

New Metal–N–H System Composed of  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  for Hydrogen Storage

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We have investigated the hydrogen storage properties of a ball-milled mixture of  $3\text{Mg}(\text{NH}_2)_2$  and  $8\text{LiH}$  after first synthesizing  $\text{Mg}(\text{NH}_2)_2$  by ball milling  $\text{MgH}_2$  under an atmosphere of  $\text{NH}_3$  gas at room temperature. The thermal desorption mass spectra of the mixture without any catalysts indicated that a large amount of hydrogen ( $\sim 7$  wt %) was desorbed from  $140^\circ\text{C}$ , and the desorption peaked at  $\sim 190^\circ\text{C}$  under a heating rate of  $5^\circ\text{C}/\text{min}$  with almost no ammonia emission. Moreover, the reversibility of the hydrogen absorption/desorption reactions was confirmed to be complete. The above results indicate that this system is one of the promising metal–N–H systems for hydrogen storage.

## 1. Introduction

In recent years, much attention has been paid to hydrogen storage materials composed of light elements, such as Mg-based metal hydrides,<sup>1,2</sup> sodium aluminum chemical hydrides,<sup>3,4</sup> carbon nanostructured materials,<sup>5,6</sup> and so on. However, there are still some unresolved problems for practical application.<sup>7</sup>

Recently Chen et al.<sup>8</sup> and Hu and Ruckenstein<sup>9</sup> investigated the system of lithium nitride,  $\text{Li}_3\text{N}$ , as one of the promising hydrogen storage materials, in which the hydrogenation and dehydrogenation were proceeded by the following two-step reversible reactions:<sup>8</sup>



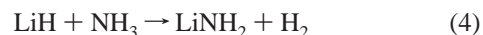
They reported that  $\text{Li}_3\text{N}$  experimentally stored 9.3 wt % hydrogen. However, it should be noted that the above reactions had already been found in the early 20th century.<sup>10,11</sup>

The enthalpy change of the first step of the reaction in eq 1 could be estimated to be 148 kJ/mol  $\text{H}_2$  and that of the second step of the reaction to be 45 kJ/mol  $\text{H}_2$ .<sup>12</sup> Since the second step of the reaction has a much smaller enthalpy change for hydrogen release than the first one and has a potential for storing still a large amount of hydrogen (6.5 wt %), we focused on the second step of the reaction which is expressed as follows:



In fact, Ichikawa et al.<sup>13</sup> in our group reported that a large amount of hydrogen (5.5–6 wt %) between  $150$  and  $\sim 250^\circ\text{C}$  was reversibly desorbed/absorbed in a ball-milled mixture of lithium amide,  $\text{LiNH}_2$ , and lithium hydride,  $\text{LiH}$ , with 1 mol % of titanium chloride  $\text{TiCl}_3$  as a catalyst. In addition, we noticed that the hydrogen desorption reaction was surprisingly fast, although it was considered to be a solid–solid reaction. In order to clarify the origin of such fast reactions, the mechanism of

desorption reaction 2 was experimentally examined in detail.<sup>12</sup> As a result of this examination, it was determined that reaction 2 proceeded by the following two elementary solid–gas reactions mediated by ammonia  $\text{NH}_3$ :



Here, reaction 3 was endothermic and the  $\text{NH}_3$  emission reaction was confirmed to be first order,<sup>12</sup> while reaction 4 between  $\text{LiH}$  and  $\text{NH}_3$  was exothermic and was confirmed to be ultrafast.<sup>12,14</sup> Hence, Ichikawa et al.<sup>12</sup> claimed that the first-order hydrogen desorption reaction 2 was mainly controlled by reaction 3.

It is known that some elements, especially those in groups I–IV, can form their nitride, hydride, and amide/imide. Therefore, we suppose that there still exist plenty of metal–N–H systems similar to those of reactions 1 and 2, which would be effective for hydrogen storage. In this letter, we report how we synthesized magnesium amide  $\text{Mg}(\text{NH}_2)_2$  and then examined the novel reaction between  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  in a series of systematic studies on high-performance hydrogen storage materials. The results in this work indicate that this system could be one of the promising metal–N–H systems for hydrogen storage.

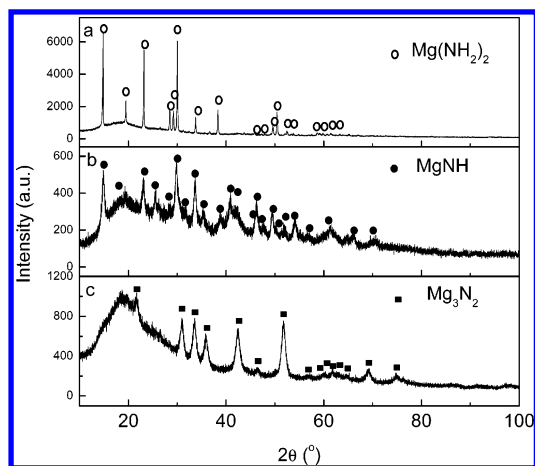
## 2. Experiments

The starting materials were purchased from Sigma-Aldrich:  $\text{LiH}$  with 95% purity and magnesium hydride  $\text{MgH}_2$  with 90% purity, respectively. All the material handling was performed in a glovebox filled with purified argon to keep a low water vapor concentration (the dew point is lower than  $190\text{ K}$ ) and a low oxygen concentration (about 1 ppm) during operation using a gas recycling purification system (Miwa MFG Co., Ltd., MP-P60W). To synthesize  $\text{Mg}(\text{NH}_2)_2$ ,  $\text{MgH}_2$  was milled under a pure  $\text{NH}_3$  gas atmosphere of 0.4 MPa using a rocking mill (SEIWA GIKEN Co., Ltd., RM-10) with a frequency of 10 Hz. In order to avoid an increase in temperature during milling, the milling process was interrupted every 15 min. The fraction of

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**Figure 1.** XRD patterns of  $\text{Mg}(\text{NH}_2)_2$  (a) after heat treatment at 300 °C under an  $\text{NH}_3$  atmosphere for 1 h, (b) after thermal desorption under a helium flow at 320 °C for 2 h, and (c) after thermal desorption under a helium flow up to 500 °C at a heating rate of 5 °C/min. The broad peak around 20° is due to grease used to fix the powder on the sample holder.

$\text{H}_2$  in the milling vessel was monitored by gas chromatographic analysis (GCA) (Shimadzu, GC8AIT). The details of the preparation of  $\text{Mg}(\text{NH}_2)_2$  are described in ref 15.

A mixture of  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  with a molar ratio of 3:8 was mechanically milled with 20 steel balls (diameter: 7 mm) in a Cr-steel pot under a hydrogen atmosphere of 1 MPa, using a planetary ball mill (Fritsch, P7) at 400 rpm for 2 h. The thermal gas desorption properties of the mixture were examined by thermal desorption mass spectroscopy (TDMS) (Anelva, M-QA200TS) combined with thermogravimetry (TG) (Rigaku, TG8120) upon heating to 500 °C at a heating rate of 5 °C/min. This equipment was specially set inside the glovebox filled with purified argon so as to not expose the samples to any air.

The identification of the phases in the products was carried out by X-ray powder diffraction (XRD) with  $\text{Cu K}\alpha$  radiation (Rigaku, RINT-2100).

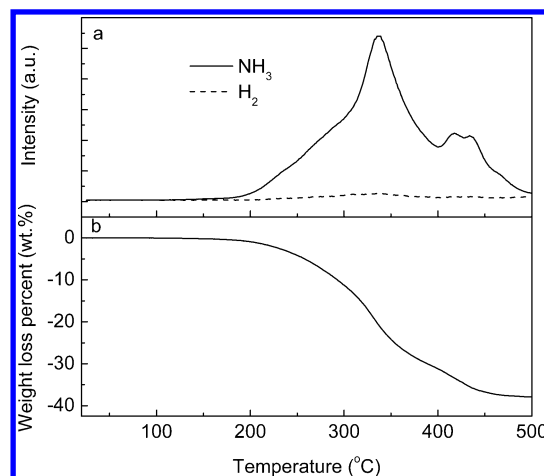
### 3. Results and Discussion

**3.1. Synthesis of Magnesium Amide  $\text{Mg}(\text{NH}_2)_2$ .** In this work,  $\text{Mg}(\text{NH}_2)_2$  was first synthesized by ball milling  $\text{MgH}_2$  in a gaseous  $\text{NH}_3$  atmosphere at room temperature prior to the examination of the hydrogen storage properties of the mixture of  $3\text{Mg}(\text{NH}_2)_2$  and  $8\text{LiH}$ . This is because we could not obtain  $\text{Mg}(\text{NH}_2)_2$  commercially. Similar to the reaction (reaction 4) of  $\text{LiH}$  with  $\text{NH}_3$ , we assumed that  $\text{Mg}(\text{NH}_2)_2$  would be synthesized at room temperature using the rocking mill method, according to the following reaction:



In order to monitor how reaction 5 proceeds in the midst of the milling process, the fraction of  $\text{H}_2$  in the milling vessel was determined by GC analysis. The results indicated that almost all of the  $\text{MgH}_2$  had reacted with  $\text{NH}_3$  by milling treatment for 13 h. The XRD profile of the product after heat treatment at 300 °C under the  $\text{NH}_3$  atmosphere indicated that the product is a single phase of  $\text{Mg}(\text{NH}_2)_2$ , which is shown in Figure 1a.

The TDMS and TG profiles of the product are shown in Figure 2. It is obvious that only  $\text{NH}_3$  gas was emitted by the two-step reactions during the heat treatment up to 500 °C. The weight loss due to the first-step desorption of  $\text{NH}_3$  is ~30 wt % until around 400 °C, suggesting that the first-step desorption of  $\text{NH}_3$  mainly corresponds to the decomposition of  $3\text{Mg}(\text{NH}_2)_2$



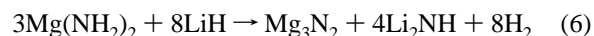
**Figure 2.** (a) Thermal decomposition mass spectrum and (b) weight loss percent due to TG analysis of  $\text{Mg}(\text{NH}_2)_2$  in the heating process up to 500 °C with a heating rate of 5 °C/min.

to  $3\text{MgNH}$  and  $3\text{NH}_3$ . With a further increase of the temperature up to 500 °C, the weight loss reached up to ~40wt % after the second-step desorption of  $\text{NH}_3$ , suggesting the appearance of further decomposition of  $3\text{MgNH}$  to  $\text{Mg}_3\text{N}_2$  and  $\text{NH}_3$ . Furthermore, the XRD profiles in parts b and c of Figure 1 indicate that the products after thermal desorption at 320 °C and 500 °C are characterized as the  $\text{MgNH}$  and  $\text{Mg}_3\text{N}_2$  phases, respectively, which really support the above suggestions. Here, it is noted that the amorphous-like background in the XRD patterns is due to the grease used to fix the powder on the sample holder.

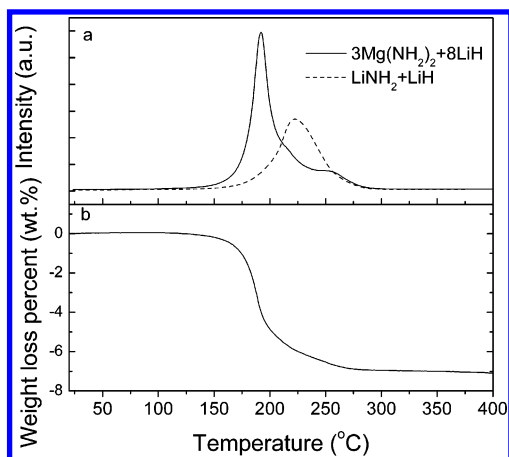
**3.2. Hydrogen Desorption Reaction between  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$ .** As described in the Introduction, we clarified that the hydrogen desorption reaction between  $\text{LiNH}_2$  and  $\text{LiH}$  was controlled by the solid–gas two-step elementary reactions mediated by  $\text{NH}_3$ . Similarly, we expect that the reaction between  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  would also proceed through  $\text{NH}_3$ -mediating solid–gas reactions as well.

In this work, a mixture of  $\text{Mg}(\text{NH}_2)_2$  and  $\text{LiH}$  with a molar ratio of 3:8 was mechanically milled under a hydrogen gas atmosphere of 1 MPa at 400 rpm for 2 h and then the hydrogen storage properties were examined. The TDMS and TG profiles of the ball-milled mixture without any catalysts are shown in Figure 3. The results showed that a large amount of hydrogen (~7 wt %) started to be desorbed at 140 °C, and the desorption peaked at 190 °C at a heating rate of 5 °C/min almost without emitting  $\text{NH}_3$ . Here, it is noteworthy that the hydrogen desorption properties of the mixture of  $3\text{Mg}(\text{NH}_2)_2$  and  $8\text{LiH}$  were much better than those of  $\text{LiH}$  and  $\text{LiNH}_2$ <sup>13</sup> from the viewpoint of both the hydrogen storage capacity and the desorption temperature. The reason may be due to the fact that  $\text{Mg}(\text{NH}_2)_2$  is less stable and more easily decomposes into the corresponding imide and nitride than does  $\text{LiNH}_2$ <sup>12</sup> because of the smaller enthalpy change or larger entropy change in the dehydrogenation reaction.

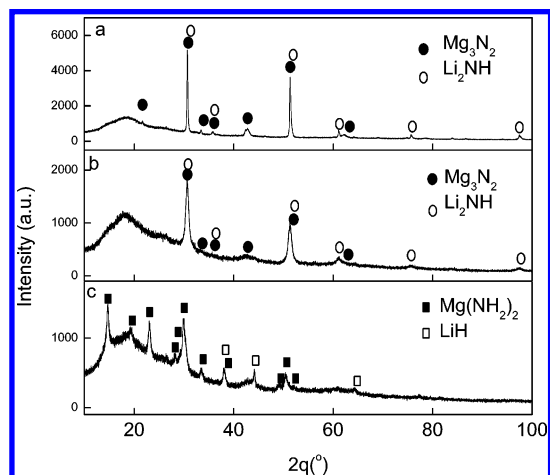
The XRD profile of the mixture after releasing hydrogen at 400 °C is shown in Figure 4a. It shows that the products are the mixed phases of  $\text{Li}_2\text{NH}$  and  $\text{Mg}_3\text{N}_2$ . This indicates that the hydrogen desorption reaction from the ball-milled mixture of  $3\text{Mg}(\text{NH}_2)_2$  and  $8\text{LiH}$  can be expressed as follows:



From reaction 6, we can theoretically calculate the amount of hydrogen capacity to be ~7 wt %, which is in good agreement with the experimental amount of desorbed hydrogen.



**Figure 3.** (a) Hydrogen desorption mass spectrum and (b) weight loss percent due to TG analysis for the mixture of 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH in the heating process up to 400 °C under a helium flow at a 5 °C/min heating rate. Here, the hydrogen desorption mass spectrum for the 1:1 mixture of LiNH<sub>2</sub> and LiH with a small amount (1 mol %) of TiCl<sub>3</sub><sup>13</sup> is also shown by the dotted line.



**Figure 4.** XRD patterns of the mixture of 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH (a) after heating to 400 °C under a helium flow at a heating rate of 5 °C/min, (b) after dehydrogenating at 170 °C in vacuum, and (c) after hydrogenating at 200 °C under 3 MPa of H<sub>2</sub>. The broad peak around 20° is due to grease used to fix the powder on the sample holder.

Next, we examined the reversibility of reaction 6 by hydrogenating the mixture at 200 °C in 3 MPa of H<sub>2</sub> after dehydrogenating the milled mixture of 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH in vacuum at 170 °C. As shown in Figure 4b, the XRD profile indicates that the dehydrogenation reaction from 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH to Mg<sub>3</sub>N<sub>2</sub> and 4Li<sub>2</sub>NH proceeds even at 170 °C in vacuum. After the second hydrogenation reaction, we notice that the product is again transformed into the original mixture of Mg(NH<sub>2</sub>)<sub>2</sub> and LiH (Figure 4c), indicating that reaction 6 is completely reversible.

Similar to the progress of the hydrogen desorption reaction between LiNH<sub>2</sub> and LiH,<sup>12</sup> the dehydrogenation reaction from the mixture of 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH should proceed by the following three kinds of elementary reactions: (1) The first one is that 3Mg(NH<sub>2</sub>)<sub>2</sub> decomposes to 3MgNH and 3NH<sub>3</sub>, and then

3MgNH continues to decompose to Mg<sub>3</sub>N<sub>2</sub> and NH<sub>3</sub> at relatively higher temperatures; (2) the second one is that the emitting 4NH<sub>3</sub> reacts with 4LiH and transforms into 4LiNH<sub>2</sub> and 4H<sub>2</sub>; (3) the third one is that 4LiNH<sub>2</sub> decomposes to 2Li<sub>2</sub>NH and 2NH<sub>3</sub>. Continuously, 2NH<sub>3</sub> again reacts with remaining 2LiH, transforming into 2LiNH<sub>2</sub> and 2H<sub>2</sub>, and then 2LiNH<sub>2</sub> decomposes to Li<sub>2</sub>NH and NH<sub>3</sub>, and such successive steps continue until 4LiNH<sub>2</sub> and 4LiH completely transform into 4Li<sub>2</sub>NH and 4H<sub>2</sub>. It seems that these successive reactions might proceed even at lower temperature through the close contact between Mg(NH<sub>2</sub>)<sub>2</sub> and LiH on a nanoscale by milling treatment.

On the other hand, the hydrogenation reaction process in eq 6 cannot be simply understood. This is because pure Li<sub>2</sub>NH is hydrogenated into LiH and LiNH<sub>2</sub>,<sup>13</sup> and similarly Mg<sub>3</sub>N<sub>2</sub> can be hydrogenated into 2MgH<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub>.<sup>16</sup> If these reactions proceed, the phases of MgH<sub>2</sub> and/or LiNH<sub>2</sub> might appear after the hydrogenation reactions. However, the above reactions do not proceed in this work. Therefore, if there exist some elementary solid–gas reactions mediated by NH<sub>3</sub> even in the hydrogenation reaction, the hydrogenation reaction can be understood as well. Currently, the mechanism of hydrogenation of this system is under investigation.

From the above results, we conclude that the novel metal–N–H system composed of 3Mg(NH<sub>2</sub>)<sub>2</sub> and 8LiH prepared by ball milling is one of the promising candidates for hydrogen storage.

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