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Hydrogen Storage in a $LiNH_2-MgH_2$ (1:1) System

Yongfeng Liu, Kai Zhong, Mingxia Gao, Jianhui Wang, Hongge Pan,* and Qidong Wang

Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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A novel $LiNH_2-MgH_2$ hydrogen storage system with a molar ratio of 1:1, which can desorb 6.1 wt % hydrogen or 3 equiv of H atoms during first ball milling and subsequent heating, was investigated. During ball milling, the NH_2 group in $LiNH_2$ and H atoms in MgH_2 switched with each other, leading to the formation of $Mg(NH_2)_2$ and LiH, and then the newly formed $Mg(NH_2)_2$ and LiH and the remaining MgH_2 reacted continuously to desorb hydrogen by absorbing heat at an elevated temperature. After heating to 390 °C, the final product was identified to be Mg_3N_2, $Li_2MgN_2H_2$, and LiH by means of XRD and IR characterization. Thermodynamic examination shows that the desorption heat effect is around 45.9 kJ/mol of H_2.

1. Introduction

Hydrogen is viewed as a new clean energy source.[1] For applications of hydrogen energy, especially as an on-board power source, hydrogen storage is one of the key enabling technologies.[2] The target set by the U.S. Department of Energy (DOE) for an automobile on-board storage system is that the hydrogen storage capacity should be higher than 6% of the system weight by 2010.[3] For achieving the DOE target, considerable work has been carried out on the research and development of new types of hydrogen storage materials,[4] in which the Li−N−H system in the reversible hydrogen storage of metal−N−H-based materials has been a successful one. In 2002, Chen et al. reported that the $LiNH_2-LiH$ system can absorb ca. 6.5 wt % hydrogen at a temperature above 200 °C by the following reaction:[4b]

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \qquad (1)$$

Although it has a relatively high storage capacity, the $LiNH_2-LiH$ system can only desorb hydrogen at 1.0 atm of hydrogen pressure at temperatures above 250 °C due to the rather high enthalpy change ($\Delta H \approx 60$ kJ/mol of H_2),[5a] which is too high for practical applications. It is necessary to tune the thermodynamic properties of the metal−N−H materials by means of component optimization for reducing the operating temperature.

Recent studies revealed that the Li−Mg−N−H ternary system has improved thermodynamic properties compared to the $LiNH_2-LiH$ system.[5] It was found that $Mg(NH_2)_2-LiH$ (1:2) and $LiNH_2-MgH_2$ (2:1) could reversibly store more than 5.5 wt % hydrogen at 180 °C with a desorption equilibrium pressure of around 20 atm. Thermodynamic calculations indicated that hydrogen desorption from the $Mg(NH_2)_2-LiH$ (1:2) system can be carried out at temperatures even below 100 °C. Further investigations indicated that the change in the molar ratio of the $Mg(NH_2)_2-LiH$ system could change the reaction process, the amount of hydrogen desorbed, and the solid products finally produced.[6]

More recently, Alpati et al. predicted the following hydrogen storage system could be energetically favorable by first-principles density function theory (DFT) calculations:[7]

$$LiNH_2 + MgH_2 \leftrightarrow (LiMgN) + 2H_2 \qquad (2)$$

This reaction yields 8.19 wt % H at completion with a calculated reaction enthalpy of 29.7 kJ/mol of H_2 at 0 K using the ultrasoft pseudopotential (USPP) approach. Furthermore, Akbarzadeh et al. inferred that the 1:1 mixture of $LiNH_2$ and MgH_2 would decompose according to the following sequential reactions by the modern first-principles calculations of total energies and vibrational free energies:[8]

$$\begin{aligned} &LiNH_2 + MgH_2 \rightarrow \frac{1}{2}Mg(NH_2)_2 + LiH + \frac{1}{2}MgH_2 \\ &\rightarrow \frac{1}{4}Mg(NH_2)_2 + \frac{1}{4}Mg_3N_2 + LiH + H_2 \\ &\rightarrow \frac{1}{4}Li_2MgN_2H_2 + \frac{1}{4}Mg_3N_2 + \frac{1}{2}LiH + \frac{3}{2}H_2 \\ &\rightarrow LiMgN + 2H_2 \end{aligned} \qquad (3)$$

Interesting enough, instead of the predicted reactions 1 and 3, Osborn et al. found experimentally the presence of a new product, $Li_2Mg_2(NH)_3$, after dehydrogenation of the

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* To whom correspondence should be addressed. Phone: +86 571 87952615. Fax: +86 571 87952615. E-mail: hgpan@zju.edu.cn.

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$LiNH_2-MgH_2$ mixture at 210 °C as expressed in the following reaction:[9]

$$LiNH_2 + MgH_2 \rightarrow \frac{1}{3}Li_2Mg_2(NH)_3 + \frac{1}{3}MgH_2 + \frac{1}{3}LiH + H_2 \quad (4)$$

However, the reversibility of the above reaction has not been ascertained yet. Therefore, it is still of scientific interest to elucidate the details of the reaction between $LiNH_2$ and MgH_2 at a molar ratio of 1:1.

In this study, the mixture of $LiNH_2-MgH_2$ was prepared at a molar ratio of 1:1 by ball milling, and its changes in structure and in hydrogen absorption/desorption behaviors during hydrogenation/dehydrogenation were systematically studied with X-ray powder diffraction (XRD), infrared (IR) spectroscopy, temperature-programmed desorption (TPD), differential scanning calorimetry (DSC), and volumetric measurement. A stepwise hydrogen desorption process was clarified.

2. Experimental Section

The starting chemicals $LiNH_2$ (95%) and MgH_2 (98%) were purchased from Alfa Aesar and were used without any further purification. A ∼1.15 g (0.05 mol) portion of $LiNH_2$ and 1.3 g (0.05 mol) of MgH_2 were weighed and loaded into a milling jar (180 mL) in a glovebox (MBRAUN) filled with pure argon to prevent air and moisture contamination. The milling jar was equipped with a gas valve which could be connected to a pressure gauge for measuring the inside pressure change. The ball-to-sample weight ratio was 60:1. The ball milling was carried out on a planetary ball mill (QM-1SP4, Nanjing) rotating at 500 rpm.

The temperature dependence of the hydrogen desorption behavior of the sample milled for 36 h was measured on a homemade TPD system with an online gas chromatograph attached. Pure Ar was used as the carrier gas. In this experiment, about 50 mg of the sample was loaded and tested. The temperature was raised gradually from 20 to 400 °C at a rate of 2 °C/min.

The amount of hydrogen desorbed and absorbed at different temperatures was determined by the volumetric method with a homemade Sieverts-type apparatus. A sample of about 500 mg was used each time. The temperature was raised at 2 °C/min for desorption and at 1 °C/min for absorption, respectively. The heat effect of hydrogen desorption from the sample milled for 36 h was measured by the DSC method on a Netzsch DSC 200 3F unit. Pure N_2 was used as the carrier gas. The heating rate was set at 10 °C/min.

N−H vibrations in all samples were identified by a Nicolet Avatar 360 infrared unit (PE). The transmission mode was adopted. The phase structures of the hydrogenated/dehydrogenated samples were identified by a Rikagu D/Max-RA X-ray diffractometer with Cu Kα radiation at 40 kV and 30 mA. A homemade container was used to prevent powder samples from contacting air and moisture.

3. Results and Discussion

During ball milling, a gas was evolved gradually, which was identified to be pure hydrogen. The amount of hydrogen released from the starting mixture was calculated by using the ideal gas law with the measured gas pressure variations within the ball-milling jar as shown in Table 1. It can be seen that no pressure rise was detected in the milling jar within the first 12 h. As the ball milling proceeded further, H_2 was gradually noticed. After 36 h of milling, about 3.0 atm of hydrogen, equivalent to 0.9 mol of H atoms per formula of $LiNH_2-MgH_2$, was released from the mixture of $LiNH_2-MgH_2$ (1:1). The fact that the two chemical components in the mixture, $LiNH_2$ and MgH_2, are both stable when ball-milled alone indicates that the hydrogen comes from the chemical reaction between these two chemicals.

Table 1. Pressure Variation and Amount of Hydrogen Released with Ball-Milling Time

ball-milling time (h)	pressure in milling jar (atm)	amt of H atoms released per $LiNH_2-MgH_2$ (mol)
2	0	0
6	0	0
12	0	0
18	0.9	0.27
24	1.4	0.4
36	3.0	0.9

For making clear the chemical reactions occurring during the ball milling process, solid residues at different ball-milling stages were collected for both IR and XRD characterizations. Figure 1a shows the IR spectra of the samples milled for 2, 6, 12, 24, and 36 h. The sample after 2 h of milling still keeps the typical doublet N−H vibration of the amide ions in $LiNH_2$ at 3258/3313 cm^{-1}. For the sample after 6 h of milling, the absorbance at 3258 cm^{-1} becomes broader and more asymmetric. It is very interesting to note that the characteristic N−H vibrations of $LiNH_2$ at 3258/3313 cm^{-1} become almost undetectable when the ball milling is prolonged to 12 h even though no hydrogen is released. Then new doublets at 3272/3326 cm^{-1} are displayed which are the characteristic N−H symmetric and asymmetric vibrations of $Mg(NH_2)_2$. This phenomenon indicates that the energetic ball milling treatment induces the exchange of the NH_2 group between $LiNH_2$ and MgH_2 and the eventual formation of $Mg(NH_2)_2$. As the milling time is prolonged to 24 h, in addition to the two absorption peaks of $Mg(NH_2)_2$,

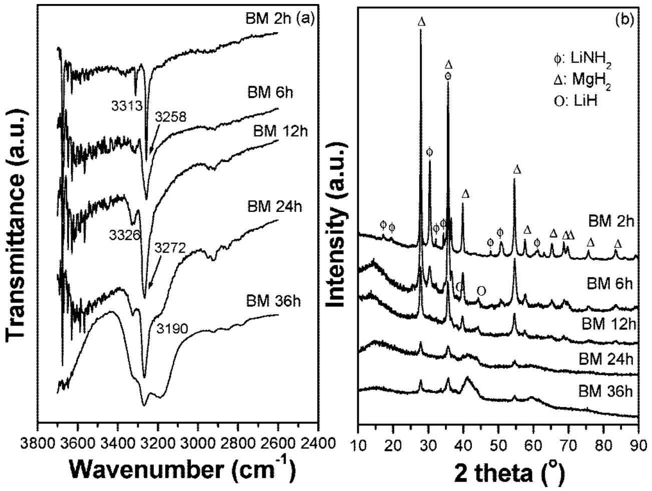

Figure 1. IR spectra (a) and XRD patterns (b) of the $LiNH_2-MgH_2$ (1:1) sample milled for 2, 6, 12, 24, and 36 h.

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a new weak absorbance appears at 3190 cm^{-1}, which is in the N−H vibration range of imide. After 36 h of ball milling, a new broad peak caused by 0.9 mol of H atoms released from $LiNH_2-MgH_2$ appears, indicating the formation of a new structure, which is possibly MgNH as proposed by Hu et al.[10] At the same time, the relative intensity of peaks at 3272/3326 cm^{-1} is decreased, implying the newly developed $Mg(NH_2)_2$ is being consumed.

The XRD patterns of the samples milled for different durations are illustrated in Figure 1b. It can be seen that the sample milled for 2 h consists of the original $LiNH_2$ and MgH_2 phases. After 6 h of milling, although the $LiNH_2$ and MgH_2 phases are still dominating in the XRD profile, two small peaks at 38.1° and 44.3° (2θ) are observed which can be assigned to the LiH phase matched with the PDF-2 database of JCPDS-ICDD. After 12 h of milling, the diffraction peaks of $LiNH_2$ become invisible, indicating the presence of a new chemical reaction between $LiNH_2$ and MgH_2 during ball milling. However, the fact that the diffraction peaks of $Mg(NH_2)_2$ then become undetectable by XRD can be attributed to the fact that the compound is easily deformed into an amorphous state under the energetic ball-milling process.[10b] The phenomenon that the XRD pattern of the sample after 24 h of milling shows a low intensity of MgH_2 peaks is interpreted by us as the gradual consumption of MgH_2 during ball milling. At the same time, two broad peaks at 41.4° and 59.8°, corresponding to the new structure observed by IR, emerge in the XRD profile. As the milling time is extended to 36 h, the intensities of the two new peaks are both enhanced. In the previous work, these two diffraction peaks at 41.4° and 59.8° were assigned to MgNH.[10]

On the basis of the above discussions, a picture of the chemical process can be given during ball milling of the $LiNH_2-MgH_2$ mixture. First, the exchange of the NH_2 group occurs between $LiNH_2$ and MgH_2 with no hydrogen release during the first 12 h of milling:

$$LiNH_2 + MgH_2 \rightarrow \frac{1}{2}Mg(NH_2)_2 + LiH + \frac{1}{2}MgH_2 \quad (5)$$

A similar metathesis reaction is also observed during the ball-milling process of the $LiNH_2-2MgH_2$ system.[5c] Then, the newly developed $Mg(NH_2)_2$ reacts with MgH_2 to form MgNH with the release of H_2. It is obvious that the sample with 0.9 mol of H atoms released after being milled for 36 h mainly consists of MgNH and LiH with a residual amount of $Mg(NH_2)_2$ and MgH_2 as shown in Figure 1. According to Hu's report, $Mg(NH_2)_2$ in the mixture of $Mg(NH_2)_2-2MgH_2$ first reacts with MgH_2 to yield MgNH and H_2 during ball milling, and then the excessive MgH_2 further reacts with MgNH.[10b] Hu's result makes us believe that the following reaction occurs with prolonged ball milling from 12 to 36 h in the present study:

$$\frac{1}{4}Mg(NH_2)_2 + \frac{1}{2}MgH_2 \rightarrow \frac{1}{2}MgNH + \frac{1}{4}MgH_2 + \frac{1}{2}H_2 \quad (6)$$

The above proposed reaction is in good agreement with the results of the amount of hydrogen released (Table 1) and our IR and XRD analyses (Figure 1).

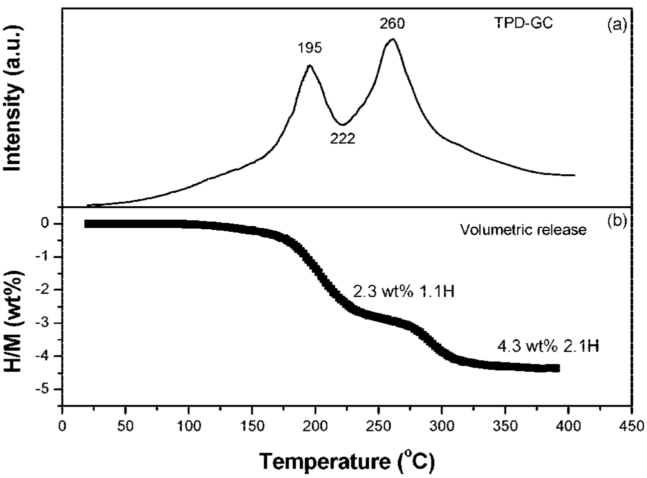

Figure 2. TPD curve (a) and volumetric release of hydrogen (b) of the $LiNH_2-MgH_2$ (1:1) sample milled for 36 h.

Figure 2a shows the TPD curve of the sample milled for 36 h. Obviously, two hydrogen desorption peaks can be detected, and the hydrogen desorption starts at ca. 50 °C, ends at ca. 390 °C, and peaks at ca. 195 and 260 °C, respectively. This reveals that the hydrogen desorption process from the $LiNH_2-MgH_2$ (1:1) system milled for 36 h is a multistep reaction. H_2 gas alone was identified in the temperature range of 20−390 °C. The quantity of hydrogen desorbed was measured subsequently with a Sieverts-type volumetric apparatus as described previously.[11a] The results are shown in Figure 2b. It can be seen that the quantity of hydrogen desorbed varies with the reaction process, which in turn is governed by the temperature of the sample, in good agreement with the TPD measurement mentioned above. Approximately 4.3 wt % hydrogen, equivalent to 2.1 mol of H atoms, was desorbed from the sample ball-milled for up to 36 h and then heated in the temperature range of 20−390 °C. With the 0.9 mol of H atoms released during ball milling also considered, 3 mol of H atoms, equivalent to 6.1% of the sample weight, was obtained from the mixture of $LiNH_2-MgH_2$ (1:1).

To ascertain the chemical process occurring during dehydrogenation, the sample was first ball-milled for 36 h and then heated slowly to desorb hydrogen at a definite heating rate, and samples at different heating stages were collected for XRD and IR analyses. Figure 3 shows the IR spectra (a) and XRD patterns (b) of the samples dehydrogenated at 210, 270, and 390 °C. As shown in Figure 3a, only one broad absorbance centered at 3178 cm^{-1} located in the typical N−H vibration range of imide can be observed after the sample is heated to 210 °C. This result indicates that the NH_2 group in the sample has been consumed and the NH group has been developed with the evolution of hydrogen. After the sample is heated to 270 and 390 °C, the absorbance becomes sharper although its position remains unchanged at 3178 cm^{-1}, especially for that at 390 °C. XRD examination shows that after the sample is heated to 210 °C, the

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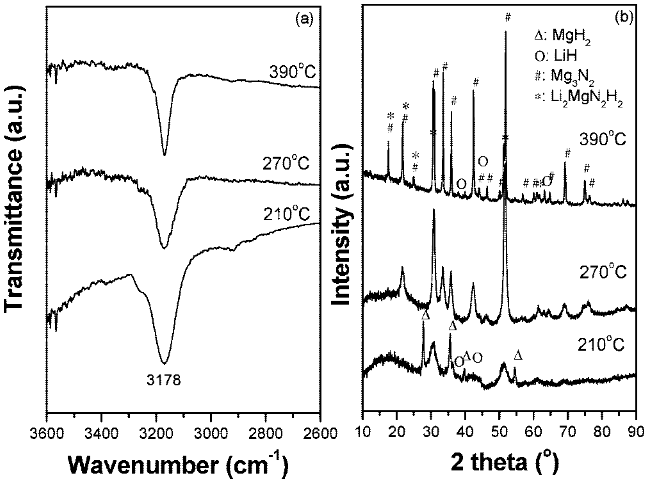

Figure 3. IR spectra (a) and XRD patterns (b) of the dehydrogenated $LiNH_2-MgH_2$ (1:1) sample at 210, 270, and 390 °C.

MgH_2 and LiH phases can be identified. In the meantime two broad peaks at 30.9° and 51.5° with much higher intensities are identified in the XRD profile. Combining these results with those of the IR spectrum analysis, we decide to assign these two diffraction peaks to an imide or nitride-like structure. On account of the presence of the constituent elements of Li, Mg, N, and H, the two strongest characteristic diffraction peaks observed here matched well with those of $Li_2MgN_2H_2$.[11] It is important for us to mention that $Li_2Mg_2(NH)_3$ reported by Osborn et al.[9] was not found in the present study. This may be attributed to the different ball-milling durations applied in these two cases. In Figure 3b for the sample heated to 270 °C, the Mg_3N_2 phase can be unambiguously identified from the peaks at 21.8°, 30.9°, 33.4°, 35.8°, 42.4°, and 51.8° despite the fact that they are broader. As the dehydrogenation temperature is increased to 390 °C, the diffraction patterns of the well-crystallized Mg_3N_2, $Li_2MgN_2H_2$, and LiH phases can be observed.

With the information obtained from IR and XRD, we can speculate on the chemical reaction process of the dehydrogenation of the ball-milled $LiNH_2-MgH_2$ mixture for 36 h and heated to specific temperatures. As mentioned above, the sample ball-milled for 36 h mainly consists of $Mg(NH_2)_2$, MgH_2, LiH, and MgNH. After the sample is heated to 210 °C, $Mg(NH_2)_2$ becomes undetectable and a new imide of $Li_2MgN_2H_2$ can be identified, as the components in the $Mg(NH_2)_2-2LiH$ system react chemically to form $Li_2MgN_2H_2$ with the release of H_2 according to the following reaction:[5]

$$Mg(NH_2)_2 + 2LiH \rightarrow Li_2MgN_2H_2 + 2H_2 \qquad (7)$$

In the present study, 1/4 mol of $Mg(NH_2)_2$ is reacting with 1/2 mol of LiH to yield 1/4 mol of $Li_2MgN_2H_2$ and 1 mol of H atoms. Accordingly, reaction 7 can be rewritten as follows:

$$\frac{1}{4}Mg(NH_2)_2 + \frac{1}{2}LiH \rightarrow \frac{1}{4}Li_2MgN_2H_2 + \frac{1}{2}H_2 \qquad (8)$$

Investigation on the quantity of hydrogen desorbed reveals that ~1.1 equiv of H atoms was released as shown in Figure 2, in which 1.0 equiv of H atoms comes from reaction 8 and the excessive 0.1 equiv of H atoms may come from reaction 6. As the sample is further heated to 390 °C, the MgH_2 phase becomes undetectable while the Mg_3N_2 phase together with the $Li_2MgN_2H_2$ and LiH phases are detected. According to Hu et al., MgNH and MgH_2 can react to yield Mg_3N_2 and H_2.[10b] From reactions 5 and 6, the sample after 36 h of ball milling should contain 1/2 mol of MgNH and 1/4 mol of MgH_2. Therefore, the reaction for hydrogen desorption in the temperature range of 220−390 °C in our sample shown in Figure 2 should be expressed as follows:

$$\frac{1}{2}MgNH + \frac{1}{4}MgH_2 \rightarrow \frac{1}{4}Mg_3N_2 + \frac{1}{2}H_2 \qquad (9)$$

The theoretical hydrogen desorption amount of 1 mol of H atoms correlates well with the result of volumetric release measurement in the temperature range of 220−390 °C as shown in Figure 2. At the same time, the exhaustion of MgNH in the reaction may be responsible for the sharpness of the absorbance at 3178 cm^{-1} observed by means of IR (Figure 2).

According to the above discussions, the hydrogen desorption reaction of $LiNH_2-MgH_2$ (1:1) can be expressed by the following four-step reaction:

$$\begin{aligned}
LiNH_2 + MgH_2 &\xrightarrow{\text{ball-milled for 12 h}} \frac{1}{2}Mg(NH_2)_2 + \\
&LiH + \frac{1}{2}MgH_2 \\
&\xrightarrow{\text{ball-milled for 36 h}} \frac{1}{2}MgNH + \frac{1}{4}Mg(NH_2)_2 + \\
&LiH + \frac{1}{4}MgH_2 + \frac{1}{2}H_2 \\
&\xrightarrow{\text{heated to 220 °C}} \frac{1}{2}Li_2MgN_2H_2 + \frac{1}{2}MgNH + \\
&\frac{1}{2}LiH + \frac{1}{4}MgH_2 + H_2 \\
&\xrightarrow{\text{heated to 390 °C}} \frac{1}{4}Mg_3N_2 + \frac{1}{4}Li_2MgN_2H_2 + \\
&\frac{1}{2}LiH + \frac{3}{2}H_2
\end{aligned} \qquad (10)$$

The total amount of hydrogen desorbed from this reaction is 6.1 wt %, which is in excellent agreement with the experimental measurement as described above. We should also report here that the product LiMgN predicted by Akbarzadeh et al.[8] has not been obtained in the present study.

For elaborating the hydrogen desorption thermodynamics, the desorption heat effect was evaluated by means of DSC. Figure 4 is the DSC curve of the $LiNH_2-MgH_2$ (1:1) sample after 36 h of ball milling. Apparently, an endothermic nature of the reaction is exhibited. There are two main endothermic peaks. By integrating the two endothermic peaks, a heat effect of 1003 J/g is obtained, which can be converted to 48.2 kJ/mol of $LiNH_2-MgH_2$ or 45.9 kJ/mol of H_2. In general, for a thermodynamically reversible hydrogen storage process, an endothermic desorption reaction with a standard enthalpy change ranging between 29 and 46 kJ/mol of H_2 is

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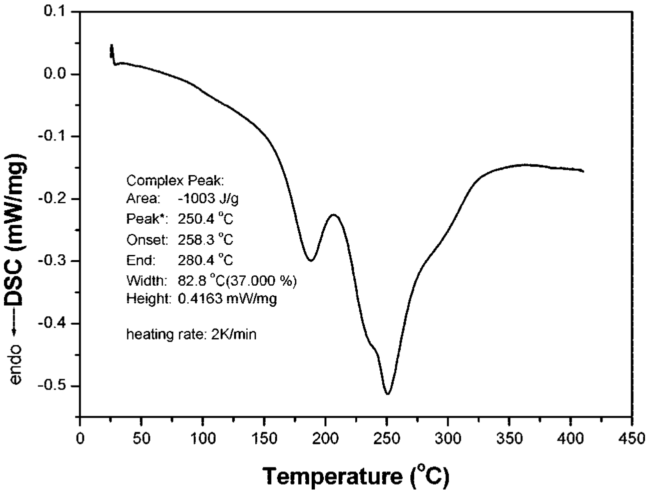

Figure 4. DSC curve of the $LiNH_2-MgH_2$ (1:1) sample milled for 36 h.

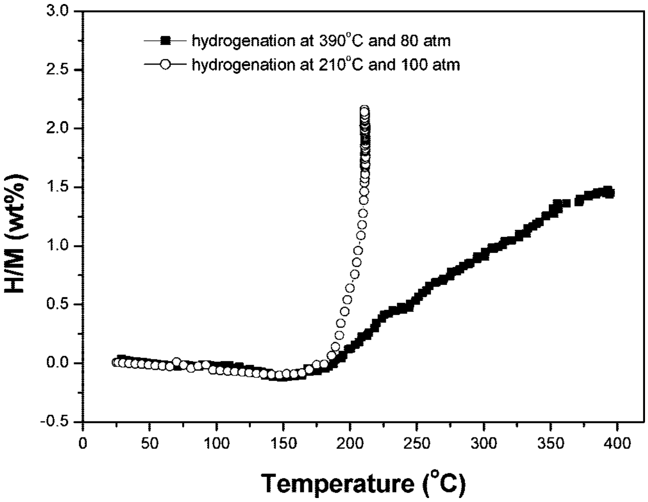

Figure 5. Volumetric soak curves of the dehydrogenated $LiNH_2-MgH_2$ (1:1) sample at 210 and 390 °C.

desired.[12] According to the above calculation, it can be deduced that the $LiNH_2-MgH_2$ (1:1) system should be a good reversible or partially reversible system.

To validate the hydrogen absorption/desorption reversibility, the hydrogenation was performed on the dehydrogenated sample of the $LiNH_2-MgH_2$ (1:1) system milled for 36 h as shown in Figure 5. A hydrogen pressure of 80 atm was applied on the system. It can be seen that the hydrogenation started at ca. 150 °C, and the hydrogen absorbed slowly reached 1.56 wt % at 390 °C, corresponding to 0.7 mol of H atoms. The amount of hydrogen reabsorbed is obviously lower than that of hydrogen desorbed from the starting mixture, implying that under the present testing conditions the dehydrogenated sample has not been reverted to its starting state. The XRD pattern and IR spectrum of the presently hydrogenated sample are shown in Figure 6. The XRD pattern apparently shows a multiphase structure, which mainly consists of a cubic Mg_3N_2 phase, a cubic LiH phase, and a tetragonal $Li_2Mg_2(NH)_3$ phase referred to the PDF-2 database of JCPDS-ICDD and the literature.[13] The diffraction peaks of $Li_2MgN_2H_2$ are not observable in the XRD profile. Moreover, two strong absorbance peaks exist at 3198 and 3163 cm^{-1} in the IR spectrum, which could be features of the N−H vibration of the ternary imide of $Li_2Mg_2(NH)_3$ according to the report of Hu et al.[14] In the meantime, two weak absorbances appear at 3313 and 3240 cm^{-1}. The absorbance at 3313 cm^{-1} can be ascribed to the N−H vibration of $LiNH_2$ as Novak et al. have reported the IR of $LiNH_2$ exhibiting two vibration absorbances at 3313 and 3258 cm^{-1}.[15] In this work, the absorbance at 3258 cm^{-1} was not discernible due to the existing strong broad absorbance. The absorbance at 3240 cm^{-1}, which is within the N−H vibration range of imide, may originate from a new imide-like structure. Since the intensity of the absorbances at 3313 and 3240 cm^{-1} is very weak, the diffraction generated from the imide is too little to be detected by means of XRD as shown in Figure 6a. On the basis of the above analysis, it can be concluded that the presently hydrogenated sample has a rather complicated composition containing mainly Mg_3N_2, LiH, $Li_2Mg_2(NH)_3$, $LiNH_2$, and a new imide-like compound, and the dehydrogenated sample is not reverted to its starting chemical conditions when it is recharged under the present conditions.

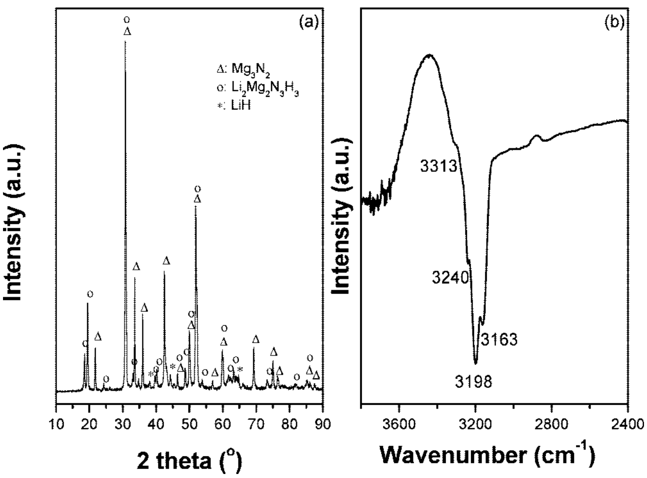

Figure 6. XRD pattern (a) and IR spectrum (b) of the hydrogenated $LiNH_2-MgH_2$ (1:1) sample at 390 °C and 80 atm.

It has been reported that $Li_2Mg_2(NH)_3$ and $LiNH_2$ play the role of intermediates in the process of hydrogenation/dehydrogenation of $Li_2MgN_2H_2$ according to the following reactions:[10b]

$$Li_2MgN_2H_2 + \frac{1}{2}H_2 \leftrightarrow \frac{1}{2}Li_2Mg_2(NH)_3 + \frac{1}{2}LiNH_2 + \frac{1}{2}LiH \tag{11}$$

$$\frac{1}{2}Li_2Mg_2(NH)_3 + \frac{1}{2}LiNH_2 + \frac{3}{2}H_2 \leftrightarrow Mg(NH_2)_2 + \frac{3}{2}LiH \tag{12}$$

Then the overall reaction can be described as follows:

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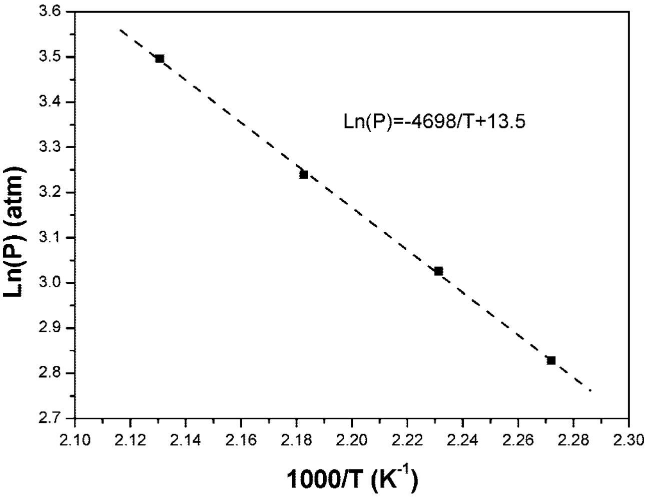

Figure 7. van't Hoff plot of H_2 desorption from the $LiNH_2-MgH_2$ sample milled for 36 h in the temperature range 165−195 °C.

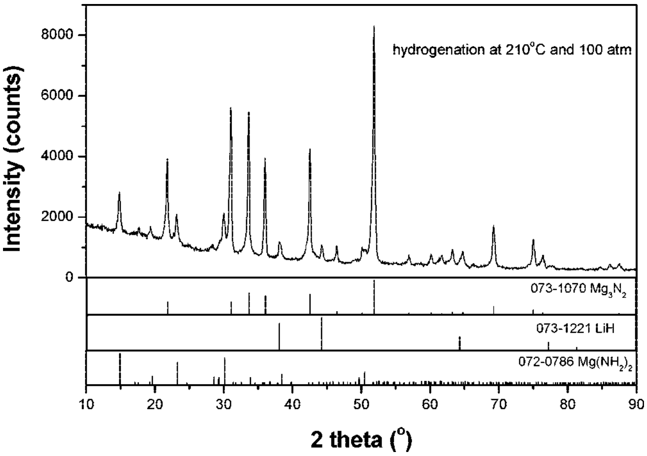

Figure 8. XRD pattern of the rehydrogenated sample at 210 °C and 100 atm.

$$Li_2MgN_2H_2 + 2H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH \qquad (13)$$

The fact that $Li_2Mg_2(NH)_3$ and $LiNH_2$ were formed with the disappearance of $Li_2MgN_2H_2$ shown in Figure 6 implies that reaction 11 should be taking place during hydrogenation at 80 atm and 390 °C. As indicated in reaction 10, there is 1/4 mol of $Li_2MgN_2H_2$ in the dehydrogenation product of the $LiNH_2-MgH_2$ mixture ball-milled for 36 h, which can only absorb 0.25 mol of H atoms according to reaction 11. This seems to be inconsistent with the 0.7 mol of H atoms absorbed as measured by volumetric soak at 80 atm and 390 °C (Figure 5). Therefore, the correct answer should have reaction 12 proceeding subsequently. On account of the above analyses, it is reasonable to suggest that reaction 13 should be the reversible reaction in the present study. Nevertheless, no trace of $Mg(NH_2)_2$ has been found by means of XRD and IR in the present study.

With the chemical reactions basically ascertained, we turned to the heat effect study of the reactions. The desorption equilibrium pressures (P_{eq}) of the sample ball-milled for 36 h were measured at 165−195 °C, and the relationship between $\ln(P_{eq})$ and $1/T$ is plotted in Figure 7, which shows a good van't Hoff relationship between the two parameters. By fitting data points into the basic equation, the van't Hoff equation for the reversible H_2 desorption/absorption was derived as

$$\ln(P) = \frac{-4698}{T} + 13.5 \qquad (14)$$

This is in good accordance with the investigations on the $Mg(NH_2)_2-2LiH$ system reported by Xiong et al.[16] This result further indicates that the reversible hydrogenation/dehydrogenation is generated from reaction 13 in this work.

According to eq 14, the calculated enthalpy change of the reversible hydrogen generation is ca. 39.1 kJ/mol of H_2, lower than the desorption heat effect (45.9 kJ/mol of H_2) obtained by DSC, which may be attributed to the fact that eq 14 is only one of the steps of reaction 10. In addition, the equilibrium pressure of reaction 13 at 390 °C is calculated to be 611 atm, much higher than the 80 atm of hydrogen pressure applied for hydrogenation in this work. These results make us believe that, owing to the low external pressure, the hydrogenation process has not been completed fully. For reducing the effect of the reverse reaction in reaction 13, the rehydrogenation of the dehydrogenated $LiNH_2-MgH_2$ sample was once more tested at 210 °C and 100 atm. The hydrogen absorption curve is also presented in Figure 5. Compared with 80 atm, the hydrogenation process of the dehydrogenated sample is sped up under 100 atm, and the amount of hydrogen absorbed is increased to ca. 2.3 wt %, which is equivalent to ca.1 mol of H atoms/mol of dehydrogenated sample.

Figure 8 shows the XRD pattern of the rehydrogenated sample at 210 °C and 100 atm. It can be seen that, after rehydrogenation at 210 °C and 100 atm, the phases of Mg_3N_2 and LiH can still be easily identified. In the meantime the $Mg(NH_2)_2$ phase with considerable intensities emerges and the specific diffraction peaks of $Li_2MgN_2H_2$ all disappear in the XRD profile. It is obvious that $Mg(NH_2)_2$ was formed accompanied by the exhaustion of $Li_2MgN_2H_2$. The new experiment on P_{eq} and $1/T$ makes us more confident in believing that eq 13 really stands for the reversible hydrogen absorption/desorption reaction in the present study. As there is only 1/4 mol of $Li_2MgN_2H_2$ in the dehydrogenated product as shown in eq 10, the reversible hydrogen absorption/desorption reaction should be expressed as

$$\frac{1}{4}Li_2MgN_2H_2 + \frac{1}{2}H_2 \leftrightarrow \frac{1}{4}Mg(NH_2)_2 + \frac{1}{2}LiH \qquad (15)$$

with the reversible hydrogen storage capacity of 1 mol of H atoms per formula unit, which correlates well with the result of experimental measurement. However, as we have repeatedly mentioned above, ~0.9 mol of H atoms was released from the $LiNH_2-MgH_2$ (1:1) sample milled for 36 h, indicating that the bonding of this part of hydrogen to the materials is weak. In other words, the recharge of hydrogen would be difficult, and the hydrogen pressure required should be high. The 100 atm of hydrogen pressure used might still not be enough for the full hydrogenation of the dehydrogenated sample in the present study.

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4. Conclusion

The reaction between lithium amide and magnesium hydride at a molar ratio of 1:1 subjected to ball milling and subsequent heating was investigated with XRD, IR, and hydrogen desorption/absorption measurements. A total of 6.1 wt % hydrogen was released from the mixture by first ball milling and subsequent heating of the sample. XRD and IR examinations showed that the exchange of the NH_2 group between $LiNH_2$ and MgH_2 occurred first to produce $Mg(NH_2)_2$ and LiH during ball milling, and the finial solid residue was composed of Mg_3N_2, $Li_2MgN_2H_2$, and LiH after heating to 390 °C. Thermodynamic analysis showed that the hydrogen desorption was an endothermic reaction, and the overall heat of reaction calculated was ca. 45.9 kJ/mol of H_2. However, only 1 equiv of H atoms can be recharged into the dehydrogenated sample to form a mixture of several compounds including Mg_3N_2, LiH, and $Mg(NH_2)_2$ under a high hydrogen pressure.

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