Hydrogen Desorption Dynamics in Li-N-H System by means of Isotopic Exchange Technique

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ABSTRACT

Hydrogen desorption dynamics in the reaction from LiH + $LiNH_2$ to Li_2NH + H_2 was examined by the TDMS, TG and FT-IR analyses for the products replaced by LiD or $LiND_2$ for LiH or $LiNH_2$, respectively. The results obtained indicate that the hydrogen desorption reaction proceeds through the following two-step elementary reactions mediated by ammonia; $2LiNH_2 \rightarrow Li_2NH + NH_3$ and $LiH + NH_3 \rightarrow LiNH_2 + H_2$, where hydrogen molecules are randomly formed from 4 equivalent hydrogen atoms in a hypothetic $LiNH_4$ produced by the reaction between LiH and NH_3 according to the laws of probability.

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Introduction

Hydrogen has been targeted as an ultimate fuel for transportation systems in future due to its abundance and environmental friendliness. To utilize hydrogen as one of the secondary energies, it is necessary to develop high-performance hydrogen storage materials [1, 2]. Especially, most of the chemical hydrides composed of light elements like alanate systems [3-6], borohydride systems [7-11], amide systems [12-22] and so on inevitably possess quite high hydrogen capacity, so that systematic investigations have vigorously been progressed all over the world.

Among them, metal-nitrogen-hydrogen (Metal-N-H) systems have been regarded as one of the most attractive hydrogen storage systems. Actually, lithium nitrides (Li_3N) can absorb/desorb a large amount of hydrogen by the following two consecutive reactions:

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH. \qquad (1)$$

Theoretically, a reversible hydrogen of 10.4 wt.% ($2H_2$ / (Li_3N+$2H_2$)) is accessible in these two reactions. So far, we have investigated the hydrogenating/dehydrogenating properties of the ballmilled mixture of $LiNH_2$ and LiH with a small amount of $TiCl_3$ as catalyst according to the following reaction [15],

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2. \qquad (2)$$

The reason is that the reaction (2) can absorb/desorb ~6.5 wt.% of hydrogen at much lower temperature due to the smaller enthalpy change ΔH than the left part in the reaction (1). In addition, we have already reported on the mechanism of the hydrogen desorption reaction (2) [18].

Concerning with the mechanism of the reaction (2), Chen et al. have claimed that H in $LiNH_2$ is positively charged while H in LiH is negatively charged, so that the strong affinity between $H^{\delta+}$ and $H^{\delta-}$ gives predominantly rise to hydrogen molecule [14]. This model suggests hydrogen gas desorption due to the direct molecule-molecule interaction, in which the LiH and $LiNH_2$

molecules should be liberated from 2 solid phases. On the other hand, we have proposed that the hydrogen desorption reaction (2) could proceed through the following two-step elementary reaction mediated by ammonia [18];

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \qquad (3) \text{ and}$$

$$LiH + NH_3 \rightarrow LiNH_2 + H_2. \qquad (4)$$

The difference between the above two models lies in whether ammonia does mediate or not in the proceeding of the reaction (2).

In this report, we give microscopic description concerning the hydrogen desorption dynamics in the reaction (2) and verify the validity of our proposed model by comparison with experimental data obtained by means of isotopic exchange technique, where LiD or $LiND_2$ is replaced by respectively LiH or $LiNH_2$ in the milled composites of $LiNH_2$ and LiH.

Reaction Model

If the ammonia mediated reaction model is valid, two kinds of the H atoms should exist in the original system with respect to the reaction (4), that is, the one is in LiH and the other is in NH_3. For example, when we employ the ballmilled mixture of lithium deutride LiD and $LiNH_2$ as the original system of the reaction (2), it is expected that a mixture of isotopic gases with some different ratios of H_2 : HD : D_2 is desorbed with an increasing temperature under a non-equilibrium condition according to the following several models, which are proposed in consideration of the H atom selectivity to make a H_2 molecule emission.

The model 1 is that the probability of forming H_2, HD or D_2 molecule from H and D atoms in LiD and NH_3 simply obeys the laws of probability without any distinctions between H and D atoms, just like the release as isotopic gases after forming a hypothetic $LiNDH_3$;

$$NH_3 + LiD \rightarrow 1/2\ LiNH_2 + 1/2\ LiNHD + 1/2\ H_2 + 1/2\ HD. \qquad (5)$$

The model 2 is that the D atom in LiD specially remains in lithium amide, like forming LiNHD without releasing as a gas molecule HD;

$$NH_3 + LiD \rightarrow LiNHD + H_2. \qquad (6)$$

The model 3 is that the D atom in LiD specially releases from the original solid state as the DH gas;

$$NH_3 + LiD \rightarrow LiNH_2 + HD. \qquad (7)$$

At the next step, the produced Li amides containing protium and/or deuterium atoms in the reactions (5), (6) and (7) decompose into the corresponding lithium imides, Li_2NH or Li_2ND and emits the corresponding ammonia molecules, NH_3, NH_2D, NHD_2 or ND_3. Then, these molecules react with the leaving LiD, transform into the corresponding Li amides and H_2, HD and D_2 gases. As a result of the following successive steps, the corresponding Li imides and hydrogen gases in the model dependent ratio can be evaluated, in which this evaluation is so complicated that the details are given in the appendix. As a result, the corresponding reactions can be expressed as follows, respectively,

Model 1: $LiNH_2 + LiD \rightarrow 4/5\ Li_2NH + 1/5\ Li_2ND + 9/25\ H_2 + 12/25\ HD + 4/25\ D_2$, (8)

Model 2: $LiNH_2 + LiD \rightarrow 2/3\ Li_2NH + 1/3\ Li_2ND + 5/9\ H_2 + 2/9\ HD + 2/9\ D_2$ and (9)

Model 3: $LiNH_2 + LiD \rightarrow Li_2NH + HD$. (10)

The above 3 models are really based on two elementary reactions (3) and (4) mediated by ammonia.

On the other hand, according to the model proposed by Chen et al. [14], the corresponding hydrogen desorbing reaction is given by the same description as the reaction (10). Moreover, if the isotopic gases are randomly desorbed after hypothetically forming Li_2NDH_2 molecule between the LiD and $LiNH_2$ according to the laws of probability without any distinctions between H and D atoms, the reaction can be written as follows, Model 4: $LiNH_2 + LiD \rightarrow 2/3\ Li_2NH + 1/3\ Li_2ND + 1/3\ H_2 + 2/3\ HD$. (11)

Here, it should be noted that the isotope effect of deuterium for hydrogen was ignored in the above description, because the desorption properties of deuterium gas from the ballmilled mixture of LiD and $LiND_2$ were almost the same as those of hydrogen gas from the mixture of LiH and $LiNH_2$. Similarly, when we employ the ballmilled mixture of LiH and $LiND_2$ as the original system of the reaction (2), we notice that the reaction descriptions for the models 1 to 4 can be given by an exchange of H for D, and vice versa, in the reactions (8). (9), (10) and (11) according to the above ignorance of the isotope effect.

Experimental Procedures

The starting materials, LiH (95 %) and LiD (95 %) were purchased from Sigma-Aldrich, and $LiNH_2$ (95 %) was from Strem Chemicals. The $LiND_2$ powder used in this work was synthesized from LiD by the ballmilling under ND_3 atmosphere according to the following reaction:

$$LiD + ND_3 \rightarrow LiND_2 + D_2. \qquad (4)'$$

This method was already reported as one of the synthesizing methods of $LiNH_2$ from LiH by the ballmilling under NH_3 atmosphere [23]. As an additive, $TiCl_3$ was employed in this work, which was purchased from Sigma-Aldrich. All the sample treatments were performed in an argon glovebox purified by gas recycling purification system (MP-P60W, Miwa MFG CO., LTD.) to minimize the oxygen and water pollutions.

To achieve nanometer-scale contact among $LiNH_2$, LiD (or $LiND_2$, LiH) and 1 mol% $TiCl_3$, the mixtures were mechanically ballmilled (P7, Fritsch) at 400 rpm under a hydrogen atmosphere of 1 MPa (99.9999 %) at room temperature for 2 h. Prior to the milling treatment, the mixed powders of ~300 mg and 20 pieces of steel balls with a diameter of 7 mm were set into a Cr steel pot with inner volume of ~30 cm^3.

The ballmilled mixtures were examined by thermal desorption mass spectroscopy measurements (TDMS; M-QA200TS, Anelva) with an increasing temperature from room temperature to 400°C at a heating rate of 5 °C/min. The TDMS equipment is especially designed and built up for using it inside the glovebox, which permitted to simultaneously perform the TDMS measurement, thermogravimetry and differential thermal analysis (TG and DTA; TG8120, Rigaku) without exposing the samples to air at all. Additionally, we have already checked by preliminary examination that it is possible to relatively estimate the ratios of amount of the isotopic gases, H_2, HD and D_2 desorbed by the TDMS measurement.

In addition to the above thermal analysis, Fourier transform infrared spectroscopy measurement (FT-IR; Spectrum One, Perkin-Elmer) was performed by a pellet method to estimate the ratio of Li_2NH to Li_2ND in the dehydrogenated product, where the pellet containing 1 wt.% samples in KBr was set in the BaF_2 folder filled with purified argon to avoid exposing the samples to air at all.

Results and Discussion

In order to clarify the mechanism of hydrogen desorption reaction from the microscopic point of view, we performed the TDMS measurements for 2 kinds of the ballmilled mixtures of LiD + $LiNH_2$ and LiH + $LiND_2$, which are shown in Fig. 1 (a) and (b), respectively. A mixture of H_2, HD and D_2 can be found as the desorbed gas and the onset and peak temperatures in the TDMS profiles are almost the same for all the isotopic gases, indicating no significant isotope effect on gaseous desorption reaction. From Fig. 1(a), the ratio of the areas of the TDMS profiles corresponding to the mass numbers 2 (= H_2), 3 (= HD) and 4 (= D_2) is estimated to be 9.0 : 13.1 : 2.9 for the mixture of LiD and $LiNH_2$, which is close to the ratio of H_2 : HD : D_2 = 9: 12:

4 evaluated by the model 1. Furthermore, the ratio for the mixture of LiH and $LiND_2$ is estimated to be 2.1 : 13.9 : 9.0 as shown in Fig. 1(b), which is almost in reverse order of that in Fig. 1 (a). This result suggests that the model 1 is acceptable as well.

Simultaneously, the TG experiments revealed that a weight loss from the ballmilled LiD + $LiNH_2$ sample reached 7.2 % by heating up to 450 °C. If the isotopic gases are desorbed with the ratio of H_2 : HD : D_2 expected from the models 1, 2 and 4, we can deduce a weight loss from the LiH + $LiND_2$ sample by reversing the ratio of H_2 : HD : D_2 for the models 1,2 and 4. Consequently, the ratio is calculated to be 8.2 %, 9.0 % or 9.0 %, respectively, according to the models. The result obtained from TG measurement for LiH + $LiND_2$ indicated that the weight loss reached 8.3 %, supporting the model 1 as well.

Furthermore, we determined the ratio of amount of Li_2NH to Li_2ND in the product by the FT-IR measurement after the desorption of the isotopic gases from the ballmilled mixtures, where the number of N-H and N-D vibration modes can be relatively distinguished. As is mentioned in reaction models, the ratio of the amount of Li_2NH to Li_2ND is evaluated to be 4 : 1, 2 : 1, 1 : 0 or 2 : 1 from the model 1, 2, 3 or 4, respectively, in the H_2 gas desorbed sample. Figure 2 shows the IR absorbance for the gas desorbed samples from the ballmilled mixtures. As references, the absorbance of mere mixtures of Li_2NH and Li_2ND with the molar ratios of 4:1, 1:1 and 1:4 are also shown in Fig.2. The two peaks corresponding to N-H and N-D stretching modes are located at ~3150 cm^{-1} and ~2350 cm^{-1}, respectively. The ratios of the peak area for the references were, respectively, 8.7:1.3, 6.3:3.7 and 3.1:6.9, indicating that the peak area corresponding to N-H mode should be equivalent to be ~1.7 times larger than those of N-D mode. Therefore, we can evaluate the number of N-D mode in the dehydrogenated mixture of LiD + $LiNH_2$ as being ~1.7 times larger than the real values of its peak area. As a result, the relative ratios of Li_2NH to Li_2ND in the dehydrogenated LiD + $LiNH_2$ and LiH + $LiND_2$ could be obtained to be 3.9:1 and 1:3.8, respectively, supporting the model 1. Therefore, the validity of the model 1 as the mechanism of the hydrogen desorption dynamics could be verified by means of the FT-IR measurements as well.

Conclusion

In this work, we have investigated the hydrogen desorption dynamics in the reaction from $LiH + LiNH_2$ to $Li_2NH + H_2$ by replacing LiD or $LiND_2$ for LiH or $LiNH_2$. From the TDMS and TG measurements, we have relatively evaluated the amount of H_2, HD and D_2 desorbed from $LiD + LiNH_2$ and $LiH + LiND_2$, and confirmed that the model 1, in which the hydrogen desorption reaction (2) is controlled by the two-step elementary reaction mediated by ammonia, is valid. Additionally, the validity of the model 1 has been confirmed by the FT-IR analysis on the N-H and N-D stretching modes in the dehydrogenated $LiD + LiNH_2$ and $LiH + LiND_2$. This model 1 microscopically indicates that LiH and NH_3 might form a hypothetic $LiNH_4$ in the hydrogen desorption process.

Finally, it is to be noted that the above discussion is concerned with the hydrogen desorption dynamics under non-equilibrium condition without reverse reactions. Under equilibrium condition, the reverse reaction corresponding to hydrogen absorption should be taken into account to describe the hydrogen gas desorption process. Therefore, more complicated considerations should be introduced to discuss the hydrogen sorption reaction in the closed system. These works are now in progress.

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Appendix

In the model 1, LiD reacts with $LiNH_2$ as follows,

$LiNH_2$ + LiD → 1/2 Li_2NH + (1/2 NH_3 + 1/2 LiD) + 1/2 LiD

→ 1/2 Li_2NH + 1/2 LiD + 1/2 (1/2 $LiNH_2$ + 1/2 LiNHD) + 1/2 (1/2 H_2 + 1/2 HD)

→ 1/2 Li_2NH + 1/4 H_2 + 1/4 HD + 1/4 ($LiNH_2$ + LiD) + 1/4 (LiNHD + LiD),

because the probability of forming one hydrogen molecule from 4 hydrogen atoms in the mixture of LiH and NH_3 simply obeys the laws of probability without any discrimination between the H and D atoms. Here, to simplify the expression, the expressions, the mixtures of $LiNH_2$ + LiD and LiNHD + LiD, are denoted by, respectively, A and B. Therefore, we can simply describe the above reaction as follows,

A → 1/2 Li_2NH + 1/4 H_2 + 1/4 HD + 1/4 A + 1/4 B.

And then,

B → 1/4 (Li_2NH + Li_2ND + NH_2D + NHD_2) + LiD

→ 1/4 (Li_2NH + Li_2ND) + 1/4 (1/2 (LiNHD + D_2) + 1/2 ($LiND_2$ + HD))

+ 1/4 (1/6 ($LiNH_2$ + D_2) + 1/6 ($LiND_2$ + H_2) + 2/3 (LiNHD + HD)) + 1/2 LiD

→ 1/4 (Li_2NH + Li_2ND) + 1/4 (1/6 H_2 + 7/6 HD+ 2/3 D_2)

+ 1/4 (1/6 ($LiNH_2$ + LiD) + 7/6 (LiNHD + LiD) + 2/3 ($LiND_2$ + LiD))

→ (1/4 Li_2NH +5/12 Li_2ND) + (1/24 H_2 + 7/24 HD + 1/3 D_2) + (1/24 A + 7/24 B).

Thus, both A and B in the right hand side contain A and B as well. Therefore, the expected total amount of the isotopic gases desorbed by proceeding the reactions A and B, which are denoted by, respectively, X_A and X_B, can be expressed by the following simultaneous equations,

X_A= 1/4 H_2 + 1/4 HD + 1/4 X_A + 1/4 X_B,

X_B = 1/24 H_2 + 7/24 HD + 1/3 D_2 + 1/24 X_A + 7/24 X_B.

From the simultaneous equations, we obtain

X_A= 9/25 H_2 + 12/25 HD + 4/25D2,

X_B = 2/25 H_2 + 11/25 HD + 12/25 D_2.

Therefore, the ratio of amount of the desorbed gases H_2 : HD : D_2 when the reaction between $LiNH_2$ and LiD proceeds is expressed to be H_2 : HD : D_2 = 9 : 12 : 4.

Similarly, with respect to the model 2, we can estimate the ratio of H_2 : HD : D_2 = 5 : 2 : 2 by the same way as the model 1 as well.

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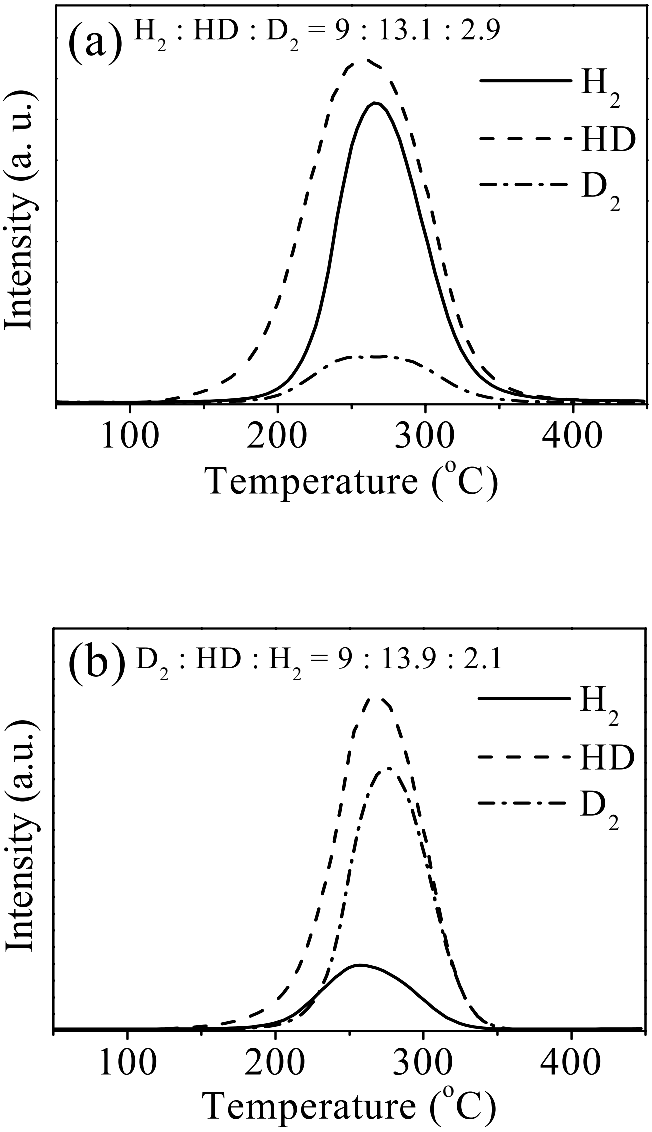
(a)
H_2 : HD : D_2 = 9 : 13.1 : 2.9
H_2
HD
D_2
Intensity (a. u.)
100
200
300
400
Temperature (°C)
(b)
D_2 : HD : H_2 = 9 : 13.9 : 2.1
H_2
HD
D_2
Intensity (a.u.)
100
200
300
400
Temperature (°C)

Figure 1

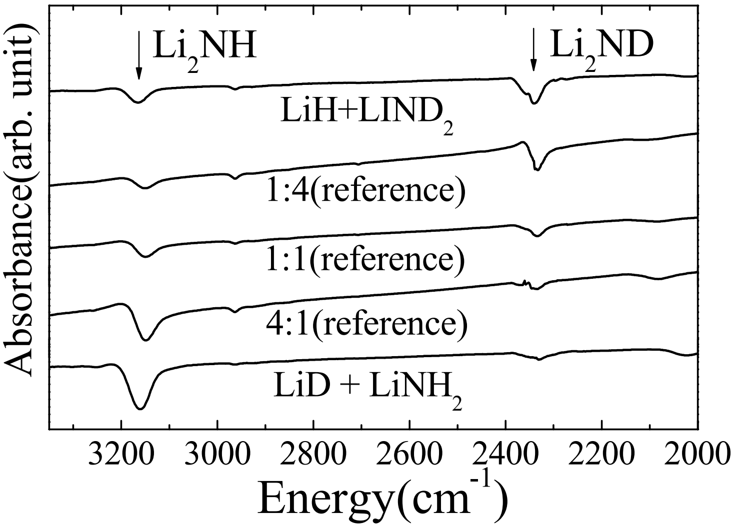
Li$_2$NH
Li$_2$ND
LiH+LIND$_2$
1:4(reference)
1:1(reference)
4:1(reference)
LiD + LiNH$_2$
Absorbance(arb. unit)
3200
3000
2800
2600
2400
2200
2000
Energy(cm^{-1})

Figure 2

Caption

Figure 1. TDMS profiles from the ball milled mixtures of (a) LiD + $LiNH_2$ and (b) LiH + $LiND_2$ examined under a helium flow at a heating rate of 5 ^{o}C/min..

Figure 2. FT-IR stectra for the gas desorbed samples from the ball milled mixtures of LiD + $LiNH_2$ and LiH + $LiND_2$. In this figure, FT-IR spectra are shopwn for the samples with the ratios of 4 : 1 1 : 1 and 1 : 4 for Li_2NH and Li_2ND as references.