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# Hydrogen storage properties and mechanisms of $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$ combination systems



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# ABSTRACT

The hydrogen storage properties and mechanisms of the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  combination systems were systematically investigated. The release of ammonia from pristine  $Mg(BH_4)_2 \cdot 2NH_3$  was completely depressed in the presence of  $MgH_2$ . Approximately 13.9 wt% of hydrogen was released from the  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$  combination system at a molar ratio of 1:1 with an onset temperature of 70 °C, which is 75 °C less relative to the onset temperature of pristine  $Mg(BH_4)_2 \cdot 2NH_3$ . In the initial dehydrogenation stage, the Lewis base  $H^{\delta-}$  in  $MgH_2$  first attacks  $H^{\delta+}$  in the  $NH_3$  group of  $Mg(BH_4)_2 \cdot 2NH_3$  to release hydrogen and generate a  $MgBH_4NH_2$  compound. Further elevation of the operating temperature results in the decomposition of  $MgBH_4NH_2$ , releasing hydrogen to form  $MgH_2$  and BN. Finally,  $MgH_2$  decomposes to release the remaining hydrogen to produce Mg. In addition, the dehydrogenated product absorbed approximately 3.7 wt% hydrogen at 450 °C with an initial hydrogen pressure of 100 bar, which demonstrates the partial reversibility for hydrogen storage.

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# 1. Introduction

Hydrogen is regarded as one of the most promising alternatives to traditional fossil fuels [1]. The safe, efficient and cost-effective storage of hydrogen is the most challenging issue in the implementation of the future "hydrogen economy". In recent years, metal borohydrides have attracted considerable interest as one of the best potential hydrogen storage materials due to their high gravimetric and volumetric hydrogen capacities [2–6]. Among the metal borohydrides studied, magnesium borohydride, which possesses a gravimetric hydrogen density of 14.9 wt% and a volumetric density of 112 g/L [5], is able to meet the ultimate system targets for practical hydrogen storage materials set by the U.S. Department of Energy [7]. In addition, an ideal overall reaction enthalpy of approximately 40 kJ/mol calculated for Mg(BH<sub>4</sub>)<sub>2</sub> favors reversible hydrogen storage [8]. However, the material's hydrogen desorption kinetics are relatively sluggish, and the dehydrogenation temperature (300-400 °C) is still too high for practical applications in mobile power systems [5,9]. Considerable effort has been devoted to exploring the hydrogen storage properties of Mg(BH<sub>4</sub>)<sub>2</sub>, including catalyst doping [10-12], nanoconfinement [13,14], and complexing with other compounds [15-20]. Hydrogen release from Mg(BH<sub>4</sub>)<sub>2</sub> co-doped with TiCl<sub>3</sub> and NbCl<sub>5</sub> was initiated at 125 °C, which is approximately 125 °C less than the onset temperature

of an additive-free sample [10]. In addition, the dehydrogenation temperature of Mg(BH<sub>4</sub>)<sub>2</sub> was even decreased to below 100 °C by doping with NbF<sub>5</sub> or TiF<sub>3</sub> [11,12]. Alternatively, incorporating  $Mg(BH_4)_2$  into activated carbon with a pore diameter of <2 nm also decreased the onset dehydrogenation temperature and improved the dehydrogenation kinetics due to a reduced activation energy barrier [13,14]. Further investigations have revealed that the thermodynamic properties of Mg(BH<sub>4</sub>)<sub>2</sub> can be improved by combining it with other compounds, such as LiH, LiNH<sub>2</sub>, LiBH<sub>4</sub>, Ca(BH<sub>4</sub>)<sub>2</sub>, LiAlH<sub>4</sub>, and NaAlH<sub>4</sub> [15–20]. Approximately 9.1 wt% hydrogen was released from the Mg(BH<sub>4</sub>)<sub>2</sub>-2NaAlH<sub>4</sub> system at an onset temperature of 101 °C [17]. The Mg(BH<sub>4</sub>)<sub>2</sub>–0.5LiH system desorbed more than 10 wt% hydrogen below 250 °C [15]. However, the dehydrogenation kinetics and reversibility of Mg(BH<sub>4</sub>)<sub>2</sub>-based hydrogen storage materials must be further improved for practical applications.

Recently, based on the discovery of amide-hydride hydrogen storage combinations, a strategy for preparing hydrogen storage materials with favorable thermodynamic and kinetic properties was proposed by creating an environment in which hydridic (H<sup>-</sup>) atoms (Lewis base) and protic (H<sup>+</sup>) atoms (Lewis acid) coexist [21]. According to this strategy, metal borohydride ammoniates were prepared and studied as a novel family of hydrogen storage materials in which the protonic H<sup> $\delta$ +</sup> in the NH<sub>3</sub> groups and the hydridic H<sup> $\delta$ -</sup> in the [BH<sub>4</sub>]<sup>-</sup> groups coexist. Without necessarily involving interface reactions, the facile local combination of H<sup> $\delta$ +</sup> in NH<sub>3</sub> and H<sup> $\delta$ -</sup> in [BH<sub>4</sub>]<sup>-</sup> is achieved and results in hydrogen

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release at much lower onset temperatures than those of the corresponding borohydrides. Recently, a series of metal borohydride ammoniates was synthesized, and the materials' hydrogen storage properties were investigated [22–27]. Among them, the diammoniate of magnesium borohydride,  $Mg(BH_4)_2$ ·2NH<sub>3</sub> began to release hydrogen at 150 °C, and released ~13.1 wt% up to 400 °C according to reaction (1), which makes it competitive as a hydrogen storage material [23].

$$3Mg(BH_4)_2 \cdot 2NH_3 \rightarrow Mg_3B_2N_4 + 2BN + 2B + 21H_2 \tag{1}$$

Unfortunately, the hydrogen that evolved from  $Mg(BH_4)_2 \cdot 2NH_3$ upon heating was contaminated by ammonia, which is highly undesirable for fuel cell applications [23]. It is well known that metal hydrides, such as  $MgH_2$  and LiH, are able to react with  $NH_3$ at an ultrafast rate to form metal amides [28,29]. Therefore, metal hydrides are considered to be ammonia-release inhibitors in N-containing hydrogen storage materials [30].

In this work, to depress ammonia release and improve the dehydrogenation properties,  $MgH_2$  was introduced into  $Mg(BH_4)_2 \cdot 2NH_3$  to form the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  combination systems. The compositional dependence of the dehydrogenation behavior of the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  combinations was elucidated by temperature-programmed desorption (TPD) and volumetric release measurements. A dramatic reduction in the onset temperature for hydrogen release was observed in the presence of  $MgH_2$ . The dehydrogenation mechanisms of the  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$  (1:1) combination as a function of temperature were also systematically examined, and a  $MgBH_4NH_2$  compound was formed as an intermediate. In addition, the dehydrogenated  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$  (1:1) system exhibited partial reversibility for hydrogen storage.

#### 2. Experimental

All handling of the samples was conducted in either a Schlenk apparatus or a glovebox (MBRAUN 200B) equipped with a circulation purifier to maintain the concentrations of  $O_2$  and  $H_2O$  below 0.1 ppm during operation.

#### 2.1. Materials and sample preparation

Sodium borohydride (NaBH<sub>4</sub>, Alfa Aesar, 98%) and anhydrous magnesium chloride (MgCl<sub>2</sub>, Alfa Aesar, 99%) were obtained commercially and used as received. First, the commercial magnesium hydride (MgH<sub>2</sub>, Alfa Aesar, 98%) was ball milled in an 80 bar hydrogen atmosphere for 24 h to fully hydrogenate the remaining metallic Mg prior to use as shown in Fig. 1. Anhydrous diethyl ether was obtained from Sinopharm Chemical and dried with calcium hydride (CaH<sub>2</sub>). Anhydrous ammonia gas (NH<sub>3</sub>, 99%) was used as received. Magnesium borohydride (Mg(BH<sub>4</sub>)<sub>2</sub>,



Fig. 1. XRD patterns of the commercial  $MgH_2$  and the ball-milled sample under a  $H_2$  atmosphere.

96%) was synthesized via a metathesis reaction between sodium borohydride and magnesium chloride in diethyl ether according to our previously reported protocol [18]. The hexaammoniate of magnesium borohydride (Mg(BH<sub>4</sub>)<sub>2</sub>,eNH<sub>3</sub>) was prepared via a ammoniation reaction of Mg(BH<sub>4</sub>)<sub>2</sub> [31], and the diammoniate of magnesium borohydride (Mg(BH<sub>4</sub>)<sub>2</sub>,2NH<sub>3</sub>) was obtained by ball milling a mixture of Mg(BH<sub>4</sub>)<sub>2</sub>.eNH<sub>3</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> with a molar ratio of 1:2 [32]. Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-xMgH<sub>2</sub> composites with different molar ratios were prepared by ball milling the corresponding chemicals in a planetary ball mill (QM-3SP4) rotating at 300 rpm for 1 h. A gas valve that could be connected to a pressure gauge to determine the pressure changes inside the milling and to limit the increase in temperature during milling, the mill was set to rotate for 0.2 h in one direction followed by a pause of 0.1 h and subsequent rotation in the reverse direction.

#### 2.2. Structural characterization

Phase identification was conducted using powder X-ray diffraction (XRD) on a PANalytical X'Pert Pro X-ray Diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA. The data were collected from 3° to 90° (2 $\theta$ ) in steps of 0.05° at ambient temperature. A specially designed sample container was used to protect the samples from contamination from oxygen and water.

The vibrational characteristics of B–H and N–H bonds were determined using a Bruker Tensor 27 Fourier Transform Infrared (FTIR) spectrometer. The spectra of all of the samples (as KBr pellets with a KBr to sample weight ratio of approximately 100:1) were acquired in the range of 4000–400 cm<sup>-1</sup> in transmission mode with a resolution of 4 cm<sup>-1</sup>.

# 2.3. Evaluation of hydrogen storage properties

Temperature-programmed desorption (TPD) measurements were performed using a homemade apparatus equipped with an online mass spectroscopy (MS, Hiden QIC-20). Approximately 40 mg of sample was loaded into a specially designed tube reactor that allowed the purge gas (pure argon) to enter upon heating. The temperature was gradually elevated from room temperature to 600 °C at a rate of 2 °C/min.

The hydrogen storage properties of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>--xMgH<sub>2</sub> systems were quantitatively evaluated with a homemade Sieverts-type apparatus. Typically, approximately 80 mg of sample was loaded into a stainless steel reactor in the glovebox and then connected to the Sieverts-type apparatus. After evacuating the system to  $10^{-3}$  bar, the sample was heated to the desired temperature at 2 °C/ min (initial in vacuum) for dehydrogenation and 1 °C/min (initial in 100 bar H<sub>2</sub>) for hydrogenation. The pressure and temperature data were automatically recorded. The amount of gas released during the experiments was calculated from the pressure change according to the equation of state.

#### 3. Results and discussion

After ball milling, no pressure increase within the milling jar was detected for the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–*x*MgH<sub>2</sub> (x = 0, 0.5, 1, 2) mixtures, which suggests that no gas evolution occurred during ball milling. Fig. 2 shows the XRD patterns and FTIR spectra of the asprepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–*x*MgH<sub>2</sub> mixtures. Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and MgH<sub>2</sub> were the only two phases in the post-milled Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–*x*MgH<sub>2</sub> combinations with x = 0.5, 1 and 2, and no new diffraction peaks were detected. This result implies that no reaction occurred during the ball milling. Additional FTIR measurements exhibited the same FTIR spectra for the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–*x*MgH<sub>2</sub> (x = 0.5, 1, 2) mixtures, which are also similar to those of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>, further confirming the presence of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> in the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–*x*MgH<sub>2</sub> samples. Therefore, the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and MgH<sub>2</sub>.

The as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-*x*MgH<sub>2</sub> composites were subjected to TPD-MS and volumetric release measurements to evaluate the dehydrogenation properties. Fig. 3 shows the TPD-MS curves of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-*x*MgH<sub>2</sub> mixtures. An apparent discrepancy in the decomposition behavior was observed for the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> combination systems compared to the pristine Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and MgH<sub>2</sub>. An additional desorption peak appeared in the TPD-MS curves of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-*x*MgH<sub>2</sub> mixtures at lower temperatures (70–150 °C). More encouragingly, the release of ammonia from Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> was completely depressed by the introduction of MgH<sub>2</sub>. In other words, only



Fig. 2. (a) XRD patterns and (b) FTIR spectra of the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-xMgH<sub>2</sub> composites.



Fig. 3. MS curves of  $Mg(BH_4)_2 \cdot 2NH_3$ ,  $MgH_2$ , and the as-prepared  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  composites.

hydrogen release was detected during heating of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–*x*MgH<sub>2</sub> samples. These results indicated that the chemical reaction between Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and MgH<sub>2</sub> should have occurred upon heating in the present study. For the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–0.5MgH<sub>2</sub> sample, the onset temperature for hydrogen release is approximately 70 °C, which was significantly reduced by 75 °C and 240 °C relative to the onset temperatures of the pristine Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> (145 °C) and MgH<sub>2</sub> (310 °C), respectively. As *x* increased, from 0.5 to 2, the dehydrogenation temperature for the dehydrogenation peaks varied, which suggested a change in the dehydrogenation quantities at different stages.

Fig. 4 shows the quantitative dehydrogenation curves of the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  mixtures as a function of temperature. The results in Fig. 4 indicates that hydrogen release from pristine  $Mg(BH_4)_2 \cdot 2NH_3$  is initiated at approximately 145 °C and reaches 14.9 wt% at 600 °C, which is in good agreement with previously reported results [32]. For  $MgH_2$ , hydrogen evolution with reasonable kinetics was detected at temperatures above 290 °C. Unlike the starting materials (i.e.,  $Mg(BH_4)_2 \cdot 2NH_3$  and  $MgH_2$ ), the onset dehydrogenation temperatures were significantly decreased to below



Fig. 4. Volumetric release curves of the as-prepared  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  composites and  $MgH_2$ . The inset shows the enlarged view of the volumetric release curves in 50–200 °C.

100 °C by combining Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> with MgH<sub>2</sub>, and the hydrogen desorption is a distinct three-step reaction at an elevated sample temperature. The total dehydrogenation amount was approximately 14.4 wt%, 13.9 wt% and 12.2 wt% for the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  composites with x = 0.5, 1 and 2, respectively, at 550 °C. As the amount of MgH<sub>2</sub> added was increased, the final temperature for hydrogen desorption gradually decreased from 535 °C (x = 0.5) to 490 °C (x = 2). In particular, the Mg(BH<sub>4</sub>)<sub>2-</sub> ·2NH<sub>3</sub>-MgH<sub>2</sub> sample with a molar ratio of 1:1 exhibited a slightly larger amount of hydrogen for the first step of the dehydrogenation at low temperatures, as shown in the inset of Fig. 4. However, the increased addition of MgH<sub>2</sub> induced a decrease in the dehydrogenation amount for the second step and an increase in this amount for the third step. The dehydrogenation behavior of the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  mixtures exhibited a compositional dependence. Approximately 3.5 wt% hydrogen was first released from the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> sample at 70-180 °C, and upon further heating, 7.3 and 3.1 wt% hydrogen were additionally liberated through the second- and third-step reactions, respectively. These amounts are equivalent to 1.98, 4.17 and 1.78 mol of H<sub>2</sub> molecules per  $[Mg(BH_4)_2 \cdot 2NH_3 - MgH_2]$  unit. In total, approximately 13.9 wt% hydrogen or 15.86 equiv. of H atoms were released from the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture at 70–550 °C. Therefore, nearly all of the hydrogen in the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture was released upon heating.

understand То the reaction mechanism between  $Mg(BH_4)_2 \cdot 2NH_3$  and  $MgH_2$ , the  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$  mixture was selected as an example, and the dehydrogenated samples at different stages were collected for XRD and FTIR measurements. The results are shown in Fig. 5. First, the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture was heated to 110 °C and then maintained at that temperature for 200 min to ensure completion of the first dehydrogenation reaction. The TPD-MS experiment performed using the sample dehydrogenated at 110 °C for 200 min revealed that the first desorption peak disappeared but the second and third peaks remained nearly unchanged, as shown in Fig. 6. This result confirms that the first dehydrogenation reaction was completed, and the second dehydrogenation reaction had not yet been initiated. After dehydrogenation at 110 °C, XRD examination reveals that the characteristic reflections of the starting chemicals (i.e., Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and MgH<sub>2</sub>) disappeared, and a new set of diffraction peaks were identified. This set of diffraction peaks is in agreement with that of MgBH<sub>4</sub>NH<sub>2</sub>, which is a novel quaternary compound analogous to Li<sub>2</sub>BH<sub>4</sub>NH<sub>2</sub> and Li<sub>4</sub>BH<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub> that was recently reported in the literatures [33–37]. FTIR analyses indicate a distinct change in the relative intensities of the N-H vibrations at 3356 and  $3273 \text{ cm}^{-1}$ , and a new N-H vibration at 3329 cm<sup>-1</sup> and a B-H vibration at 2296 cm<sup>-1</sup> were detected, which can be assigned to MgBH<sub>4</sub>NH<sub>2</sub>. In addition, the B-H absorbance at 1408 cm<sup>-1</sup> splits into two peaks at 1438 and 1403 cm<sup>-1</sup> due to the local interaction between the BH<sub>4</sub> groups and the NH<sub>2</sub> groups in MgBH<sub>4</sub>NH<sub>2</sub>. These results indicate that Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> reacts with MgH<sub>2</sub> to release hydrogen and form a quaternary hydride (i.e., MgBH<sub>4</sub>NH<sub>2</sub>) during the initial heating process. The reaction process can be expressed as follows:

$$Mg(BH_4)_2 \cdot 2NH_3 + MgH_2 \rightarrow 2MgBH_4NH_2 + 2H_2$$
(2)

Theoretically, this reaction can desorb 2.00 mol of hydrogen molecules, which is in excellent agreement with the experimental results shown in Fig. 4 ( $\sim$ 1.98 mol).

It should be noted that the  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$  mixture expanded dramatically during the dehydrogenation process, as shown in Fig. 7. Foaming was observed for the  $Mg(BH_4)_2$ 



Fig. 6. TPD-MS curves of the as-prepared  $Mg(BH_4)_2\cdot 2NH_3-MgH_2$  composite and  $MgBH_4NH_2.$ 



Fig. 7. Photos of the (a) as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–MgH<sub>2</sub> mixture, (b) the decomposed Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–MgH<sub>2</sub> sample at 150 °C and (c) the decomposed MgBH<sub>4</sub>NH<sub>2</sub> at 310 °C.

 $2NH_3-MgH_2$  mixture heated to 150 °C and was similar to the phenomenon observed during the dehydrogenation processes of AB, LiNH<sub>2</sub>BH<sub>3</sub> and NaNH<sub>2</sub>BH<sub>3</sub> [38,39]. In contrast, MgBH<sub>4</sub>NH<sub>2</sub>, which is the product of the decomposition of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture at 150 °C, did not exhibit any detectable foaming upon



Fig. 5. (a) XRD patterns and (b) FTIR spectra of the dehydrogenated Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> composite at different stages.

further heating. A previous investigation reported the expansion and melting of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> at temperatures above 100 °C [23], which are responsible for the foaming of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture upon heating.

After dehydrogenation at 360 °C, which is the temperature at which the second-step dehydrogenation is completed, the typical diffraction peaks of MgH<sub>2</sub> dominate the XRD profile with the disappearance of the newly developed MgBH<sub>4</sub>NH<sub>2</sub>. This observation is different from the thermal decomposition of pristine  $Mg(BH_4)_{2}$ ·2NH<sub>3</sub> because no MgH<sub>2</sub> was observed as a decomposition product [23]. In addition, two bumps with relatively weak intensities were also detected located in the  $2\theta$  range of  $20-30^{\circ}$  and  $40-50^{\circ}$ . According to Kim's report, these two bumps originate from boron nitride (BN) [40]. The FTIR results indicate that the intensities of the B-H and N-H absorbances decreased significantly, which is indicative of their consumption in this dehydrogenation step. In addition, the absorbance centered at  $1393 \text{ cm}^{-1}$  is also visible. which corresponds to the stretching vibration of the B-N bonds [41], confirming the presence of BN. Therefore, the second dehydrogenation reaction originates from the local combination of  $H^{\delta+}$ in  $[NH_2]^-$  and  $H^{\delta-}$  in  $[BH_4]^-$ , and the dehydrogenation product consists of MgH<sub>2</sub> and BN.

$$MgBH_4NH_2 \rightarrow MgH_2 + 2BN + 2H_2 \tag{3}$$

According to reaction (2), 2.00 mol of MgBH<sub>4</sub>NH<sub>2</sub> can only release 4.00 mol of hydrogen molecules. However, 4.17 mol of hydrogen were released, which is slightly larger than the theoretical value. It is well known that Mg(NH<sub>2</sub>)<sub>2</sub> can react with MgH<sub>2</sub> due to the strong affinity of the Lewis base H<sup> $\delta$ -</sup> in MgH<sub>2</sub> and the Lewis acid H<sup> $\delta$ +</sup> on the nitrogen of Mg(NH<sub>2</sub>)<sub>2</sub> to produce MgNH, as reported by Hu et al. [42]. In this case, we believe that there is a similar reaction between the newly developed MgH<sub>2</sub> and MgBH<sub>4</sub>NH<sub>2</sub>, which releases the additional H<sub>2</sub> and produces an imide group (-NH) according to the following process.

$$2MgBH_4NH_2 + MgH_2 \rightarrow Mg_3(BH_4)_2(NH)_2 + 2H_2$$
(4)

This proposed explanation was confirmed by heating mixtures of MgBH<sub>4</sub>NH<sub>2</sub>–xMgH<sub>2</sub> (x = 0, 0.25, 0.5, 1 and 2). As shown in Fig. 8, approximately 7.6 wt% hydrogen, which is equivalent to 4.16 mol H atoms, was released from MgBH<sub>4</sub>NH<sub>2</sub> in the temperature range of 150–300 °C, which corresponds to the second step of dehydrogenation for the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–MgH<sub>2</sub> system. Interestingly, the presence of extra MgH<sub>2</sub> induced the release of additional hydrogen atoms over this temperature range. Approximately 4.18, 4.28, 4.49 and 4.77 mol H atoms were liberated from the MgBH<sub>4</sub>NH<sub>2</sub>–xMgH<sub>2</sub> mixtures with x = 0.25, 0.5, 1 and 2,



Fig. 8. Volumetric release curves of the  $MgBH_4NH_2-xMgH_2$  mixtures. The inset shows the amount of hydrogen released.

respectively, as shown in the inset of Fig. 8. This result further suggests that a chemical reaction between MgBH<sub>4</sub>NH<sub>2</sub> and MgH<sub>2</sub> occurs as a side reaction during the thermal decomposition process of MgBH<sub>4</sub>NH<sub>2</sub>, which may be responsible for the additional hydrogen release in the second-step dehydrogenation of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>–MgH<sub>2</sub> system.

After further increasing the temperature to 510 °C, the reflections of Mg and BN were detected in the XRD profile in the absence of MgH<sub>2</sub>. The FTIR spectrum exhibits only the absorption peak of B-N bonding at 3192 cm<sup>-1</sup>, and there is no B-H and N-H absorbance in the dehydrogenation product. Therefore, the resulting product after the third dehydrogenation step is composed of metallic Mg and BN. In other words, the third dehydrogenation process primarily originates from the decomposition of MgH<sub>2</sub>. Here, it should be noted that the decomposition temperature of the in situ formed MgH<sub>2</sub> is higher than that of the pure pristine  $MgH_2$ , as shown in Figs. 3 and 4. This result is attributable to the materials' different formation conditions. As mentioned above, the pristine MgH<sub>2</sub> was ball milled in an 80 bar hydrogen atmosphere for 24 h to fully hydrogenate the remaining metallic Mg. This process decreases the particle and/or grain sizes of the pure pristine MgH<sub>2</sub>, which is confirmed by the significantly reduced peak intensities in the XRD profile (Fig. 1), resulting in lower dehydrogenation temperatures. In the decomposition of MgBH<sub>4</sub>NH<sub>2</sub>, MgH<sub>2</sub> was formed in situ at relatively higher temperatures, which leads to an increase in the grain and/or particle sizes, enhancing the dehydrogenation temperatures. Further comparison of the TPD curves of the as-received, post-milled and in situ formed MgH<sub>2</sub> provides powerful evidence for the above hypothesis. As shown in Fig. 3, the thermal decomposition of the as-received and in situ formed MgH<sub>2</sub> occurs in a similar temperature range, which is distinctly higher than that of the post-milled pristine MgH<sub>2</sub>.

According to the above discussion, the overall dehydrogenation process of the  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$  mixture upon heating can be expressed as follows:

$$Mg(BH_{4})_{2} \cdot 2NH_{3} + MgH_{2} \xrightarrow{RT-160 \ ^{\circ}C} 2MgBH_{4}NH_{2} + 2H_{2}$$
$$\xrightarrow{160-360 \ ^{\circ}C} 2MgH_{2} + 2BN + 6H_{2}$$
$$\xrightarrow{360-510 \ ^{\circ}C} 2Mg + 2BN + 8H_{2}$$
(5)

As shown in reaction (5), the decomposition of MgH<sub>2</sub> primarily contributes to the third step of dehydrogenation of the  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  composites, which is most likely the primary reason for the strong dependence of the dehydrogenation amount of the different reaction steps on the MgH<sub>2</sub> content, as shown in Fig. 4. In addition, a new Mg-B-N-H compound with a composition corresponding to MgBH<sub>4</sub>NH<sub>2</sub> was formed while heating the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture at 110 °C. Such a process appears to produce MgBH<sub>4</sub>NH<sub>2</sub> more readily by reacting Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> with MgH<sub>2</sub> in a molar ratio of 1:1 compared to previous work [35-37], in which MgBH<sub>4</sub>NH<sub>2</sub> was synthesized by heating the post-milled Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> mixture at 180 °C. It is well known that the hydridic anion  $H^{\delta-}$  is a strong Lewis base that readily donates electrons. By contrast,  $H^{\delta +}$  in the  $NH_3$  group of athe ammoniate acts as a Lewis acid, which accepts electrons transferred from a Lewis base. Upon heating, the Lewis base  $H^{\delta-}$  in the magnesium hydride attacks the positively charged hydrogen atoms bonded to the nitrogen of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> in which the NH<sub>3</sub> groups are linked to the central Mg<sup>2+</sup> cation through coordination bonds with no interaction between the  $NH_3$  and  $BH_4^-$  groups [23]. Therefore, the positively charged hydrogen atoms are transferred from Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and combine with the H<sup>-</sup> atoms in MgH<sub>2</sub> resulting in the release of hydrogen molecules and the formation of the MgBH<sub>4</sub>NH<sub>2</sub> compound. We believe that the local



Fig. 9. (a) Hydrogenation and (b) re-dehydrogenation curves of the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> composite as a function of temperature.

combination of the positively charged H atoms and the negatively charged H atoms drives the formation of MgBH<sub>4</sub>NH<sub>2</sub>, which is similar to the formation mechanism of LiNH<sub>2</sub>BH<sub>3</sub> and Ca(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub> [43]. A similar phenomenon was observed in the dehydrogenation process of the LiBH<sub>4</sub>·NH<sub>3</sub>-LiH mixture resulting in the formation of Li<sub>4</sub>(BH<sub>4</sub>)

(NH<sub>2</sub>)<sub>3</sub> [44].

In addition, a hydrogenation experiment was conducted using the fully dehydrogenated product of the  $Mg(BH_4)_2 \cdot 2NH_3 - MgH_2$ mixture to evaluate the hydrogen storage reversibility. Fig. 9a shows the hydrogenation curve for an initial hydrogen pressure of 100 bar. The hydrogen uptake begins at approximately 97 °C and reaches approximately 3.7 wt% as it was heated to 450 °C. Further examination of the re-dehydrogenation confirms a reversible hydrogen storage capacity of 3.7 wt%, as shown in Fig. 9b. However, it should be noted that the reversible hydrogen storage capacity is distinctly lower than the dehydrogenation amount of the as-prepared Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> sample, indicating that only some hydrogen can be recharged into the fully dehydrogenated sample. As shown in Fig. 10, the typical reflections of MgH<sub>2</sub> were observed in the XRD profile with the disappearance of metallic Mg after hydrogenation. Therefore, we believe that reversible hydrogen storage in the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> composite



Fig. 10. XRD patterns of the dehydrogenated and hydrogenated  $Mg(BH_4)_2\cdot 2NH_3-MgH_2$  system.

primarily originates from the hydrogenation of metallic Mg to form  $\rm MgH_{2}.$ 

### 4. Conclusions

 $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  mixtures were prepared by ball milling the corresponding chemicals, and their hydrogen storage properties and mechanisms were systematically investigated. The results indicated that the as-prepared  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$ samples are the physical mixtures of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> and MgH<sub>2</sub>. Upon heating, only hydrogen was released from the as-prepared  $Mg(BH_4)_2 \cdot 2NH_3 - xMgH_2$  samples. Hydrogen release reached 13.9 wt% for the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> sample in a three-step reaction with an onset temperature of 70 °C. In the initial dehydrogenation process (70–150 °C), Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> reacted with MgH<sub>2</sub> to release hydrogen and form a quaternary hydride (i.e. MgBH<sub>4</sub>NH<sub>2</sub>). As the temperature increased (150-320 °C), the newly developed MgBH<sub>4</sub>NH<sub>2</sub> decomposed to produce MgH<sub>2</sub> and BN with the release of hydrogen. In addition, a side reaction between MgBH<sub>4</sub>NH<sub>2</sub> and MgH<sub>2</sub> induced the release of a minor amount of hydrogen. Upon further heating of the sample to 510 °C, the decomposition of MgH<sub>2</sub> resulted in the desorption of the remaining hydrogen. Further hydrogenation measurements demonstrated that the partial reversibility of hydrogen storage in the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub>-MgH<sub>2</sub> mixture was approximately 3.7 wt% hydrogen, which was recharged into the fully dehydrogenated sample. In addition, the reaction between the metal borohydride ammoniates and the corresponding metal hydrides can be a facile approach to preparing novel metal-B-N-H compounds.

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