Hydrogen storage properties in Ti catalyzed Li–N–H system

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Abstract

The Li–N–H system expressed by $LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$ can be expected as a promising candidate for the hydrogen storage materials because of possessing a large amount of reversible hydrogen (6.5 wt.%), a satisfactorily fast kinetics and a relatively small enthalpy change. In this work, we investigated the hydrogen storage properties of the Li–N–H system from three different points of view. Firstly, we claim that the ball milled 1:1 mixture of lithium amide ($LiNH_2$) and lithium hydride (LiH) containing a small amount (1 mol %) of titanium chloride ($TiCl_3$) shows superior hydrogen storage properties; a large amount of H_2 gas desorbs in the temperature range from 150 to 250 °C at a heating rate of 5 °C/min and it reveals an excellent reversibility. Secondly, we clarify that the above hydrogen desorption reaction is composed of two kinds of elementary reactions: The one is that $2LiNH_2$ decomposes to Li_2NH and emits ammonia (NH_3). The other is that the emitted NH_3 reacts with LiH and transforms into $LiNH_2$ and H_2, indicating that NH_3 plays an important role on this H_2 desorption reaction. Finally, we examined the reaction of LiH and LiOH to clarify the influence of exposing the product to air. This is because due to the fact that LiOH is easily produced by exposing LiH and $LiNH_2$ to air. The reaction between LiH and LiOH indicated better kinetics but worse durability and an extra H_2 desorption due to transforming into Li_2O.
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Keywords: Hydrogen storage materials; Nanostructures; Gas–solid reactions; High-energy ball milling; Thermal analysis

1. Introduction

As early as 1910, Dafert and Miklauz [1] had already reported that the reaction between Li_3N and H_2 proceeded at 220–250 °C. Recently, Chen et al. [2] and Hu and Ruckenstein [3] have independently reported hydrogen storage properties of the Li_3N system. After that, much attention has been paid to this system [4–11], where the hydrogenation and dehydrogenation of Li_3N have been described by the following two consecutive reversible reactions;

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \tag{1}$$
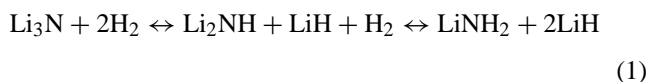
Here, the enthalpy change of the first reaction in chemical formula (1) could be calculated to be -148 kJ/mol H_2, while that of the second one -44.5 kJ/mol H_2, respectively. Since the small enthalpy change and possession of a large amount of hydrogen 6.5 wt.% for the latter reaction are considered to be still suitable for hydrogen storage system, we focused only on the latter reaction [5] and examined the hydrogen storage properties in details, which is expressed by the following chemical formula;

$$LiH + LiNH_2 \leftrightarrow Li_2NH + H_2 \tag{2}$$
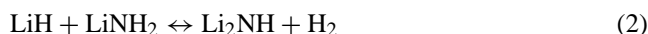
In this paper, we will discuss the catalytic effects on the hydrogen storage properties and the reversibility of the reaction (2), and also discuss the mechanism of the hydrogen desorption reaction from LiH and $LiNH_2$ to Li_2NH and H_2. Finally, we will describe the influence of exposing the Li-based materials to air (the water vapor in air).

2. Experimental details

The starting materials, LiH (95%) and LiOH (98%) were purchased from Sigma-Aldrich, whereas $LiNH_2$ (95%) from

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Strem Chemicals. As additives, the dry metals Fe, Co and Ni with particle size of several tens of nanometer were purchased from Shinku-Yakin, and $TiCl_3$ and VCl_3 were from Sigma-Aldrich. All the samples were treated in a glovebox filled with purified argon by gas recycling purification system (MP-P60W, Miwa MFG CO., LTD.) to minimize the oxygen and water pollution.

To achieve nanometer-scale contact among $LiNH_2$, LiH and the respective additives, and between LiH and LiOH, their mixtures were mechanically ball-milled (P7, Fritsch) at 400 rpm under a hydrogen atmosphere of 1 MPa (99.9999%) at room temperature for 2 h. For the milling treatment, the mixed powders of ∼300 mg and 20 pieces of steel balls with a diameter of 7 mm were brought into a Cr steel pot. After the ball-milling of the mixed powders, the products were examined by thermal desorption mass spectroscopy measurements (TDMS; M-QA200TS, Anelva) with the increase of temperature from ∼25 to 400 °C at a heating rate of 5 °C/min. This equipment is especially designed and built up for using it inside the glovebox filled with purified argon, which permitted simultaneously performing the TDMS measurement, thermogravimetry and differential thermal analysis (TG and DTA; TG8120, Rigaku) without exposing the samples to air at all.

To proceed the solid–gas reaction of LiH and NH_3, we performed the milling treatment for LiH under a NH_3 gas atmosphere of 0.4 MPa. After the treatment, the H_2 component in the milling vessel was monitored by gas chromatography (GC; GC8AIT, Shimadzu).

The identification of phases in the samples was examined by X-ray powder diffraction method with Cu Kα radiation (XRD; RINT-2100, Rigaku).

3. Results and discussions

First of all, we examined the catalytic effects on hydrogen desorption properties of ball milled mixtures with 1:1 molar ratio of $LiNH_2$ and LiH. As effective catalysts for improving the reaction rate, a small amount (1 mol %) of Ni, Fe and Co nanometer sized particles and titanium and vanadium chlorides ($TiCl_3$ and VCl_3) with particle size of micron meter were added to the mixtures before the ball milling. It is well-known that the former metal elements can act as a catalyst for the hydrogen molecule dissociation and the latter two chlorides can act as an excellent catalyst in the alanate system [12].

Fig. 1 shows the H_2 desorption and the NH_3 emission profiles (TDMS) of the mixtures containing the respective additives. We can notice that the mixtures doped with $TiCl_3$ and VCl_3 show very sharp and symmetrical hydrogen desorption curves in the temperature range from 150 to 280 °C. This indicates that the additives $TiCl_3$ and VCl_3 really act as an excellent catalyst in improving the reaction rate. Furthermore, it is noteworthy that no NH_3 gas emission was detected in the TDMS measurement up to 400 °C within our exper-
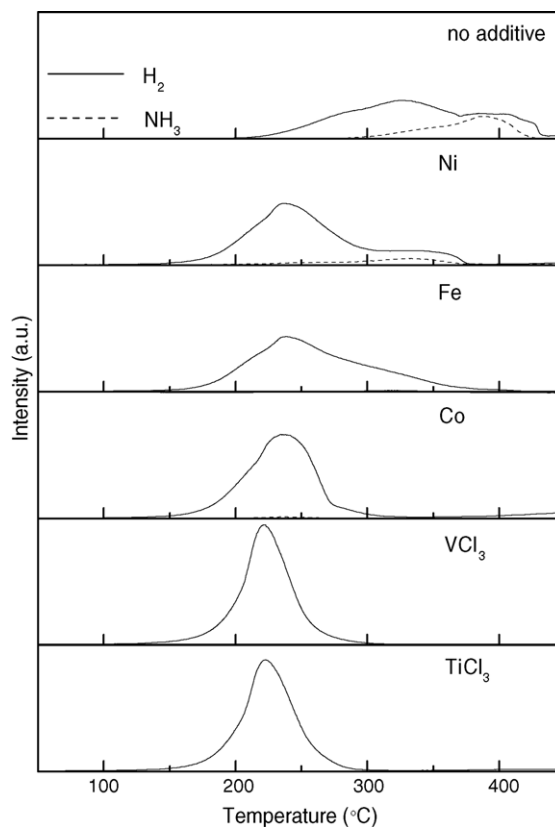

Fig. 1. Thermal desorption spectra of H_2 and NH_3 of the ball milled mixtures of 1:1 $LiNH_2$ and LiH, in which a small amount (1 mol %) of Ni, Fe and Co nanometer sized metals, and VCl_3 and $TiCl_3$ are added as additives before milling.

imental accuracy. These results indicate that all $LiNH_2$ has been consumed as a result of complete reaction with LiH and transformation into Li_2NH.

On the other hand, for nano-particle Ni, Co or Fe additives, a little emission of NH_3 is observed above ∼300 °C as shown in Fig. 1. This result indicates that the reaction rate is so low that a small amount of $LiNH_2$ remains unreacted up to 300 °C and starts to decompose into Li_2NH emitting NH_3 over 300 °C. From this fact, we suppose that the NH_3 emission plays an important role on the H_2 desorption reaction (2), because the H_2 desorption actually synchronizes with the NH_3 emission as is evident from Fig. 1. As a result of deep consideration, we could assume suitable elementary reactions for the reaction (2) as follows:

$$2LiNH_2 \rightarrow Li_2NH + NH_3, \text{ and} \tag{3}$$

$$LiH + NH_3 \rightarrow LiNH_2 + H_2, \tag{4}$$
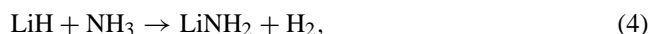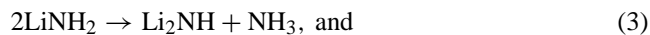
where the enthalpy change of reaction (3) and (4) could be calculated to +84 kJ/mol NH_3 and −42 kJ/mol H_2, respectively. The progress of the former reaction is confirmed around 380 °C as is evident from Fig. 1. On the other hand, since the latter reaction would be exothermic, it might proceed even at room temperature by exposing LiH to a NH_3 gas atmosphere. For the acceleration of this reaction,
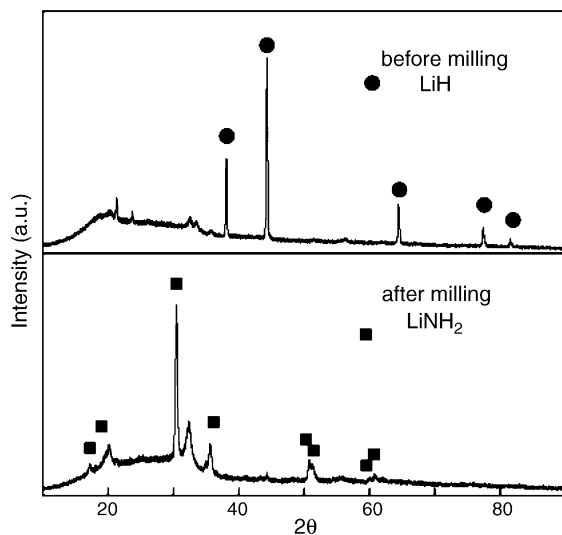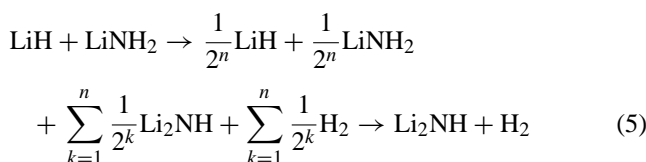
Fig. 2. X-ray diffraction patterns before and after ball milling LiH under the NH_3 gas atmosphere for 30 min at room temperature. We can see that $LiNH_2$ was produced after LiH had reacted with NH_3 by ball milling.

the ball milling treatment for the LiH powder was performed for 30 min under a NH_3 gas atmosphere of 0.4 MPa. The gas chromatography (GC) analysis for remaining gases in the milling vessel indicated that about 70% of NH_3 reacted with LiH and changed to H_2. In Fig. 2 the XRD-patterns of the products are shown before and after the ball milling. We can recognize that the above two elementary reactions are really essential for the hydrogen storage reaction (2). The elementary reactions (3) and (4) have been partly discussed by Hu and Ruckenstein [3], in which they claimed that the reaction (4) was so fast that the NH_3 formation was suppressed during the hydrogenation of Li_3N and the NH_3 emission was also suppressed during the dehydrogenation process.

According to the above two-step elementary reactions model mediated by NH_3, the hydrogen desorption reaction (2) can be expressed as follows;

$$LiH + LiNH_2 \rightarrow \frac{1}{2^n}LiH + \frac{1}{2^n}LiNH_2$$
$$+ \sum_{k=1}^{n}\frac{1}{2^k}Li_2NH + \sum_{k=1}^{n}\frac{1}{2^k}H_2 \rightarrow Li_2NH + H_2 \qquad (5)$$

This indicates that: At the first step $LiNH_2$ decomposes into $Li_2NH/2$ and $NH_3/2$, and then the emitting $NH_3/2$ quickly reacts with LiH/2, transforming into $LiNH_2/2$ and $H_2/2$. At the next step, the product $LiNH_2/2$ decomposes into $Li_2NH/4$ and $NH_3/4$, and then $NH_3/4 + LiH/4$ transform into $LiNH_2/4 + H_2/4$, and such successive step reactions continue until $LiNH_2$ and LiH completely transform into Li_2NH and H_2. These successive reactions might be realized even at low temperature through the close contact among $LiNH_2$, LiH and $TiCl_3$ in a nanometer scale which produced by ball milling.

Next, we examined the reversibility of the product with a small amount (1 mol %) of $TiCl_3$ as a catalyst. The reversibility was tested through the following cyclic processes: the first
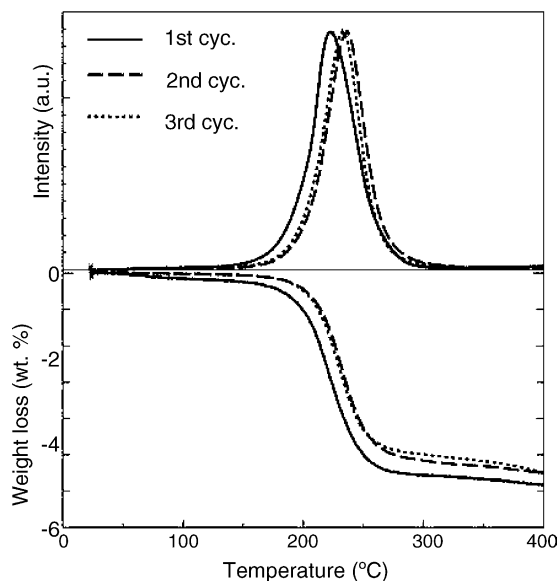

Fig. 3. Thermal desorption spectra of the H_2 gas and corresponding weight loss of the 1:1 mixture of $LiNH_2$ and LiH catalyzed with $TiCl_3$ which were mixed by ball milling. The solid, dashed and dotted lines correspond to the first, second and third cycles, respectively.

dehydrogenation from the mixture was performed by holding the sample at 220 °C for 12 h under high vacuum, and then the hydrogenation was performed under a pure hydrogen gas up to 3 MPa at 180 °C for 12 h. After these hydrogen desorbing/absorbing cycles, we examined the hydrogen desorption properties by the TG and TDMS equipment. The results obtained are shown in Fig. 3. The amount of desorbed hydrogen slightly decreases after the 2nd cycle, indicating that a small amount of stable materials, that is Li_2O or LiCl, might be generated during the first heating process. However, since the effective hydrogen capacity is still higher than 5 wt.% after the initial dehydrogenation process and the reaction rate has almost not changed between the 2nd and 3rd cycles, we can say that the reversibility should essentially be good.

What we have mentioned above is concerned with the hydrogen storage properties under the clean condition with an ideal inert gas atmosphere, such as almost no water vapor and no oxygen partial pressure. On the other hand, it is of interest to investigate the influence of exposing the product to air, especially a low vapor pressure of water. In principle, both of LiH and $LiNH_2$ react with water vapor and transform into LiOH desorbing H_2 or NH_3 at room temperature if the product would be exposed to the air. Therefore, if the products exposed to air are heated up for hydrogen release, the host LiH and the created LiOH would react with each other to form Li_2O and release excess H_2 gas in addition to the desorption of H_2 due to the reaction (2). As is evident from Fig. 4, the H_2 desorption due to this reaction occurs from room temperature since the reaction from LiH and LiOH to Li_2O and H_2 would be exothermic (−22.5 kJ/mol H_2). Thus, we claim that the H_2 desorption from Li-Based materials under dirty condition, such as the exposure of the product to air, occur with less
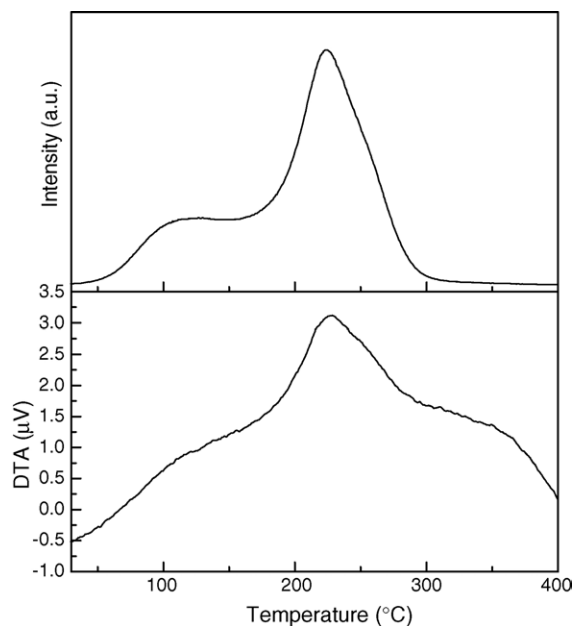
Fig. 4. Thermal desorption spectrum of the H_2 gas and corresponding differential thermal analysis of the 1:1 mixture of LiOH and LiH which were mixed by ball milling.

durability but, apparently, better kinetics and an extra H_2 desorption.

4. Conclusion

We examined the catalytic effects on hydrogen desorption properties of ball milled mixture with 1:1 molar ratio of $LiNH_2$ and LiH with a small amount (1 mol %) of additives, such as the Fe, Co, Ni metal nano-particles, and Ti and V chlorides. The product containing 1 mol % $TiCl_3$ shows the best hydrogen desorption properties among all the trials; $\sim$5.5 to 6 wt.% of hydrogen was desorbed in 150 $\sim$ 250 °C with a relatively high reaction rate. The reversibility was also essentially good because the effective hydrogen capacity was still higher than 5 wt.% until at least 3rd cycles and the reaction rate did almost not changed until 3rd cycles.

The hydrogen desorption reaction from the product was clarified to be composed of two elementary reactions mediated by NH_3. Particularly the reaction between NH_3 and LiH could play an important role on the hydrogen storage reaction (2). Finally, we discussed the influence of exposing the product to air, especially, a water vapor. The results indicated that the exposure of the product to air led to not only worse durability but also an extra H_2 desorption.

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