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Investigation of reaction between $LiNH_2$ and H_2

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Abstract

The reactions for $LiNH_2$ under a H_2 and an Ar flow were investigated, respectively. The results showed that $LiNH_2$ can be converted into LiH and NH_3 by reacting with H_2 under a H_2 flow condition, whereas $LiNH_2$ is converted into Li_2NH and NH_3 by decomposition under an Ar flow. Moreover, the reaction between $LiNH_2$ and H_2 can be accelerated by mixing $LiNH_2$ with LiH as well as doping $LiNH_2$ with $TiCl_3$. The confirmation of reaction between $LiNH_2$ and H_2 is helpful for the deeper insight in the systems of Li–N–H and Li–Mg–N–H for hydrogen storage materials.

Keywords: Hydrogen storage materials; Gas–solid reaction; X-ray diffraction

1. Introduction

In order to develop high-performance solid-state hydrogen storage materials for on-board application, recently, much attention has been paid to complex metal hydride [1–4]. Since the Li–N–H system was reported by Chen et al. to be one of the most promising hydrogen storage materials [3], many efforts have focused on the development of this novel hydrogen storage system. Ichikawa et al. [5] has first reported that by doping with 1 mol% $TiCl_3$, the ball-milled mixture of $LiNH_2$ and LiH reversibly desorbs/absorbs a large amount of H_2 (5.5–6 mass%) between 150 and 250 °C according to the following reaction:

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

Subsequently, it has been clarified that the above hydrogen desorption reaction proceeds through the following two elementary reaction steps [6,7]:

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \quad (2)$$

$$LiH + NH_3 \rightarrow LiNH_2 + H_2 \quad (3)$$

On the basis of the above mechanism model, we have successfully designed and developed a novel Li–Mg–N–H system, which reversibly stores ∼7 mass% H_2 according to the following reaction [8]:

$$8LiH + 3Mg(NH_2)_2 \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2 \quad (4)$$

Similar to the mechanism of the hydrogen desorption reaction (1), it has been proved that the hydrogen desorption reaction (4) was also possible to be mediated by NH_3 [8,9]. Furthermore, the mechanism of the hydrogenation process of reaction (4) has been investigated as well, indicating that Li_2NH is first hydrogenated into LiH and $LiNH_2$, and then the mixture of $LiNH_2$ and Mg_3N_2 is hydrogenated into LiH and $Mg(NH_2)_2$. Finally, the following reactions were proposed as the hydrogenation process [10]:

$$4Li_2NH + 4H_2 \rightarrow 4LiH + 4LiNH_2 \quad (5)$$

$$4LiNH_2 + 4H_2 \rightarrow 4LiH + 4NH_3 \quad (6)$$

$$Mg_3N_2 + 4NH_3 \rightarrow 3Mg(NH_2)_2 \quad (7)$$

The reactions (5) and (7) have been proved before, but the reaction (6) has not been confirmed yet [10]. On the other hand, a direct molecule–molecule reaction model due to the strong affinity between $H^{\delta+}$ in metal amides and $H^{\delta-}$ in metal hydride was proposed for understanding a hydrogen desorption mechanism in the Li–N–H and Li–Mg–N–H systems [11,12]. Therefore, the

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study on the reaction between $LiNH_2$ and H_2 seems to be helpful to understand the dominant mechanism of hydrogen storage in this system and provides clues for future research on hydrogen storage materials.

Previously, our results showed that the LiH phase was not detected in the XRD profile after heating $LiNH_2$ at 200 °C under a static hydrogen pressure in a closed space [10]. On the other hand, a similar reaction between $NaNH_2$ and H_2 was already investigated one century ago [13,14]. Miles [13] reported that $NaNH_2$ was partially converted into NaH in a stream of hydrogen at temperatures between 200 and 300 °C. Therefore, he thought that the following reaction took place:

$$NaNH_2 + H_2 \rightarrow NaH + NH_3 \quad (8)$$

However, Titherley [14] could not find the proceeding of the reaction (8) when $NaNH_2$ was heated under a hydrogen gas atmosphere in an enclosed space up to 300 °C. These results suggest that the equilibrium pressure of NH_3 for the decomposition of $NaNH_2$ is too low and/or the activation energy for the desorbing NH_3 from the surface of the sample is too high for proceeding of the reaction (8). Motivated by the above results, we planed in this work to investigate the reaction between $LiNH_2$ and H_2 under a H_2 flow in an open space, which can lead the NH_3 partial pressure to almost zero on the surface of $LiNH_2$ and can progress the reaction (6) even if the equilibrium pressure of NH_3 is low. In addition, we also studied the doping effect of $TiCl_3$ and the mixing effect with LiH on the reaction between $LiNH_2$ and H_2, since the hydrogen storage properties of the mixture of $LiNH_2$ and LiH were significantly improved by doping with 1 mol% $TiCl_3$. As comparison, the two contrastive experiments under a close static hydrogen pressure (close space) as well as an Ar gas flow (open space) were carried out in this work.

2. Experimental

The starting material $LiNH_2$ (95%), LiH (95%) and $TiCl_3$ (98%) were purchased from Sigma–Aldrich. Four kinds of samples, i.e. $LiNH_2$, 1 mol% $TiCl_3$-doped $LiNH_2$, the mixture of $LiNH_2$ and LiH, and the mixture of $LiNH_2$ and LiH doped with 1 mol% $TiCl_3$, were prepared by ball milling the mixtures for 2 h under a 1 MPa H_2 atmosphere. The thermal analyses of their samples were carried out by differential scanning calorimetry (DSC) equipment (Q10 PDSC, TA Instruments) under a H_2 or Ar flow with a flow rate of 100 ml/min. The DSC equipment was especially installed in a glovebox filled with purified argon, so that the samples were never exposed to air. The samples were first heated up to 200 °C at a rate of 5 K/min and kept at 200 °C for 4 h. A temperature of 200 °C was chosen to be the same temperature as the hydrogenation temperature of reaction (4) [10]. The pressure of H_2 flow was employed to be 1 MPa, and that of Ar to be 0.25 MPa. The identification of structure was carried out by the X-ray powder diffraction (XRD) method with a Cu Kα radiation (Rigaku, RINT-2100). In addition, Fourier transform infrared spectroscopy measurement (FT-IR, Spectrum One, Perkin-Elmer) was employed to check the identification of products obtained under an Ar flow as well.

3. Results and discussion

As shown in Fig. 1a, there are small amount of LiOH and Li_2O in the ball-milled $LiNH_2$ sample, which are the main impurities of the starting material $LiNH_2$. In the following XRD profiles, although the relative intensity of these impurities looks stronger comparing with the very poor scatterer of LiH, these impurities have no noticeable effect on the results and our discussion. In order to compare the most intense $LiNH_2$ peaks with the tiny LiH ones, the smaller inserts have been added in the corresponding XRD figures which show the poor diffraction peaks of LiH in the narrow region from 37° to 46°. As shown in Fig. 1b, $LiNH_2$ is partially converted into LiH after the heat treatment at 200 °C for 4 h under a 1 MPa H_2 flow, indicating that reaction (6) takes place in an open system, i.e. the $LiNH_2$ is hydrogenated into LiH and NH_3. However, in a close space even at the same temperature and pressure, reaction (6) does not proceed (Fig. 1c), which is consistent with our previous results [10]. When the temperature is further increased up to 300 °C, $LiNH_2$ is partially converted into LiH even in a close space (Fig. 1d), while under a H_2 flow (in an open space) it is completely converted into LiH (Fig. 1e). The above results indicate that the equilibrium pressure of NH_3 for the decomposition of $LiNH_2$ is too low for reaction (6) to progress at low temperature of 200 °C and/or the activation energy for releasing NH_3 from the surface of $LiNH_2$ is too high for proceeding of reaction (6) at 200 °C in a close space. However, when NH_3 is taken away from the system by flowing H_2-gas, reaction (6) can easily proceed (Fig. 1b and e). The confirmation of the reaction between $LiNH_2$ and H_2 is helpful for the deeper insight in the systems of Li–N–H and Li–Mg–N–H for hydrogen storage materials. In our previous work [10], we claimed that the mixture of $4LiNH_2$ and Mg_3N_2 was able to be hydrogenated into 4LiH and $3Mg(NH_2)_2$ at 200 °C, because $4NH_3$ and 4LiH could be formed by reacting $4LiNH_2$ with $4H_2$, and then the produced $4NH_3$ is consumed by reacting with Mg_3N_2 to form $3Mg(NH_2)_2$. These results well suggest that the NH_3 mediated reaction mechanism is acceptable

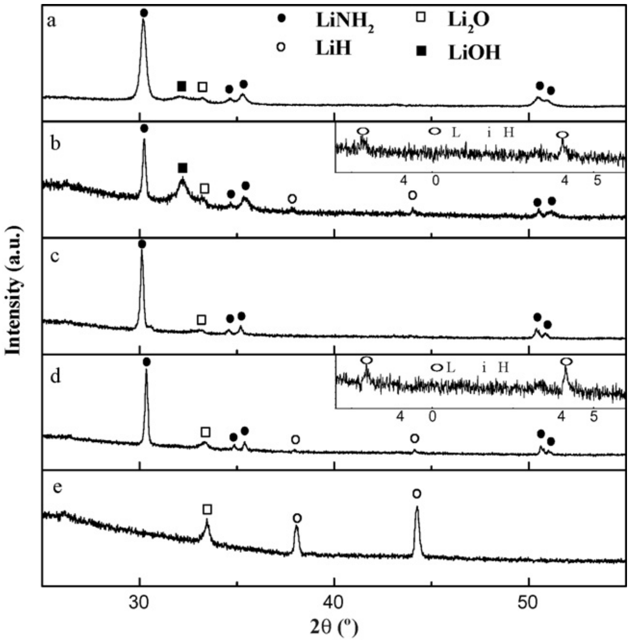

Fig. 1. XRD profiles of the ball-milled $LiNH_2$ (a) before heat treatment, (b) after heat treatment at 200 °C for 4 h under a 1 MPa H_2-gas pressure flow with a rate of 100 ml/min, (c) after heat treatment at 200 °C for 4 h under 1 MPa H_2 in a close space, (d) after heat treatment at 300 °C for 4 h under 1 MPa H_2 in a close space and (e) after heat treatment at 300 °C for 4 h under 1 MPa H_2 with a flow rate of 100 ml/min, respectively.