

Desorption behaviours from metal–N–H systems synthesized by ball milling

H.Y. Leng^{a,*}, T. Ichikawa^b, S. Isobe^a, S. Hino^a, N. Hanada^a, H. Fujii^b

^a Graduate School of Advanced Sciences of Matter, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

^b Materials Science Center, N-BARD, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

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Abstract

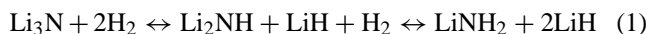
Three metal amides LiNH_2 , NaNH_2 and $\text{Mg}(\text{NH}_2)_2$ were synthesized by ball milling the metal hydrides under gaseous ammonia NH_3 at room temperature. The decomposition behaviours from these metal amides were investigated by thermal desorption mass spectroscopy and thermogravimetry analysis methods. The results showed that LiNH_2 decomposed at $T > 230^\circ\text{C}$ and was transformed into the imide Li_2NH with emitting NH_3 , while $\text{Mg}(\text{NH}_2)_2$, decomposed at $T > 180^\circ\text{C}$ and was transformed into MgNH and finally into Mg_3N_2 with emitting NH_3 within 500°C . Then, a new metal–N–H system composed of $\text{Mg}(\text{NH}_2)_2$ and LiH with a molar ratio of 3:8 was designed by ball milling treatment and examined the hydrogen storage properties. The results showed that this system could reversibly absorb/desorb a large amount of hydrogen (~ 7 wt.%) at a moderate temperature and pressure, which was better than the system of LiNH_2 and LiH for hydrogen storage.

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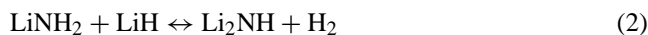
Keywords: Hydrogen storage materials; Mechanochemical synthesis; X-ray diffraction; Thermal analysis

1. Introduction

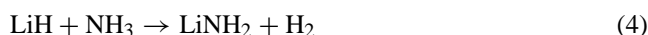
An ideal solid hydrogen storage material for practical applications should reversibly store hydrogen with the minimum amount capacity of 6.5 wt.% at a moderate desorption temperature range of 60 – 120°C for both the economic and environmental reasons [1]. In recent years, some non-interstitial hydrides with high hydrogen capacity have attracted particular interest as potential high-performance hydrogen carriers [2–11]. Among them, metal nitrides or imides have become one of the promising families for hydrogen storage media since the reports of Chen et al. [10] and Hu and Ruckenstein [11]. They reported that the system of Li_3N could reversibly stored a high amount of hydrogen (10.4 wt.%) by the following two-step reactions:



Here, the second step reaction was considered to be worth to investigate for hydrogen storage and was intensively investigated by Ichikawa et al. [12,13], because of its large amount of hydrogen capacity (6.5 wt.%) and much lower standard enthalpy change of desorption (44.5 kJ/mol H_2) compared with that of the first step reaction (148 kJ/mol H_2). The reaction is expressed as follows:



The mechanism of the desorption reaction (2) was experimentally examined in details [12,14], and was clarified that the reaction (2) proceeded as the following two elementary reactions:



The reaction between LiH and NH_3 was exothermic and confirmed to be ultra-fast during the desorption reaction (2) [12,14].

* Corresponding author. Tel: +81 82 424 5744; fax: +81 82 424 7486.

E-mail address: hyleng@hiroshima-u.ac.jp (H.Y. Leng).

Some elements, especially those in groups of I–IV, formed their nitride, hydride and amide/imides. Therefore, it is supposed that there still exist plenty of metal–N–H systems similar to the reactions of (1) and (2) which are effective for hydrogen storage. In this paper, we synthesized the metal amides by ball milling MH_x (M = alkali metals or alkali earth metals, like Li, Na and Mg) with gaseous NH_3 at room temperature and investigated the decomposition behaviours of these metal amides. Finally, a new metal–N–H system was successfully designed and developed for hydrogen storage material.

2. Experiments

The starting materials were purchased from Sigma-Aldrich: LiH and NaH with 95% purity, and MgH_2 with 90% purity. To synthesize metal amides, LiH, NaH, and MgH_2 were respectively milled under a pure NH_3 gas atmosphere of 0.4 MPa using a rocking milling equipment (SEIWA GIKEN Co., Ltd. RM-10) with a frequency of 10 Hz. The fraction of H_2 in the milling vessel was monitored by a gas chromatography analysis (GCA) (Shimadzu, GC8AIT). The details of preparation of metal amides are described in ref. [15]. The products after milling were examined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation (Rigaku, RINT-2100) and oxygen combustion analysis (OCA) (Perkin Elmer 2400 α CHN).

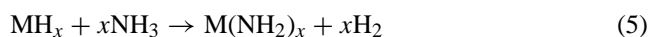
The thermal decomposition behaviours of the products were examined by a thermal desorption mass spectroscopy (TDMS) (Anelva, M-QA200TS) combined with thermogravimetry (TG) (Rigaku, TG8120) upon heating up to 500 °C with a heating rate of 5 °C/min under a helium flow. This equipment was especially set inside the glovebox filled with purified argon, which permitted simultaneous measurements by TG and TDMS without exposing the samples to air at all.

To design the new metal–N–H systems for hydrogen storage, the product of $Mg(NH_2)_2$ was mixed with LiH and MgH_2 in the molar ratios of 3:8 and 1:2, respectively, using a planetary ball milling equipment (Fritsch, P7) with 400 rpm for 2 h.

3. Results and discussion

3.1. Synthesis of metal amides

Motivated by the reaction (4), we proposed that the reactions for the alkali and alkali earth metal hydrides with gaseous NH_3 would proceed by ball milling even at room temperature as follows:



Here, M represents alkali or alkali earth metal. By monitoring the amounts of H_2 in the milling vessel using GCA, the proceeding of reaction (5) can be predicted. The GCA results

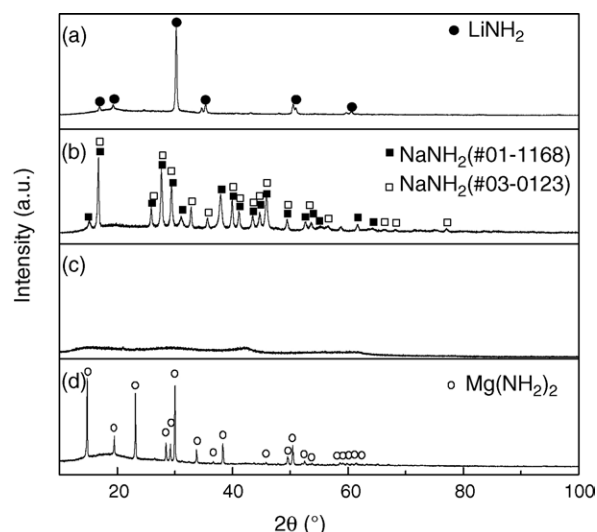


Fig. 1. XRD patterns of the products obtained: (a) by milling LiH under 0.4 MPa NH_3 for 2 h; (b) by milling NaH under 0.4 MPa NH_3 for 1 h; (c) by milling MgH_2 under 0.4 MPa NH_3 for 13 h; (d) by annealing at 300 °C in NH_3 atmosphere after milling MgH_2 under 0.4 MPa NH_3 for 13 h. The symbols of #01-1168 and #03-0123 are the numbers of JCPDS file. The broad peak around 20° is due to the grease using for fixing the powder on the sample holder.

suggested that the full amount of LiH, NaH and MgH_2 reacted with NH_3 within 2, 1 and 13 h milling, respectively.

To confirm whether the corresponding metal amides would be synthesized with a high purity or not, the products were examined by XRD experiment. As shown in Fig. 1(a) and (b), it is noticeable that almost the single phases of $LiNH_2$ and $NaNH_2$ are produced by the reactions of LiH and NaH with gaseous NH_3 after milling. On the other hand, the XRD pattern in Fig. 1(c) indicates that the product after 13 h milling for the Mg system is nano-structured or amorphous phase. Since it was difficult to clarify the formation of the $Mg(NH_2)_2$ by XRD, the OCA method was employed to chemically analyze the concentrations of H and N in the products. The mass ratio of N to H was estimated to be 7.0 ± 0.2 wt.%, which is in good agreement with the theoretical value of 6.95 for $Mg(NH_2)_2$. In addition, we confirmed that the product after heat treatment at 300 °C under NH_3 atmosphere was the single phase of $Mg(NH_2)_2$, as shown in Fig. 1(d) as well.

3.2. Thermal decomposition of the metal amides

The thermal decompositions of the products were investigated by TDMS and TG methods. As shown in Fig. 2(a), only NH_3 gas was emitted at $T > 230$ °C from $LiNH_2$ with two peaks, which may be caused by the difference of desorption rates between the surface and body of the particles of $LiNH_2$. The weight loss up to 500 °C due to NH_3 emission is ~ 37 wt.%, corresponding to the decomposition of $LiNH_2$ into Li_2NH and NH_3 . The XRD profile also indicated that $LiNH_2$ was fully transformed into Li_2NH after decomposition (Fig. 3(a)). As is shown in Fig. 2(b), we notice that

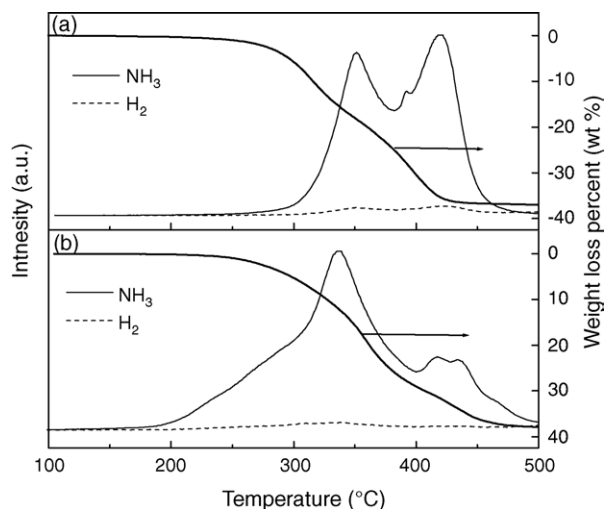


Fig. 2. Thermal desorption mass spectrum and TG profiles of the products in the heating process up to 500 °C under a 5 °C/min heating rate: (a) the products by milling LiH under 0.4 MPa NH₃ for 2 h; (b) the products by milling MgH₂ under 0.4 MPa NH₃ for 13 h.

only NH₃ gas was emitted from Mg(NH₂)₂ at $T > 180$ °C by two-step reactions during the heat treatment up to 500 °C. The weight loss due to the first step desorption of NH₃ is ~30 wt.% until around 400 °C, mainly corresponding to the decomposition of 3Mg(NH₂)₂ to 3MgNH and 3NH₃, while the weight loss due to the second step desorption of NH₃ reaches up to ~40 wt.% until 500 °C, mainly corresponding to the decomposition of 3MgNH into Mg₃N₂ and NH₃. Actually, the XRD profiles in Fig. 3(b) and (c) indicate that the products after thermal desorption at 320 °C and 500 °C for 2 h under a helium flow could be identified as MgNH and Mg₃N₂, respectively. Here we note that the amorphous-like background in the XRD patterns is due to the grease using for fixing the powder on the sample holder.

According to the above results, it seems that the ammonia desorption properties depend on the electronegativity of alkali or alkali earth metals. Actually, the electronegativity of Li is a little bit smaller than that of Mg, so that the ionic bond between the cation Li⁺ and anion [NH₂]⁻ should be stronger than that between Mg²⁺ and [NH₂]⁻ ions. This leads to a lower decomposition temperature for the Mg(NH₂)₂, and also a longer time for the synthesis of Mg(NH₂)₂ compared with LiNH₂ as well, which is consistent with the results of synthesis by ball milling described in Section 3.1. Furthermore, it is noteworthy that Mg(NH₂)₂ decomposes into MgNH and finally into Mg₃N₂ within 500 °C, while LiNH₂ decomposes into only Li₂NH but not Li₃N in the same condition. Thus, we claim that the Mg(NH₂)₂ system would become one of the promising metal–N–H systems for hydrogen storage.

Unfortunately, we could not observe the decomposition of NaNH₂ into the imide, because it easily reacted with the sample holder made of Au or Al used in this work above 300 °C, and volatilized at higher temperature. A much better method is needed to investigate its decomposition behaviour at higher temperature.

3.3. New metal–N–H system of Mg(NH₂)₂ and LiH/MgH₂ for hydrogen storage

According to the thermal decomposition properties of Mg(NH₂)₂ and LiNH₂, two new metal–N–H systems were designed by ball milling the mixture of Mg(NH₂)₂ and LiH with a molar ratio of 3:8 and the mixture of Mg(NH₂)₂ and MgH₂ with a molar ratio of 1:2, respectively. The Hydrogen storage properties of these mixtures were examined by the TDMS, TG and XRD methods.

As shown in Fig. 4, the mixture of 3Mg(NH₂)₂ and 8LiH without any additives started to desorb a large amount of H₂ (~7 wt.%) from 140 °C and took a desorption peak at 190 °C under a heating rate of 5 °C/min almost without NH₃ emission. It is noteworthy that the hydrogen desorption properties of the mixture of 3Mg(NH₂)₂ and 8LiH are much better than those of LiNH₂ and LiH [13]. This is due to the lower decomposing temperature of Mg(NH₂)₂ than that of LiNH₂ as shown in Fig. 2. On the other hand, the mixture of Mg(NH₂)₂ and 2MgH₂ did start to desorb a large amount of H₂ (~7.3 wt.%) from 80 °C but took no clear peak until at ~415 °C at the same condition (Fig. 4). Here, the lower decomposing temperature of Mg(NH₂)₂ also leads to a much lower starting temperature of H₂ desorption, while the H₂ desorption in wide temperature range might be due to the slower reaction between MgH₂ and NH₃. In these senses, the starting temperature of the H₂ desorption for above two mixtures should be the same as each other, however we found that the starting temperature for H₂ desorption was different between the two mixtures. This is because that LiNH₂ is formed on the surface of LiH particles at the first step of H₂ desorption in the system of 3Mg(NH₂)₂ and 8LiH, which is

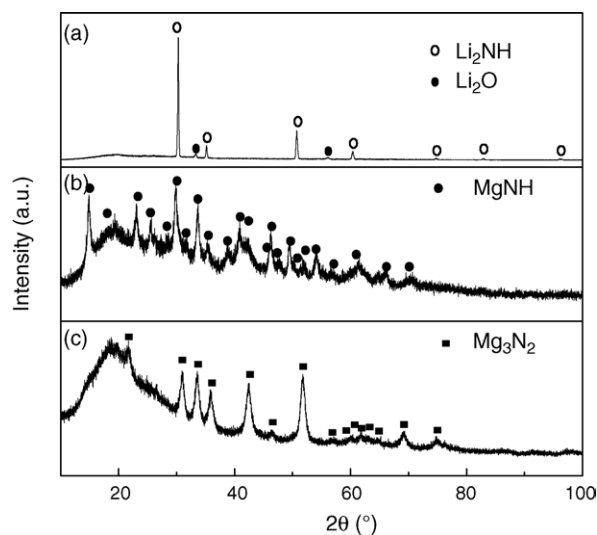


Fig. 3. XRD patterns of the products after thermal decomposition: (a) the product of LiNH₂ after heating up to 500 °C under a helium flow; (b) the product of Mg(NH₂)₂ after thermal desorption under a helium flow at 320 °C for 2 h; (c) the product of Mg(NH₂)₂ after heating up to 500 °C under a helium flow. The broad peak around 20° is due to the grease using for fixing the powder on the sample holder.

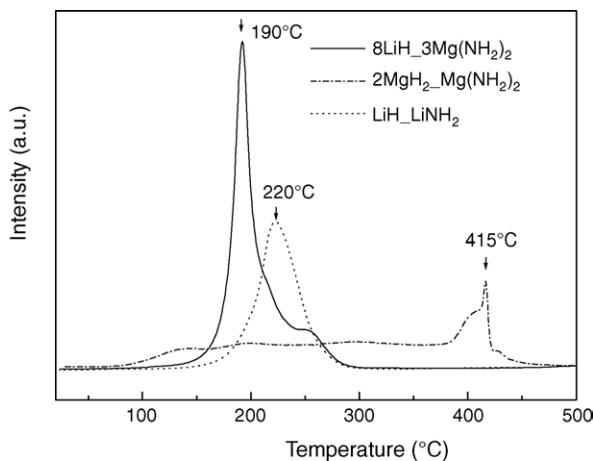


Fig. 4. Hydrogen desorption mass spectrum from the mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH shown in the solid line and from the mixture of $\text{Mg}(\text{NH}_2)_2$ and 2MgH_2 shown in the dashed line in the heating process up to 500°C under a helium flow at a $5^\circ\text{C}/\text{min}$ heat rate. Here, the hydrogen desorption mass spectra for the 1:1 mixture of LiNH_2 and LiH with a small amount (1 mol) of TiCl_3 [13], is also shown by the dotted line.

more stable than $\text{Mg}(\text{NH}_2)_2$ formed on the surface of MgH_2 particles in the system of $\text{Mg}(\text{NH}_2)_2$ and 2MgH_2 .

According to the above results, the system of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH has the best hydrogen desorption properties. The XRD profile of this mixture after releasing hydrogen at 500°C is shown in Fig. 5(a). We can see that the product is composed of the mixed phases of Li_2NH and Mg_3N_2 . This indicates that the hydrogen desorption reaction from the mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH can be expressed as follows:

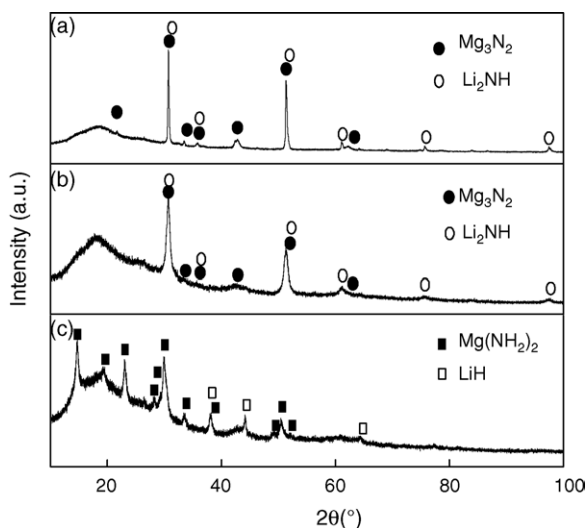
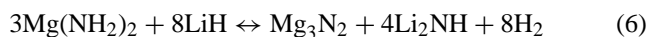


Fig. 5. XRD patterns of the mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH : (a) after heating up to 500°C under a helium flow at a heating rate of $5^\circ\text{C}/\text{min}$; (b) after dehydrogenating at 170°C in vacuum; (c) after hydrogenating at 200°C under 5 MPa H_2 . The broad peak around 20° is due to the grease using for fixing the powder on the sample holder.

from which we can theoretically calculate a hydrogen capacity of $\sim 7\text{ wt}\%$. This is in good agreement with the experimental result. Finally, we examined the reversibility of the reaction (6) by hydrogenating the mixture at 200°C in 5 MPa H_2 after dehydrogenating the mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH in vacuum at 170°C . As shown in Fig. 5(b), the XRD profile indicates that the dehydrogenation reaction (6) proceeds even at 170°C in vacuum. After the second hydrogenation reaction, we noticed that the products were hydrogenated into $\text{Mg}(\text{NH}_2)_2$ and LiH again (Fig. 5(c)), indicating the reaction (6) is completely reversible.

4. Conclusion

Three metal amides LiNH_2 , NaNH_2 and $\text{Mg}(\text{NH}_2)_2$ were successfully synthesized by the novel reaction between the corresponding metal hydride and gaseous NH_3 at room temperature during ball milling. The produced LiNH_2 decomposed into its imide in the range of $230\text{--}500^\circ\text{C}$, while $\text{Mg}(\text{NH}_2)_2$ decomposed into its imide MgNH and nitride Mg_3N_2 in the temperature range of $180\text{--}500^\circ\text{C}$. However, we could not observe the decomposition of NaNH_2 into its imide because it reacted with the sample holder made of Al or Au above 300°C . On the basis of the above results, the new metal–N–H system composed of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH was designed by ball milling treatment and showed a superior hydrogen storage properties to the system of $\text{Mg}(\text{NH}_2)_2$ and 2MgH_2 and the system of LiNH_2 and LiH , in which a large amount of hydrogen ($\sim 7\text{ wt}\%$) can be reversibly absorbed and desorbed at moderate temperature and pressure.

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