sub>4</sub><sup>-</sup> units in LiBH<sub>4</sub>.<sup>26</sup> After heat treatment at 500 °C, two new peaks at -3.1 and 19.9 ppm are observed, suggesting that the chemical environment of a fraction of the B atoms shifts to lower field compared to the tetrahedral BH<sub>4</sub><sup>-</sup>, due to the formation of HBN<sub>2</sub> and/or BN<sub>3</sub>.<sup>27</sup> In addition, the chemical shift which is assigned to BH<sub>4</sub><sup>-</sup> is still observed at -40.149 ppm, which is similar to the product of decomposed LiAB and NaAB.<sup>28</sup>

From the TG results in Figure 1, the weight loss of the first step is about 7.2 wt %, which corresponds to 3 equiv of H<sub>2</sub> evolved from the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio 1:1) by 300 °C. As the B-H bonds at 2296 and 2230 cm<sup>-1</sup> still exist after heating to 300 °C (Figure 5), we surmise that intermediate phases of Li-N-B-H and/or Mg-B-H<sup>14</sup> were formed. After heating to 500 °C, no B-H bonds were identified from the decomposition products, and the Li-Mg alloy was formed, as shown in Figure 6, indicating that the intermediate phases are transformed to Li-Mg and a BN-related polymer at high temperature, with the transformation accompanied by a second weight loss of 4.2 wt %.

The improved decomposition in the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> system might be due to a combination reaction of [BH<sub>4</sub>] with



**Figure 8.** MS results for Ca(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> (mole ratio of 1:1) compared with pure Ca(BH<sub>4</sub>)<sub>2</sub> with a heating rate of 10 deg min<sup>-1</sup>.

[NH<sub>2</sub>], in which the [BH<sub>4</sub>] consists of negatively charged hydrogen, while positively charged hydrogen is bonded to N atoms in [NH<sub>2</sub>]. In this case, the reaction of H<sup>δ+</sup> + H<sup>δ-</sup> → H<sub>2</sub> might be the driving force making the chemical reaction take place, which has been demonstrated in the LiNH<sub>2</sub>/LiH, LiNH<sub>2</sub>/MgH<sub>2</sub>, and LiNH<sub>2</sub>BH<sub>3</sub> systems,<sup>28-30</sup> as well as by our recent results on the Mg(NH<sub>3</sub>)<sub>n</sub>Cl<sub>2</sub>/LiBH<sub>4</sub> system,<sup>31</sup> in which the NH<sub>3</sub> molecules can react with BH<sub>4</sub> anions to generate H<sub>2</sub> at low temperature. According to the combination reaction of [BH<sub>4</sub>] with [NH<sub>2</sub>], it seems that the decomposition of the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> system is similar to that of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>. However, the states of Mg in the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> system are different from the case of decomposed Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>, in which magnesium boronitrides are formed. This may result from a different bond formation mechanism for [NH<sub>2</sub>] between the two systems, in which the [NH<sub>2</sub>] forms an ionic bond with Li<sup>+</sup> in Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub>, but coordinates with Mg<sup>2+</sup> in Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>. As a result, magnesium boronitrides instead of Li-Mg were formed from the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>.<sup>20</sup>

Guided by the above combination mechanism, we have investigated another system of Ca(BH<sub>4</sub>)<sub>2</sub>/LiNH<sub>2</sub> mixtures where improved dehydrogenation was also achieved. Figure 8 shows the MS results for Ca(BH<sub>4</sub>)<sub>2</sub>/LiNH<sub>2</sub> (1:1) compared with pure Ca(BH<sub>4</sub>)<sub>2</sub>. Ca(BH<sub>4</sub>)<sub>2</sub> released hydrogen above 350 °C, with two peaks appearing at 378 and 455 °C, respectively. In the case of Ca(BH<sub>4</sub>)<sub>2</sub>/LiNH<sub>2</sub> (1:1), the dehydrogenation temperature of the two peaks was shifted to 297 and 405 °C, respectively, which represents a significant decrease compared to that of the pure Ca(BH<sub>4</sub>)<sub>2</sub>, exhibiting similar dehydrogenation performance to the Mg(BH<sub>4</sub>)<sub>2</sub>/LiNH<sub>2</sub> system. Therefore, further screening of various borohydride/amide systems may open up significant opportunities for developing more effective hydrogen storage materials.

#### 4. Conclusions

In summary, we have demonstrated a binary system of Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub>, which exhibits a significant improvement in dehydrogenation compared with Mg(BH<sub>4</sub>)<sub>2</sub> alone. In all studied samples, the Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> sample with a mole ratio of 1:1 delivered a two-step weight loss of 7.2 wt % below 300 °C and 4.2 wt % from 300 to 500 °C, associated with a two-step activation energy  $E_a$  of 121.7 and 236.6 kJ mol<sup>-1</sup>, respectively. It is proposed that the improved dehydrogenation in Mg(BH<sub>4</sub>)<sub>2</sub>-LiNH<sub>2</sub> results from a combination reaction between the [BH<sub>4</sub>] and [NH<sub>2</sub>]. This combination mechanism can also extend to other complex systems such as Ca(BH<sub>4</sub>)<sub>2</sub>/LiNH<sub>2</sub>.

**Acknowledgment.** The authors would like to acknowledge Dr Tania Silver for her help in editing the manuscript. This

work was partially supported by the Program for New Century Excellent Talents in Universities (NCET-08-0135), the Shanghai Leading Academic Discipline Project (B113), Shanghai Pujiang Programs (08PJ14014), and an Australian Research Council (ARC) Discovery project (DP0878661).

**Supporting Information Available:** Figure showing the XRD pattern for the synthesized Mg(BH<sub>4</sub>)<sub>2</sub>, MS-TG results for LiNH<sub>2</sub> with heating, FT-IR spectra of hand-milled Mg(BH<sub>4</sub>)<sub>2</sub>–LiNH<sub>2</sub> and pure LiNH<sub>2</sub>, and XRD results for Mg(BH<sub>4</sub>)<sub>2</sub> dehydrogenated at 500 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JP910547S