

Synthesis and dehydriding studies of Mg–N–H systems

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Abstract

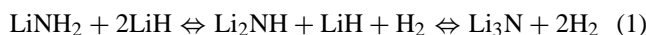
Light-elemental amides and imides are recently regarded as potential candidates for high-performance hydrogen storage materials. In this studies, the single phases magnesium amide ($\text{Mg}(\text{NH}_2)_2$) and magnesium imide (MgNH) were successfully prepared by solid–gas reactions of MgH_2 with ammonia at 613 K and 653 K, respectively. Subsequently, $\text{Mg}(\text{NH}_2)_2$ was mixed with different molars of MgH_2 or LiH in order to systematically investigate the dehydriding properties. With increasing temperature, the mixtures of $\text{Mg}(\text{NH}_2)_2$ and MgH_2 desorb ammonia at approximately 630 K, similar to the decomposition reaction of $\text{Mg}(\text{NH}_2)_2$ alone. On the other hand, the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 M of LiH desorbs only hydrogen during heating because of the “ultra-fast” reaction of LiH with ammonia from $\text{Mg}(\text{NH}_2)_2$, unlike MgH_2 .

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1. Introduction

Experimental and theoretical studies on complex hydrides such as NaAlH_4 [1–6], $\text{Mg}(\text{AlH}_4)_2$ [7], LiBH_4 [8–10], and LiNH_2 [11–16] have been of great interest from the viewpoint of the application of reversible solid state hydrogen storage functions for fuel cell technologies [17,18]. For example, the mixture of 1 M of LiNH_2 (lithium amide) and 2 M of LiH can store 10.4 mass% of hydrogen totally, via the formation of lithium imide (Li_2NH), as follows [11]:



One of the effective methods to promote the dehydriding reaction (left-to-right direction in Eq. (1)) of LiNH_2 is partial substitution of Li by other elements having larger electronegativities, such as Mg [15]. At the start of the reaction, the dehydriding temperatures decrease with increasing Mg concentrations, down to approximately 370 K for MgNH_2 with $\text{M} = \text{Li}$ –30 at.% Mg [16].

In this study, we focus on the hydriding and dehydriding properties of magnesium amide ($\text{Mg}(\text{NH}_2)_2$) and magnesium imide (MgNH), which have not been clarified yet. $\text{Mg}(\text{NH}_2)_2$ has been reported to be synthesized by the reactions of Mg_3N_2 or Mg with ammonia (gas and liquid) and the time taken for the reaction to be completed is in the order of years [19,20]. The solid–gas reaction of MgH_2 with ammonia was employed in this study to prepare the single phases $\text{Mg}(\text{NH}_2)_2$ and MgNH .

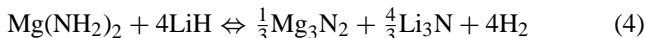
The prepared $\text{Mg}(\text{NH}_2)_2$ was mixed with different molars of MgH_2 or LiH to systematically investigate the dehydriding properties.

2. Experimental

$\text{Mg}(\text{NH}_2)_2$ and MgNH were prepared as follows: approximately 100 mg of MgH_2 (90% of hydride phase, and remainder Mg, Aldrich Co. Ltd.) was placed in a Mo crucible in a glove box filled with purified argon (dew point below 180 K). The crucible with MgH_2 was then sealed into a reaction tube equipped with a connection valve for evacuation and introduction of ammonia. After evacuation at 1×10^{-4} Pa, 0.5 MPa of ammonia (5N) was introduced into the reaction

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tube and this was heated up to a temperature of 603–653 K for 1 week. Using an analogy similar to that of Eq. (1), $\text{Mg}(\text{NH}_2)_2$ thus prepared was mixed with 1 M of MgH_2 , 2 M of MgH_2 , and 4 M of LiH (99.9%, Serac Co. Ltd.) to investigate the possible dehydriding and hydriding reactions as follows:



Each of the equations given above may be composed of more than two reaction steps, similar to Eq. (1).

The dehydriding and hydriding reactions were examined by powder X-ray diffraction measurement (PANalytical, X'PERT, Cu- $K\alpha$), thermal desorption spectroscopy (TDS) detected by gas chromatography (GL Science, GC323, argon flow under 0.1 MPa with a heating rate of 10 K/min), and thermogravimetry and differential thermal analysis (TG-DTA, Bruker AXS, TG-DTA 2000SA, Ar flow under 0.1 MPa with a heating rate of 10 K/min). The sample was placed in a gas-tight container (equipped with gas-exchanging and heating unit for the TDS measurements) in the glove box to avoid the exposure to air, except for the TG-DTA measurements.

3. Results and discussion

3.1. Synthesis and decomposition of $\text{Mg}(\text{NH}_2)_2$ and MgNH

Fig. 1 shows the powder X-ray diffraction profiles of MgH_2 heated up at various temperatures in 0.5 MPa of ammonia. The starting material was identified as MgH_2 , whereas remainder Mg could not be detected by the powder X-ray diffraction measurement. The sample heated up to 603 K was identified as a mixture of $\text{Mg}(\text{NH}_2)_2$ and un-reacted MgH_2 . The single phase $\text{Mg}(\text{NH}_2)_2$ was detected in the sample heated up to 613 K. Judging from the increase of weight

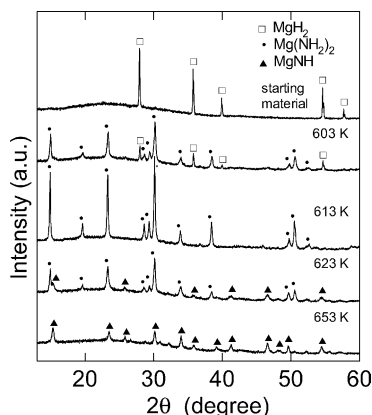


Fig. 1. Powder X-ray diffraction profiles of MgH_2 heated up at various temperatures in 0.5 MPa of ammonia. Opened squares, closed circles and closed triangles show the peak positions of MgH_2 in ref. [21], $\text{Mg}(\text{NH}_2)_2$ in ref. [19], and MgNH in ref. [19], respectively.

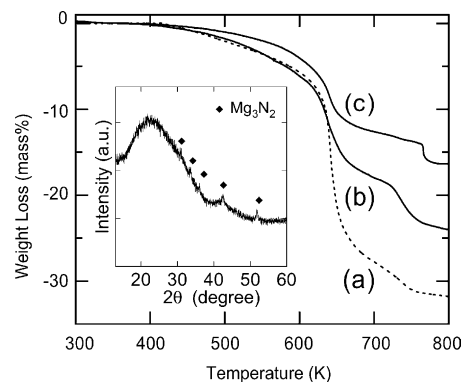
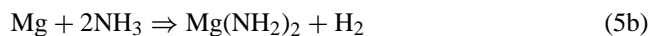
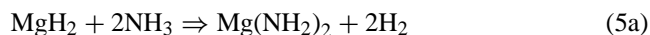


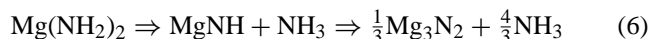
Fig. 2. Thermogravimetry of (a) $\text{Mg}(\text{NH}_2)_2$ mixed without MgH_2 , (b) $\text{Mg}(\text{NH}_2)_2$ mixed with 1 M of MgH_2 and (c) $\text{Mg}(\text{NH}_2)_2$ mixed with 2 M of MgH_2 in argon flow at 0.1 MPa with a heating rate of 10 K/min. The inset shows the powder X-ray diffraction profile after the measurement of (a) i.e., $\text{Mg}(\text{NH}_2)_2$ without MgH_2 . The peak positions of Mg_3N_2 in ref. [22] were represented by closed diamonds.

during reaction, approximately 97% of the starting material (90% of MgH_2 , and remainder Mg) became $\text{Mg}(\text{NH}_2)_2$ under heat treatment at 613 K. Conceivable reactions are as follows:



The peak at around 20° and the triad peaks at around 30° and 50° seem to be characteristic of $\text{Mg}(\text{NH}_2)_2$. With increasing reaction temperatures, those peaks became to small, while the peaks at around 15° , 25° , and 40 – 50° , which are characteristic of MgNH , began to appear. Finally the single phase MgNH was obtained at 653 K.

The decomposition process of $\text{Mg}(\text{NH}_2)_2$ was examined by TG-DTA, as shown in Fig. 2(a). The weight loss begins at approximately 400 K, and the decomposition reactions clearly occur at approximately 630 K and 720 K, corresponding to 25 mass% and 32 mass% of weight losses, respectively. After heating up to 873 K, only Mg_3N_2 was detected in the X-ray diffraction profile, as shown in the inset of Fig. 2. Thus, by combining the results shown in Fig. 1, the two-step decomposition process of $\text{Mg}(\text{NH}_2)_2$ can be explained as follows:



The differences between the weight losses detected experimentally by the TG-DTA measurements, and those expected from ideal equations (30 mass% and 40 mass%, respectively) might arise from the surface oxidation/hydroxidation. Presently, we are installing the TG-DTA apparatus inside the glove box to completely isolate the measuring samples from air.

3.2. Decomposition of the mixture of $\text{Mg}(\text{NH}_2)_2$ and MgH_2

The possible dehydriding reactions (left-to-right directions) in Eqs. (2) and (3) were examined by TG-DTA, and

the results are also shown in Fig. 2(b) and (c). The weight loss reactions clearly occur at approximately 630 K and 720–750 K. The weight losses are approximately 24 mass% and 16 mass% for the $\text{Mg}(\text{NH}_2)_2$ with 1 M of MgH_2 and the $\text{Mg}(\text{NH}_2)_2$ with 2 M of MgH_2 , respectively. However, these values are much larger than the estimated dehydrating reactions, 4.9 mass% and 7.4 mass% according to Eqs. (2) and (3), suggesting that not only hydrogen but also ammonia was desorbed during heating. Judging from these results, we infer that the mixture of $\text{Mg}(\text{NH}_2)_2$ and 1 M of MgH_2 (or 2 M of MgH_2) also decomposes in a manner similar to Eq. (6); first into MgNH at approximately 630 K, and then into Mg_3N_2 up to approximately 720 K.

The dehydrating reactions according to Eqs. (2) and (3) cannot be confirmed, at least under the present condition with a heating rate of 10 K/min under 0.1 MPa of argon. The intrinsic reason is the limited kinetics of reaction between MgH_2 and ammonia to form $\text{Mg}(\text{NH}_2)_2$. As described in Section 3.1, it required approximately 1 week to form $\text{Mg}(\text{NH}_2)_2$ completely, indicating that the reaction of MgH_2 with ammonia is in the order of day. On the other hand, it was reported that the reaction of LiH with ammonia is ultra-fast (25 ms) [13]. Therefore, LiH should be mixed with $\text{Mg}(\text{NH}_2)_2$ in order to suppress the desorption of ammonia, and to enhance the desorption of only hydrogen.

3.3. Dehydrating reaction of $\text{Mg}(\text{NH}_2)_2$ with LiH according to Eq. (4)

The possible dehydrating reaction (left-to-right direction) in Eq. (4) was examined by TG-DTA, and the results are shown in Fig. 3. The weight loss reaction begins at approximately 420 K, and the value is approximately 6.5 mass% up to 873 K under present condition, corresponding to 71% of the estimated value according to Eq. (4). The preliminary results indicated that Eq. (4) contains more than two reaction steps, similar to Eq. (1). For example, there are thermodynamically

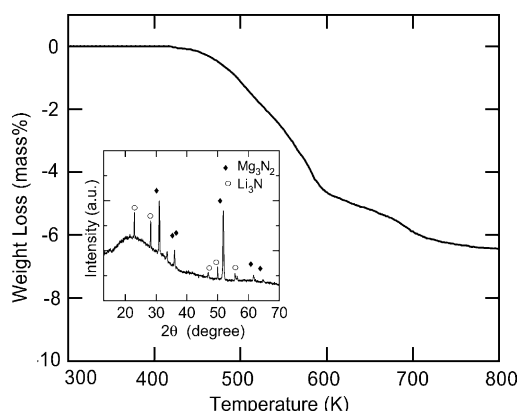


Fig. 3. Thermogravimetry of the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 M of LiH in argon flow at 0.1 MPa with a heating rate of 10 K/min. The inset shows the powder X-ray diffraction profile after dehydrating reaction of the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 M of LiH. The closed diamonds and open circles show the peak positions of Mg_3N_2 and Li_3N in refs. [22,23], respectively.

stable intermediate products of Li_2NH , which was confirmed by the powder diffraction measurements. This is the cause of difference weight loss between measurement and theoretical one. As shown in the inset of Fig. 3, the diffraction peaks corresponding only to Mg_3N_2 and Li_3N were observed after the dehydrating reaction in vacuum up to 750 K. This indicates that the dehydrating reaction actually according to Eq. (4). We have also confirmed by gas chromatography that the gas component from the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 M of LiH contains only hydrogen without ammonia.

It should be emphasized that the dehydrating reaction of the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 M of LiH begins at approximately 420 K under the present condition, while that of the mixture of LiNH_2 and 2 M of LiH began at approximately 550 K with a heating rate of 10 K/min under 0.1 MPa of argon by gas chromatography [15]. The difference is probably due to the lower decomposition temperature of $\text{Mg}(\text{NH}_2)_2$ as compared to that of LiNH_2 , with respect to the formation of ammonia. Moreover, the mixed LiH could suppress the desorption of ammonia from $\text{Mg}(\text{NH}_2)_2$, and enhance the desorption of only hydrogen.

We have also reported in detail the hydriding reaction (right-to-left direction) in Eq. (4) of the mixture of 4 M of Li_3N and 1 M of Mg_3N_2 under appropriate conditions [24]. Moreover, detailed reaction path of Eq. (4) is now being investigated by synchrotron radiation X-ray diffraction and neutron diffraction experiments. The reversible reaction according to Eq. (4) achieves solid state hydrogen storage more than 9 mass% of hydrogen. $\text{Mg}(\text{NH}_2)_2$ is a preferable candidate for hydrogen storage, since it has a lower dehydrating temperature, less activity to air, and also a lower cost, comparing to LiNH_2 .

4. Conclusions

The single phase $\text{Mg}(\text{NH}_2)_2$ prepared by the solid–gas reaction of MgH_2 with ammonia was mixed with different molars of MgH_2 or LiH to systematically investigate the dehydrating properties. With increasing temperature, the mixtures of $\text{Mg}(\text{NH}_2)_2$ and MgH_2 desorb ammonia at approximately 630 K, similar to $\text{Mg}(\text{NH}_2)_2$ without MgH_2 . On the other hand, the mixture of $\text{Mg}(\text{NH}_2)_2$ and 4 M of LiH desorbed only hydrogen, because LiH can react ultra-fast with ammonia from $\text{Mg}(\text{NH}_2)_2$, unlike MgH_2 .

Acknowledgements

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