

Mechanism of Novel Reaction from LiNH_2 and LiH to Li_2NH and H_2 as a Promising Hydrogen Storage System

Takayuki Ichikawa,^{*,†} Nobuko Hanada,[‡] Shigehito Isobe,[‡] Haiyan Leng,[‡] and Hironobu Fujii[†]

Natural Science Center for Basic Research and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan, and Graduate School of Advanced Sciences of Matter, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

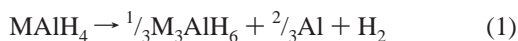
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The mechanism of the hydrogen desorption (HD) reaction from the 1:1 mixture of lithium amide (LiNH_2) and lithium hydride (LiH) to lithium imide (Li_2NH) and hydrogen (H_2) has been proposed on the basis of our experimental results in this paper. The proposed model is constituted by 2 kinds of elementary reactions: the one is that 2LiNH_2 decomposes to Li_2NH and ammonia (NH_3), the other is that the emitted NH_3 reacts with LiH and transforms into LiNH_2 and H_2 . Since the former and the latter reactions are, respectively, endothermic and exothermic, the HD reaction corresponding to the latter reaction occurs as soon as LiNH_2 has decomposed into Li_2NH and NH_3 . Therefore, the HD reaction can be understood by the following processes: at the first step, LiNH_2 decomposes into $\text{Li}_2\text{NH}/2 + \text{NH}_3/2$, and then the emitted $\text{NH}_3/2$ quickly reacts with $\text{LiH}/2$, transforming into $\text{LiNH}_2/2 + \text{H}_2/2$; at the second one, the produced $\text{LiNH}_2/2$ decomposes to $\text{Li}_2\text{NH}/4 + \text{NH}_3/4$, and then $\text{NH}_3/4 + \text{LiH}/4$ transform to $\text{LiNH}_2/4 + \text{H}_2/4$, and such successive steps continue until LiNH_2 and LiH completely transform into Li_2NH and H_2 , even at low temperatures, by the catalytic effect of TiCl_3 .

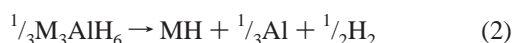
1. Introduction

For realizing hydrogen energy systems in the near future, it is important to establish suitable energy storage and transportation technologies. One of the key technologies on that way is the development of high-performance hydrogen storage systems. It is well-known that conventional metal hydride systems can store more hydrogen than in liquid hydrogen or high-pressure hydrogen in a safe and efficient way. However, those materials are too heavy for commercial applications.

To overcome the disadvantages, some chemical hydrides composed of light elements such as lithium (Li) and sodium (Na) have been deeply attracted as new hydrogen storage materials these days. In particular, the hydrogen storage properties of some Alanate systems, studied by many researchers, show the following clear 2-step reactions:



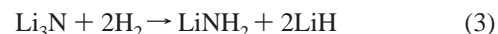
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Here, the total hydrogen capacities for $\text{M} = \text{Na}$ and Li are theoretically calculated to be 5.6 and 8.0 wt %, respectively.^{1,2} The enthalpy changes of both reactions 1 and 2 for $\text{M} = \text{Na}$ were estimated to be endothermic, and the reversibility of both the reactions were experimentally confirmed. Then, some catalysts containing Ti or Zr elements were doped for improving reaction rate.^{1,3–9} On the other hand, the enthalpy changes of reactions 1 and 2 for $\text{M} = \text{Li}$ have been estimated to be,

respectively, exothermic and endothermic by DTA measurements.^{2,10–12} So, only reaction 2 for $\text{M} = \text{Li}$ should be reversible for hydrogen storage. However, the hydrogenating reaction could not be confirmed so far, because the reaction rate might be too slow for realizing the hydrogenating reaction under moderate temperature and H_2 gas pressure.

As early as 1910, Dafert and Miklauz¹³ reported that the reaction between Li_3N and H_2 generated Li_3NH_4 . However, the product was proved to be a mixture of lithium amide and lithium by Ruff and Goerges¹⁴ as follows:



Furthermore, the mixture was decomposed to release H_2 on heating:¹⁴



Recently, Chen et al.¹⁵ and Hu et al.¹⁶ had investigated the system Li_3N as one of the hydrogen storage materials, where the hydrogenation and dehydrogenation of Li_3N were performed by the following 2-step reversible reactions:



They claimed that a large amount of hydrogen (10.4 wt %) could be reversibly stored in this system. Since then, the hydrogen storage properties of the $\text{Li}-\text{N}-\text{H}$ systems have been also examined in other laboratories.^{15–20} Here, the enthalpy change of the first reaction in eq 5 could be calculated to be -148 kJ/mol H_2 and that of the second reaction of eq 5 to be -44.5 kJ/mol H_2 ,²¹ respectively. Because the small enthalpy change and possessing still a large amount of hydrogen 6.5 wt % for the latter reaction are considered to be still suitable for a hydrogen storage system, we focused on that reaction and

* Corresponding author: E-mail: tichi@hiroshima-u.ac.jp.

[†] Natural Science Center for Basic Research and Development.

[‡] Graduate School of Advanced Sciences of Matter.

investigated the hydrogen storage property,¹⁸ which is expressed by the following chemical equation:



In our previous experiments, we used LiH and LiNH₂ as starting materials and prepared their 1:1 mixture by ball milling for 2 h under a hydrogen gas atmosphere of 1 MPa. For improving the reaction rate, we doped 1 mol % TiCl₃ in the LiH and LiNH₂ mixture, which was homogeneously dispersed on the surface of the mixture by ball milling. The mixture reversibly desorbed/absorbed a large amount of hydrogen (~5.5 wt %) at 150–200 °C under a heating rate of 5 °C/min.¹⁸ In our paper,¹⁸ the reaction kinetics for the hydrogen desorption process has also been examined, and the chemical reaction between LiNH₂ and LiH was estimated to be of first order. Usually, it is very difficult to understand the appearance of the first-order solid–solid reaction, because the reaction rate should be controlled by the diffusion process of elements between the solid phases and/or the growth of the nuclei of the Li₂NH phase.

On the other hand, Hu and Ruckenstein have claimed that the ultrafast reaction between LiH and NH₃ emitted by the decomposition of LiNH₂ should be very important on the hydrogen absorbing and desorbing processes for the solid–solid reaction.²⁰ In addition, Chen et al. have examined the dehydrogenation reaction from the mixture of LiNH₂ and 2LiD, and they have confirmed that the desorbing gas was a mixture of H₂, HD, and D₂, all of which were desorbed in the temperature range from 150 to 400 °C. These results could not be understood by a simple solid–solid reaction model.¹⁷

In this paper, we discuss the mechanism of the hydrogen desorbing reaction from LiH and LiNH₂ to Li₂NH and H₂, on the basis of some of our experimental results. Finally, we emphasize that the existence of LiH near the surface of LiNH₂ is very important for the progress of the reaction at temperatures lower than 200 °C.

2. Experimental Section

The starting material LiNH₂, with 95% purity, was purchased from Strem Chemicals; also the starting materials LiH and NaH, with 95% purity, and dry catalyst TiCl₃, with 98% purity, were purchased from Sigma-Aldrich. All the samples were handled in a glovebox filled with purified argon to minimize oxidation and water adsorption by the gas recycling purification system (MP-P60W, Miwa Mfg. Co., Ltd.).

To achieve nanometer-scale contact among LiNH₂, LiH, NaH, and the catalyst, the mixture of powders was milled by a mechanical ball milling method (Fritsch P7). In the milling process, 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, and milled with 400 rpm under a hydrogen gas pressure of 1.0 MPa at room temperature for 2 h. After homogenizing the mixed powders by the above method, the samples were examined by thermal desorption mass spectroscopy (TDMS) measurements (Anelva M-QA200TS) as the temperature was increased from ~25 °C to 400 °C with a heating rate of 5 °C/min. This equipment was especially designed and built for using it inside the glovebox filled with purified argon, which permitted simultaneously performing of differential thermal analysis (DTA) without exposing the samples to air.

To confirm the solid–gas reaction of LiH and NH₃, we milled LiH under an NH₃ gas atmosphere of 0.4 MPa. After the milling treatment, the examination of remaining gases in the milling vessel was estimated by gas chromatography (GC) (Shimadzu, GC8AIT).

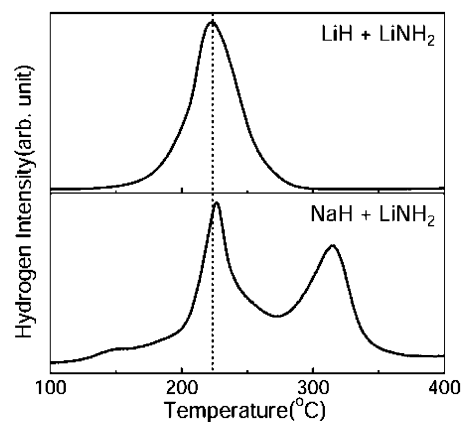
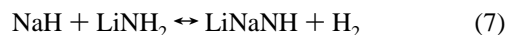


Figure 1. Hydrogen desorption profiles from the 1:1 mixtures of LiNH₂ + LiH (A) and LiNH₂ + NaH (B), respectively, obtained by TDMS measurements. Both of the mixtures were catalyzed with TiCl₃, which were prepared by ball milling for 2 h in a H₂ gas atmosphere.

In addition, the phase identification of the products after the reaction was performed by X-ray diffraction (XRD) measurement with Cu K α radiation (Rigaku, RINT-2100).

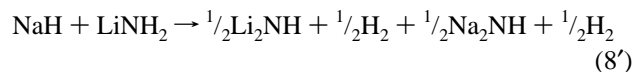
3. Results and Discussion

3.1. Experimental Evidence for Formation of LiNH₂ due to Reaction of LiH with NH₃. Figures 1(A) and 1(B) show the results of the TDMS measurement for the product prepared by ball milling the mixture of MH + LiNH₂ where M = Li and Na. From Figure 1(A), we can see that the hydrogen desorption from the milled mixture of LiH and LiNH₂ catalyzed with TiCl₃ shows a clear single peak around 220 °C under a 5 °C/min heating rate, while, as shown in Figure 1(B), hydrogen desorption from the milled mixture of NaH and LiNH₂ prepared by the same method as the case of LiH and LiNH₂ indicates clear double peaks around 220 °C and 310 °C. If reaction 7 could be realized under the same heating condition as reaction 6 shown in Figure 1(A),



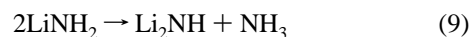
then the hydrogen desorption should show a single peak. However, the TDMS result clearly indicated two step reactions, in which the lower peak temperature was almost the same as that of the mixture LiH and LiNH₂. Furthermore, differential thermal analysis (DTA) showed that all of those hydrogen desorbing reactions were endothermic.

From these results, we guess that at least two kinds of products are formed in the hydrogen desorbing process. Furthermore, we guess that the 2 hydrogen desorption processes should be chemically similar to each other. Then, we suppose that the above 2-step reactions could be expressed by a following chemical reaction:



where the H₂ desorptions corresponding to the low and the high-temperature peaks might occur by the formation of Li₂NH and Na₂NH, respectively.

It is well-known that LiNH₂ decomposes into 1/2Li₂NH and 1/2NH₃,^{17,18,20}



which might play an important role on the above reaction.

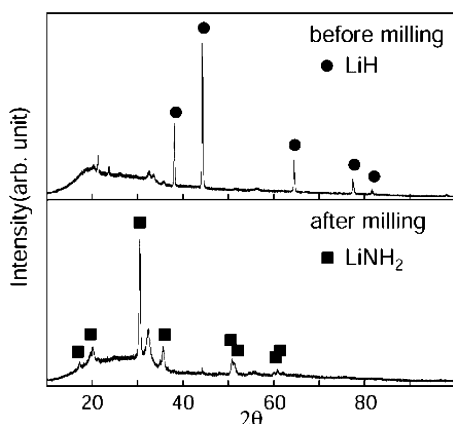
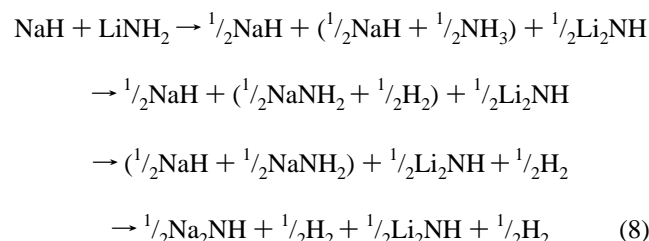


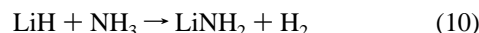
Figure 2. X-ray diffraction patterns before and after ball milling LiH under an NH₃ gas atmosphere for 30 min at room temperature. We can see that LiNH₂ was produced after LiH reacted with NH₃ by ball milling.

Therefore, we easily presume that after the reaction of LiNH₂ → 1/2Li₂NH + 1/2NH₃ occurs, the emitted 1/2NH₃ reacts with NaH and transforms into 1/2Na₂NH and H₂. However, if this 2-step reaction occurs, then a single peak structure should appear, but it is not realized. Therefore, we assume that the emitted 1/2NH₃ reacts with 1/2NaH and transforms into 1/2NaNH₂ and 1/2H₂. If this type of reaction is realized in the Na system, we would expect the following reaction processes:



and we could understand the two peak structure in the TDMS profile. Thus, we can also expect the appearance of similar reaction in case of the Li system.

Actually, since the following reaction:



is calculated to be exothermic (~42 kJ/mol) from the literature,²¹ the reaction might progress in the milling process of LiH under NH₃ gas atmosphere even at room temperature. Then, we performed 30 min ball milling for LiH of 40 mg under NH₃ gas atmosphere of 0.4 MPa at room temperature, in which the molar ratio of LiH and NH₃ corresponds to 1:1. In Figure 2, the XRD-patterns of the products before and after ball milling are shown. We can see that the XRD profile of the initial mixture before milling is almost assigned by the LiH phase, and that of the final product is mainly assigned by the LiNH₂ phase as well. In addition, the gas chromatography (GC) for remaining gases in the milling vessel after milling indicated that about 70% of NH₃ reacted with LiH and changed to H₂ during milling for 30 min. Furthermore, we performed the TDMS measurement for the final product, and the result is shown in Figure 3. In principle, LiNH₂ should emit only NH₃ gas, but H₂ gas was also detected in the experiment. This is because the product still remains 30% of LiH without reacting with NH₃, and the remaining LiH reacts with LiNH₂, leading to the H₂ emission according to reaction 6 as well. From the above experiments, we conclude that the following two elementary reactions are

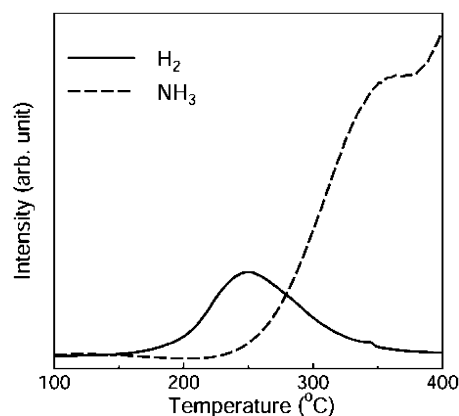
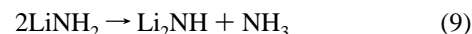
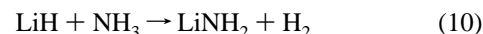


Figure 3. Hydrogen and ammonia emission profiles measured by thermal desorption mass spectroscopy (TDMS) equipment from the resultant sample produced by reacting LiH with NH₃ by ball milling for 30 min at room temperature.

essential for the hydrogen storage reaction 6:

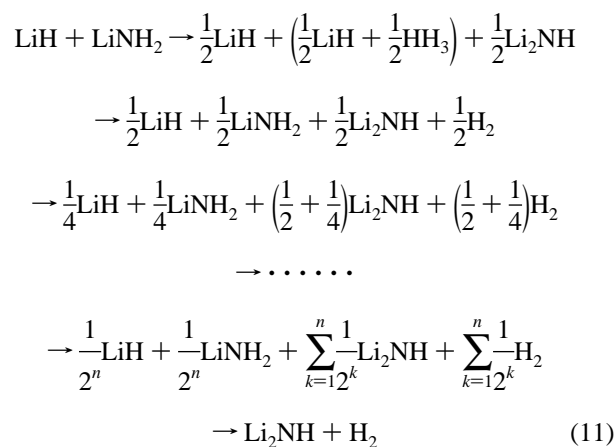


and



Reaction 10 has been already confirmed by Hu and Ruckenstein.²⁰ In their paper, they claimed that reaction 10 was so fast that the NH₃ formation was suppressed during the hydrogenation of Li₃N and the NH₃ emission was also suppressed during the dehydrogenation process. However, they did not discuss the mechanism of reaction 6 in detail.

If we accept this two-step elementary reaction model, the HD reaction can be expressed as follows:



That is to say: At the first step, LiNH₂ decomposes into Li₂NH/2 and NH₃/2, and then the emitted NH₃/2 quickly reacts with LiH/2, transforming into LiNH₂/2 and H₂/2. At the second step, the produced LiNH₂/2 decomposes into Li₂NH/4 + NH₃/4 and then NH₃/4 + LiH/4 transform to LiNH₂/4 + H₂/4, and such successive steps continue until LiNH₂ and LiH completely transform into Li₂NH and H₂.

This successive multistep reaction might be realized at low temperature by doping some appropriate catalysts such as TiCl₃.

3.2. Clarification of the Appearance of Two-Step Elementary Reactions in the Hydrogen Desorption Process. To clarify the appearance of the two-step reactions, we examined the decomposition process of some two-layered samples composed of LiNH₂ and LiH by the TDMS measurements, the

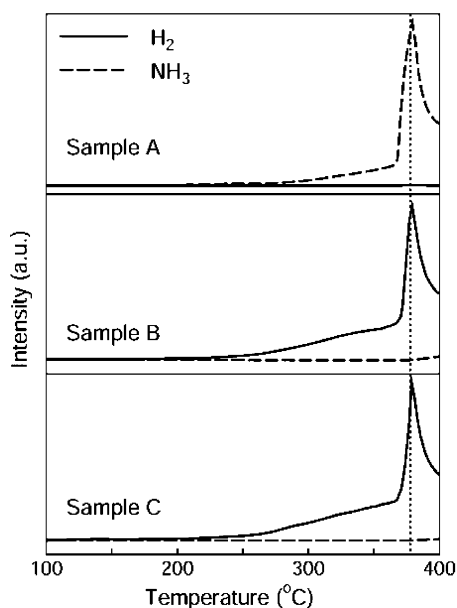


Figure 4. Hydrogen and ammonia emission profiles from Samples A, B, and C which were detected by the TDMS measurements. Here, sample A is the raw LiNH_2 powder purchased from Strem Chemicals, Sample B is a two-layer sample in which the milled LiH powder was placed directly on the raw LiNH_2 powder as is schematically drawn in Figure 5(i), and Sample C is a two-layered product in which TiCl_3 -doped (ball milled) LiH was placed directly on the raw LiNH_2 powder shown in Figure 5(ii).

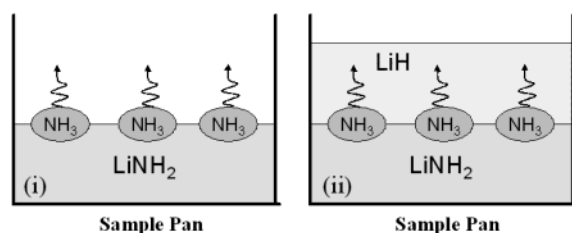


Figure 5. Schematic figure for sample arrangements of (i) LiNH_2 alone, and (ii) a two-layered sample with LiH on LiNH_2 used for TDMS analysis, both of which were put in the sample pan. Here, NH_3 is emitted by decomposition of LiNH_2 to Li_2NH .

results of which are shown in Figure 4. Similar experiments were independently done by Hu and Ruckenstein,²⁰ but they did not show experimental details in their paper. You can see from Figure 4 that Sample A, the raw LiNH_2 powder as is schematically drawn in Figure 5(i), slowly emits NH_3 from $\sim 200^\circ\text{C}$ and rapidly emits NH_3 from $\sim 370^\circ\text{C}$. In the two-layer Sample B where the milled LiH powder was placed directly on the raw LiNH_2 powder in the sample pan as drawn in Figure 5(ii), we can see that LiH reacts with NH_3 which desorbed from LiNH_2 , and emits H_2 . It should be noted that the shape of the H_2 emission curve in Sample B is quite similar to that of the NH_3 emission curve in sample A. This result indicates that the NH_3 emitted from LiNH_2 immediately reacts with LiH . On the other hand, in the two-layer Sample C, in which the catalyzed LiH with TiCl_3 by ball milling was put directly on the raw LiNH_2 powder in the sample pan, TiCl_3 does not act as a catalyst for reaction 10. In addition, we notice that the onset of the H_2 desorbing temperature of Samples B and C is lower than the onset of NH_3 emission temperature of Sample A. This suggests that the existence of some special interaction on their boundaries between LiH and LiNH_2 surfaces is important for desorbing H_2 at low temperature.

Next, we examined the milling effect on the above two-step elementary reactions. Figure 6 shows the profiles of NH_3 and

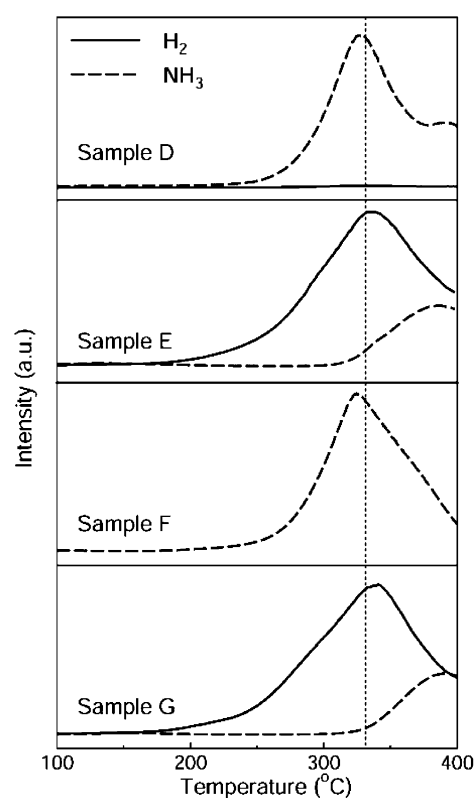


Figure 6. Hydrogen and ammonia emission profiles from Samples D, E, F, and G, which were detected by the TDMS equipment. Here, sample D is the milled LiNH_2 powder, Sample E is a two-layer sample in which the milled LiH powder was placed directly on the milled LiNH_2 powder, Sample F is a milled powder of LiNH_2 and a small amount of TiCl_3 , and Sample G is a two-layered product in which TiCl_3 -doped (ball milled) LiH was placed directly on the milled powder of LiNH_2 and a small amount of TiCl_3 .

H_2 emissions from Sample D, which is the milled LiNH_2 powder as in Figure 5(i), and the two-layered Sample E where the milled LiH was placed on the milled LiNH_2 in the sample pan as in Figure 5(ii). We notice that the emission profile of NH_3 from LiNH_2 becomes broad due to milling, but shifts to the low-temperature side. Similarly, the temperature of H_2 emission from two-layered Sample E is lower than that of NH_3 emission from Sample D, although both emission curves are synchronized. This also suggests that the emitted NH_3 from LiNH_2 immediately reacts with LiH . In addition, the doping effects of TiCl_3 in LiNH_2 on the NH_3 and H_2 emissions were examined for Samples F and G, which correspond to the milled LiNH_2 with a small amount of TiCl_3 and two layered sample of LiH on TiCl_3 -doped LiNH_2 , respectively. The results of the TDMS measurements are shown in Figure 6. We notice that the catalytic effect of TiCl_3 on LiNH_2 gives no strong influence on the HD process as well.

3.3. Catalytic Effect of TiCl_3 and LiH on the HD Reaction.

The experimental results also indicated that the HD reaction in the TiCl_3 -doped 1:1 mixture of LiH and LiNH_2 prepared by ball milling occurs at a much lower temperature than that in Samples E or G (compare Figure 1 with Figure 6), although the additive TiCl_3 could not act as a catalyst for both elementary reactions 9 and 10 themselves. Therefore, it seems likely that the catalyst TiCl_3 acts as a role for the transfer of NH_3 molecule from LiNH_2 to LiH in nanometer scale. In the near future, we will discuss that in detail.²³

Moreover, the above results suggest that the LiH plays a role of something like a catalyst for the decomposition of LiNH_2 in

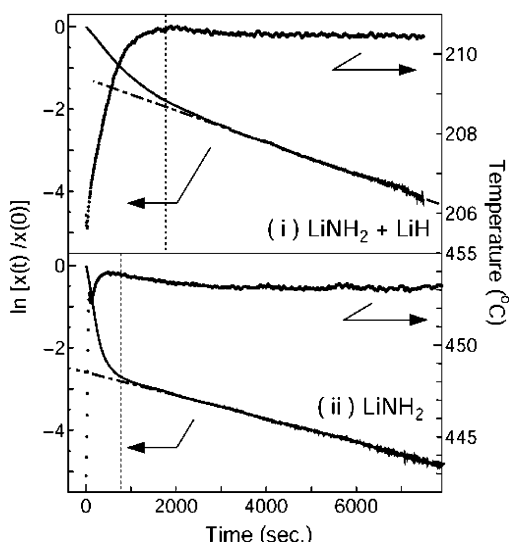


Figure 7. Relative (i) hydrogen and (ii) ammonia concentrations $x(t)/x(0)$ as a function of time, which were desorbed from the 1:1 mixture of LiH and LiNH₂ catalyzed with a small amount of TiCl₃ by ball milling for 2 h and the raw LiNH₂ without any treatment, respectively. Here, $x(t)$ in (i) and (ii) are the hydrogen and ammonia contents at the reaction time of t in the desorption processes, respectively, which were estimated from the TG measurements after reaching constant temperatures. In these figures, the temperature fluctuations are also shown as a function of time. The values of $x(t)/x(0)$ were deduced under no partial pressure of hydrogen and ammonia (using He gas as a flow gas for TDMS measurement).

the ball milled mixture, because the H₂ emission temperature of the mixture is actually much lower than the NH₃ emission temperature from LiNH₂ itself. A preliminary Raman scattering measurement for LiNH₂ indicated that a quite small amount of NH₃ molecule started to be liberated from the LiNH₂ particle surface around 70 °C,²⁴ although the decomposition of LiNH₂ normally starts to occur from higher temperature than 200 °C and transforms into Li₂NH and NH₃. This phenomenon indicates the existence of a relatively high surface potential for NH₃ liberation on the LiNH₂ surface. If some action can remove the NH₃ molecule which sticks on the surface part of the LiNH₂ as a precursor, the decomposition of the LiNH₂ should progress at low temperatures. Therefore, we consider that the interaction between LiH and LiNH₂ decreases the decomposing temperature of LiNH₂, and consequently the H₂ emission temperature synchronously decreases down to about 150 °C by a quick reaction between LiH and NH₃ emitted from LiNH₂.

3.4. Kinetics of the Hydrogen Desorption Reaction. Finally, we discuss the kinetics of the novel HD reaction 6 under no partial pressure of hydrogen (using a He gas as a carrier for TDMS measurement). Figures 7(i) and (ii), respectively, show the features of the relative hydrogen and ammonia concentrations $x(t)/x(0)$ and temperature fluctuations as a function of time. Here, $x(t)$ in Figure 7(i) is the hydrogen content desorbed from the 1:1 mixture of LiNH₂ and LiH catalyzed by TiCl₃ at about 210 °C, and $x(t)$ in Figure 7(ii) is the ammonia content emitted from LiNH₂ at about 450 °C at the reaction time of t in the dehydrogenation process, which was estimated from the TG measurement during the hydrogen desorption process after reaching constant temperature. The above results indicate that the logarithmic relative ratios of residual hydrogen and ammonia concentrations in the 1:1 mixture and LiNH₂, respectively, follow a good straight line for both systems. In our previous paper, we reported that the hydrogen desorbing reaction 6 is surprisingly of first order as shown in Figure 7(i), because a

good linearity for the change of logarithmic hydrogen desorption ratio under a constant temperature is realized as shown in Figure 7(i). On the other hand, we can see from Figure 7(ii) that the reaction of NH₃ emission is also of the first order. Therefore, we finally conclude that the reaction of hydrogen desorption from the mixture is controlled by the endothermic reaction of the NH₃ emission expressed by reaction 9 because the exothermic reaction of the H₂ emission expressed by reaction (10) immediately occurs after LiNH₂ decomposes into Li₂NH and NH₃.

4. Conclusion

We have investigated the mechanism of the H₂ desorbing (HD) reaction from the 1:1 mixture of LiNH₂ and LiH to Li₂NH and H₂. The results indicate that the reaction composes of two kinds of elementary reactions. One is that 2LiNH₂ decomposes into Li₂NH and NH₃. The other is that the emitted NH₃ reacts with LiH and transforms into LiNH₂ and H₂. Since the former and the latter reactions are, respectively, endothermic and exothermic, the HD reaction corresponding to the latter reaction occurs as soon as LiNH₂ has decomposed into Li₂NH and NH₃. Therefore, the HD reaction can be understood by the following processes: In the first step, LiNH₂ decomposes into Li₂NH/2 and NH₃/2, and then the emitted NH₃/2 quickly reacts with LiH/2, transforming into LiNH₂/2 and H₂/2. In the second step, the produced LiNH₂/2 decomposes into Li₂NH/4 + NH₃/4 and then NH₃/4 + LiH/4 transform to LiNH₂/4 + H₂/4, and such successive steps continue until LiNH₂ and LiH completely transform into Li₂NH and H₂.

We also examined how the catalyst TiCl₃ acts on these two elementary reactions. In conclusion, the additive TiCl₃ could not act as a catalyst for both elementary reactions 9 and 10 themselves, even though TiCl₃ is quite effective for improving the kinetics of the reaction 6. So, we could guess that TiCl₃ acts as a catalyst for the transfer of the NH₃ molecule from LiNH₂ to LiH. In addition, our results indicate the existence of LiH near the LiNH₂ surface can be very important for the decomposition of the LiNH₂ into the Li₂NH and NH₃ at lower temperature, compared with its own decomposition temperature.

We have also discussed what kind of elementary reactions could control the H₂ desorption of reaction 6. Generally, a solid-state reaction tends to be complicated because the progress of the reaction could be controlled by diffusion of elemental composed atoms and/or growth of some molecule nuclei. It was surprising that the HD reaction of the mixture was of first order, which was observed in our previous report. In this paper, we confirmed that the LiNH₂ decomposition reaction with NH₃ emission was also of first order. Therefore, we conclude that this reaction can be controlled by the decomposition of LiNH₂, after which the fast reaction, LiH + NH₃ → LiNH₂ + H₂, occurs.

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