

# Hydrogen Ab/Desorption of LiH-KH Composite and Ammonia System

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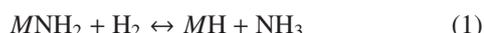
Lithium hydride-Potassium hydride (LiH-KH) composite prepared by ball-milling is focused in order to modify the kinetic properties of the reaction between LiH and gaseous ammonia (NH<sub>3</sub>). The LiH-NH<sub>3</sub> system is recognized as one of the most promising hydrogen storage system because it generates hydrogen at room temperature by ammonolysis reaction, is regenerated below 300°C, and possesses more than 8.0 mass% hydrogen capacity. From the experimental results, it is confirmed that the hydrogen generation from the reaction between NH<sub>3</sub> and the LiH-KH composite shows much higher reaction rate than that of the simple summation of each component, which can be recognized as a synergetic effect. Then, double-cation metal amide (MNH<sub>2</sub>) phases such as LiK(NH<sub>2</sub>)<sub>2</sub>, which are not assigned to any amides reported before, are formed as the reaction product. Moreover, it is confirmed that hydrogenation of the generated amide can proceed to form LiH-KH composite and NH<sub>3</sub>. [doi:10.2320/matertrans.M2016071]

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## 1. Introduction

Ammonia (NH<sub>3</sub>) is recognized as an attractive hydrogen (H<sub>2</sub>) carrier because it has a high hydrogen capacity of 17.8 mass% and it is easily liquefied under about 1 MPa at room temperature<sup>1,2</sup>. The annual production of NH<sub>3</sub> in the world reached about 1.3 hundred million tons in 2010<sup>3</sup>, suggesting that infrastructures have been already established for mass production and transportation of NH<sub>3</sub>. However, more than 400°C is required to generate H<sub>2</sub> by decomposition of NH<sub>3</sub> itself even in the presence of transition metal catalyst<sup>4,5</sup>. Besides, production of NH<sub>3</sub> needs high temperature of 400–600°C and high pressure of 20–40 MPa, which is well known as Haber-Bosch process. Therefore, it is necessary to realize an efficient conversion technique between NH<sub>3</sub> and H<sub>2</sub>. Based on this point of view, we focus on NH<sub>3</sub> and metal hydride (MH; M = Li, Na, K) systems as a reversible NH<sub>3</sub>-H<sub>2</sub> conversion technique<sup>6–13</sup>. By using this system, MNH<sub>2</sub> can react with H<sub>2</sub> to form MH and NH<sub>3</sub> below 300°C under H<sub>2</sub> flow condition of a moderate pressure by following left to right reaction (eq. (1)), which means that H<sub>2</sub> is chemically compressed in the form of MH and NH<sub>3</sub> as a high H<sub>2</sub> density state<sup>7,11,13</sup>. In addition, H<sub>2</sub> can be generated even at room temperature by exothermic ammonolysis reaction of MH described as following right to left reaction (eq. (1)), and it was confirmed that the reaction rate became higher in the order of periodic table of alkali metal (Li < Na < K)<sup>13</sup>.



Although KH-NH<sub>3</sub> system has the highest reaction rate for hydrogen generation reaction (ammonolysis), the gravimetric

H<sub>2</sub> density is much lower than that of LiH-NH<sub>3</sub> system. On the other hand, the reaction of LiH-NH<sub>3</sub>, which has the highest H<sub>2</sub> density, is considerably slow. Therefore, several studies concerning kinetic improvement of LiH-NH<sub>3</sub> system were reported so far<sup>6,8</sup>. Since the reaction of NH<sub>3</sub> and MH is a gas-solid phase reaction, it is possibly assumed that MNH<sub>2</sub> formed on the surface blocks the contact of NH<sub>3</sub> molecule to MH, leading to the limited reaction rate. However, considering that the ammonolysis reaction of KH-NH<sub>3</sub> system proceeds rapidly with 100% reaction yield, it is inconsistent with the explanation of the gas-solid phase reaction. Herein, it is again assumed that the NH<sub>3</sub> molecule could reach the interface of MH-MNH<sub>2</sub> by forming ammoniate (MNH<sub>2</sub>·xNH<sub>3</sub>) as a consistent reaction model<sup>14</sup>. On this reaction model, the reaction rate is influenced by the interaction between MNH<sub>2</sub> and NH<sub>3</sub>. Therefore, it is expected that the reaction rate can be improved by modification of the solid MNH<sub>2</sub>. Actually, when two kinds of metal hydrides are mixed to form a composite, the reaction properties of this composite should be changed, for instance, melting point becomes possibly lower than that of the components in the case for a eutectic phenomenon. Moreover, the generated amide after the reaction between mixed MH and NH<sub>3</sub> could show a different interaction between the amide product and NH<sub>3</sub>.

In this work, we focused on the LiH-KH composite and investigated the reactivity with NH<sub>3</sub>, which was expected to show practically better reaction properties in the viewpoint of reaction rate by potassium and gravimetrically high H<sub>2</sub> density by lithium.

## 2. Experimental Procedure

### 2.1 Sample preparation

Lithium hydride (LiH) (99.4%, Alfa aesar), potassium hydride (KH) (dispersion in mineral oil, Aldrich), lithium amide (LiNH<sub>2</sub>) (95%, Aldrich), potassium amide (KNH<sub>2</sub>) synthesized from KH and NH<sub>3</sub> (99.999%) were used for the experi-

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ment.

LiH-KH composite, activated LiH, and activated KH were prepared by the following procedure for the investigation of their ammonolysis reaction. A mixture of LiH and KH with a molar ratio of LiH/KH = 1, as-purchased LiH, and as-purchased KH were independently ball-milled for 10 h under 1.0 MPa of H<sub>2</sub> pressure by using a stainless steel container and balls in a planetary ball mill apparatus (Fritsch, P7) at 370 rpm. Then, the milled samples were heat-treated at 220°C under 1.0 MPa of H<sub>2</sub> pressure.

A metal amide compound was synthesized from LiNH<sub>2</sub> and KNH<sub>2</sub> by the following procedure for the investigation of its hydrogenation reaction. A mixture of LiNH<sub>2</sub> and KNH<sub>2</sub> with a molar ratio of LiNH<sub>2</sub>/KNH<sub>2</sub> = 1 was ball-milled for 10 h under 0.1 MPa of Ar atmosphere by using the planetary ball mill apparatus.

These samples were identified by X-ray diffraction (XRD) measurement (Rigaku, RINT-2100, CuK $\alpha$  radiation) and fourier transform infrared spectroscopy (FT-IR) measurement (Perkin-Elmer, Spectrum One). The sample handling was performed in a glove box (Miwa MFG, MP-P60 W) filled with purified Ar (> 99.9999%) to avoid oxidation and hydration due to oxygen and water.

## 2.2 Investigation for hydrogen generation reaction of MH with NH<sub>3</sub> (Ammonolysis reaction)

The ammonolysis properties were investigated in a closed system at room temperature by the following procedure. First of all, a weighed amount of MH was loaded into a reaction cell (= 8.99 cc) in the glove box, then 0.8 MPa NH<sub>3</sub> with a molar ratio of NH<sub>3</sub>/MH = 1 was introduced in the cell, and the reaction of MH with NH<sub>3</sub> was performed for 360 min as the total time. During this process, the reaction was interrupted at 10, 60, 180 min. In each interrupt, reactor was evacuated and the weight gain of the sample was measured to estimate the reaction yield. After that, the reactor was again refilled with the same amount of NH<sub>3</sub> as the initial one. The products after the ammonolysis reaction were identified by XRD and FT-IR measurements.

## 2.3 Investigation for hydrogenation reaction of MNH<sub>2</sub>

Hydrogenation process of the amide compound synthesized from LiNH<sub>2</sub> and KNH<sub>2</sub> was investigated in closed system by using the gas circuit system<sup>15</sup>). A reaction cell loading a weighed amount of the sample was connected to the gas circuit system and 0.5 MPa H<sub>2</sub> was introduced. After that, the experiments were carried out under gas circulated condition with 100 sccm of flow rates at 160°C and 220°C. The products after the hydrogenation reaction were identified by XRD measurement.

## 3. Result and Discussions

### 3.1 Investigation for hydrogen generation reaction of MH with NH<sub>3</sub> (Ammonolysis reaction)

In this study, activated MH and MH composite were prepared by ball-milling, where these MH samples were activated due to appearance of a fresh MH surface, decrease of crystalline size, and structural distortion. Considering a practical use for the MH-NH<sub>3</sub> system, it is expected that such an active

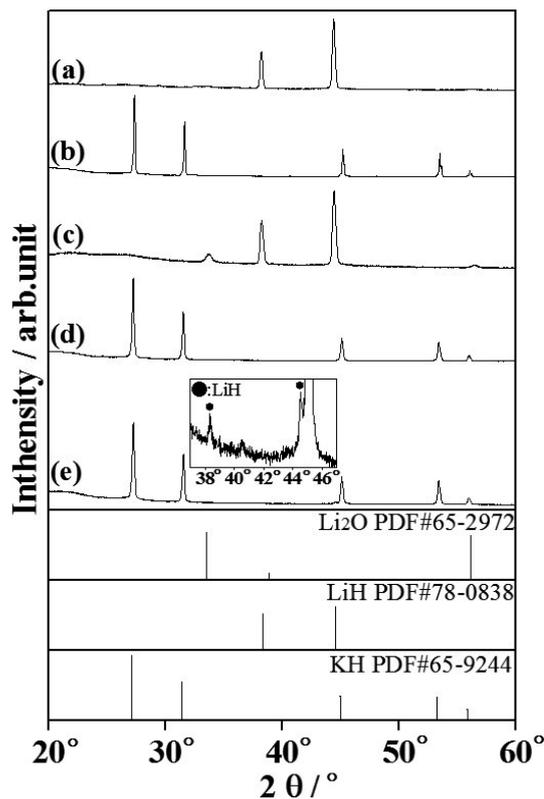


Fig. 1 XRD patterns of as purchased LiH: (a), KH: (b), ball-milled and heat-treated LiH: (c), KH: (d), and LiH-KH composite: (e). The inset shows the enlarged figure for the profile of LiH-KH composite to find the peaks of LiH; XRD pattern of Li<sub>2</sub>O (PDF#65-2972), LiH (PDF#78-0838), KH (PDF#65-9244) are referred from databases.

state with small crystalline size and structural distortion would be lost after the repeated uses because a temperature of more than 200°C is necessary for the hydrogenation of MNH<sub>2</sub> to form MH and NH<sub>3</sub>. Therefore, in order to know the characteristic properties for the practical application, ball-milled MH were heat-treated at 220°C, which was chosen as a possible temperature to regenerate amide phases in this work, to restore the structural disorder by the crystallization. Figure 1 (a), (b), (c), (d), and (e) show XRD patterns of as-purchased LiH, as-purchased KH, activated LiH, activated KH, and LiH-KH composite, respectively. It was confirmed that the diffraction peaks of activated LiH, activated KH, and LiH-KH composite were sharpened even though those profiles just after ball-milling were quite broad, indicating that the structural disorder added by ball-milling was restored by heat treatment. Here, the peaks corresponding to LiH in the profile of LiH-KH composite, which were quite weak due to its much smaller constitutive diffraction intensity than that of KH, were observed as shown in the inset in Fig. 1. Therefore, it was considered that LiH-KH composite prepared by ball-milling was not an MH compound but a physical mixture of LiH and KH, that should be named an MH composite. Besides, Li<sub>2</sub>O phase observed in the profile of activated LiH would be derived from impurity in the reagent. Since X-ray diffraction intensity is proportional to square of the atomic number of the material components, the diffraction intensity of Li<sub>2</sub>O should be observed more strongly than the diffraction intensity of LiH. Then, it is considered that the amount of the

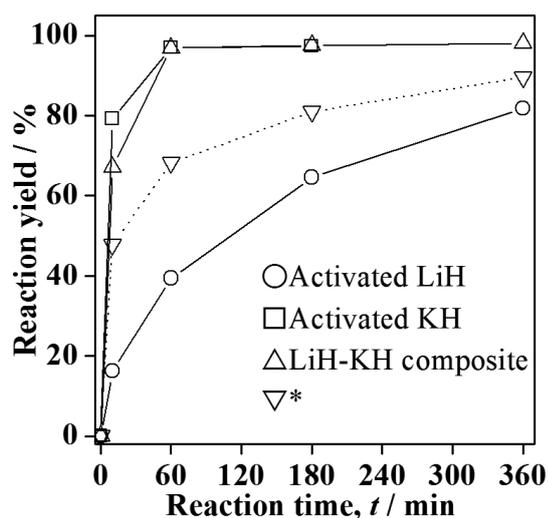


Fig. 2 Hydrogen generation profiles for the reactions of activated LiH, activated KH, and LiH-KH composite with  $\text{NH}_3$ . The broken line is the expected reaction yield of mixture of LiH and KH without interaction each other ( $*$  =  $0.5 \times$  reaction yield of activated LiH +  $0.5 \times$  reaction yield of activated KH).

impurity was small by taking account of the intensity of LiH phase and  $\text{Li}_2\text{O}$  phase. Thus, any effects of the impurity into the essential reaction could be negligible.

Figure 2 shows the reaction yields as a function of the time for the ammonolysis reaction of activated LiH, activated KH, and LiH-KH composite at room temperature. The reaction rates were higher in the order of periodic table of alkali metal ( $\text{Li} < \text{K}$ ), where this trend is well consistent with the previous results<sup>13</sup>. Then, the reaction yield of the simple mixture of activated LiH and activated KH ( $\text{LiH}/\text{KH} = 1 \text{ mol/mol}$ ) calculated from the results of each single hydride ( $= 0.5 \times$  reaction yield of activated LiH +  $0.5 \times$  reaction yield of activated KH) is also plotted as a comparison, which is shown as broken line in Fig. 2, for the evaluation of the reaction rate of LiH-KH composite. From these results, it was confirmed that the LiH-KH composite showed a characteristic reactivity with  $\text{NH}_3$ , namely much higher reaction yield than the expected value. Here, it was noteworthy that the reaction yield of LiH-KH composite for 60 min was 96.9%, which was 28.7% higher than the expected reaction yield as 68.2% ( $= 0.5 \times 39.4\% + 0.5 \times 96.9\%$ ). Considering the reaction process for the solid-gas reaction in the  $\text{NH}_3$ -MH system, it is expected that the reaction rate at initial and late stages are controlled by the surface reaction and  $\text{NH}_3$  diffusion in the product, respectively. Thus, the higher diffusion rate due to higher solubility of  $\text{NH}_3$  than that in the LiH- $\text{NH}_3$  system would be realized after the reaction of LiH-KH composite with  $\text{NH}_3$ .

Figure 3 (a), (b), and (c) show XRD patterns of the products after the ammonolysis reaction of activated LiH, activated KH, and LiH-KH composite, respectively. The diffraction pattern for the reaction product of activated LiH with  $\text{NH}_3$  showed  $\text{LiNH}_2$  phase, where diffraction peak of remaining LiH was not obvious at this scale because of its relatively weak intensity. The diffraction pattern for the reaction product of activated KH with  $\text{NH}_3$  showed only  $\text{KNH}_2$  phase without KH phase, indicating that the reaction was almost com-

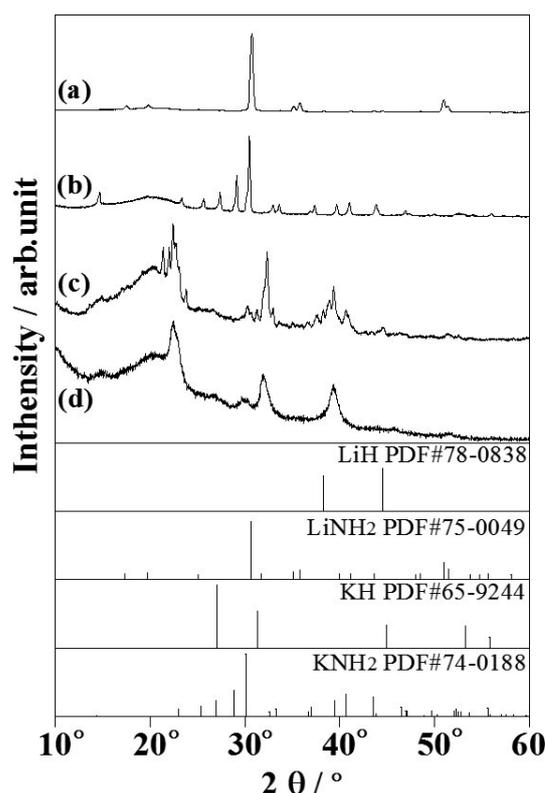


Fig. 3 XRD patterns of reaction products of activated LiH: (a), activated KH (b), LiH-KH composite: (c) with  $\text{NH}_3$ , and amide compound synthesized from  $\text{LiNH}_2$  and  $\text{KNH}_2$  by ball-milling process: (d); XRD pattern of LiH (PDF#78-0838),  $\text{LiNH}_2$  (PDF#75-0049), KH (PDF#65-9244),  $\text{KNH}_2$  (PDF#74-0188) are referred from databases.

pleted. On the other hand, in the diffraction pattern for the reaction product of LiH-KH composite with  $\text{NH}_3$ , unknown phase appeared, where the observed peaks were not assigned by any crystal structures of  $\text{LiK}_2(\text{NH}_2)_3$ ,  $\text{LiK}(\text{NH}_2)_2$ ,  $\text{Li}_3\text{K}(\text{NH}_2)_4$ , and  $\text{Li}_7\text{K}(\text{NH}_2)_8$  reported before<sup>16,17</sup>, and others listed in the ICDD database. Besides, the peak intensity of the unknown phase was relatively weak compared with the products of activated LiH and activated KH with  $\text{NH}_3$ .

In order to characterize the unknown phase, FT-IR measurement for the product was performed. Figure 4 (a), (b), and (c) show the IR spectra of commercial  $\text{LiNH}_2$ ,  $\text{KNH}_2$ , and the reaction product of LiH-KH composite with  $\text{NH}_3$ , respectively. The two absorption peaks observed here are located in the energy range corresponding to stretching mode of the  $-\text{NH}_2$  group, which were not equivalent to those of neither  $\text{LiNH}_2$  nor  $\text{KNH}_2$ , indicating that a double-cation amide compound ( $\text{LiK}(\text{NH}_2)_2$ ) could be formed by the reaction of LiH-KH composite with  $\text{NH}_3$ . However, the  $-\text{NH}_2$  group peaks of the unknown phase didn't seem to be a simple doublet but multiple doublets, which would indicate coexistence of some different phases having a quite similar composition with  $\text{LiK}(\text{NH}_2)_2$ . Thus, it was considered that the relatively lower diffraction intensity of the unknown phase could be attributed to the coexistence of the several amides which have almost the same structure as each other. In this paper, the unknown phases are represented together as "complex  $\text{LiK}(\text{NH}_2)_2$ " for convenience in the following discussion.

From the above results, the reactivity of the LiH-KH composite is briefly summarized as follows. The LiH-KH com-

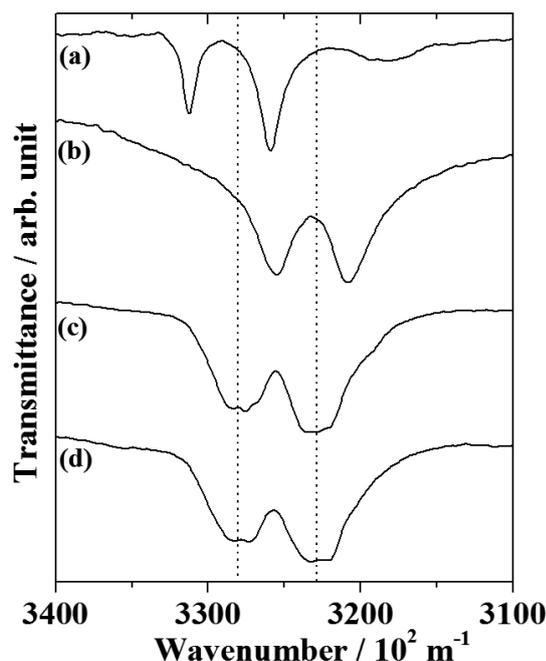


Fig. 4 FT-IR spectra of as-purchased  $\text{LiNH}_2$ : (a), as-purchased  $\text{KNH}_2$ : (b), reaction product of  $\text{LiH-KH}$  composite with  $\text{NH}_3$ : (c), and amide compound synthesized from  $\text{LiNH}_2$  and  $\text{KNH}_2$  by ball-milling process: (d).

posite synthesized by ball-milling shows high reaction rate even at the late-stage, where it is expected that complex  $\text{LiK}(\text{NH}_2)_2$  as the reaction product would have a similar behavior to  $\text{KNH}_2$ , e.g. high solubility and diffusion rate of  $\text{NH}_3$  into complex  $\text{LiK}(\text{NH}_2)_2$ , which needs further investigation to provide supportive evidence in future.

### 3.2 Investigation for hydrogenation reaction of complex $\text{LiK}(\text{NH}_2)_2$

Hydrogenation reaction of complex  $\text{LiK}(\text{NH}_2)_2$  to form  $\text{LiH-KH}$  composite and  $\text{NH}_3$  was investigated to demonstrate its feasibility and understand the hydrogenation process. In this study, the hydrogenation reaction was performed under  $\text{H}_2$  circulated condition in closed system, where  $\text{NH}_3$  trap by using liquid  $\text{N}_2$  is equipped into the circulating line. As a result, the partial pressure of the generated  $\text{NH}_3$  gas around the sample could be sufficiently reduced so that the endothermic hydrogenation reaction proceeded under the non-equilibrium condition<sup>15</sup>.

Figure 3 (d) and Fig. 4 (d) show XRD pattern and IR spectrum of the amide compound synthesized from  $\text{LiNH}_2$  and  $\text{KNH}_2$  by ball-milling process, respectively. In the comparison between the diffraction patterns in Fig. 3 (d) and Fig. 3 (c), it was confirmed that the product after the ball-milling process showed diffraction peaks similar to those of complex  $\text{LiK}(\text{NH}_2)_2$  formed by the ammonolysis of  $\text{LiH-KH}$  composite, which were weakened and broadened due to the milling effects. However, some peaks in the diffraction pattern of the ammonolysis product in Fig. 3 (c), e.g. the peaks around  $21^\circ$  and  $41^\circ$ , were not observed in that of the product after the ball-milling process in Fig. 3 (d). As mentioned above, the product after the ammonolysis of  $\text{LiH-KH}$  composite would be composed of some different phases having a quite similar composition with  $\text{LiK}(\text{NH}_2)_2$ . Then, it is considered that the

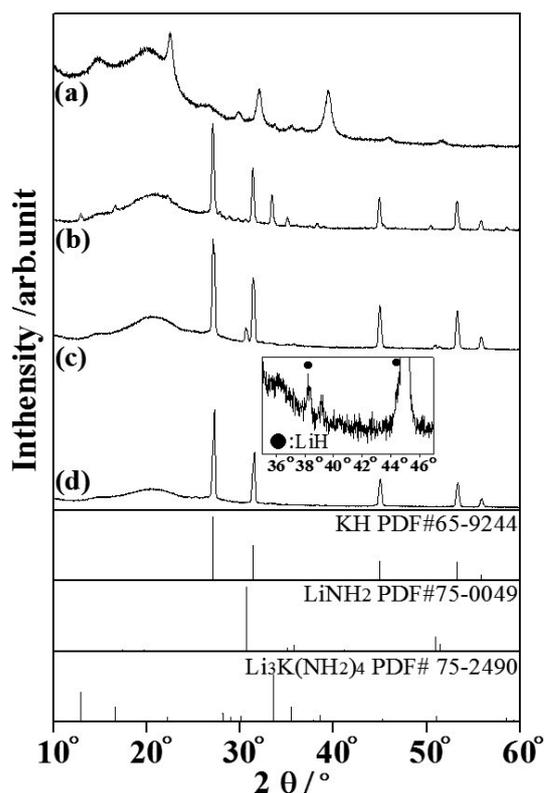
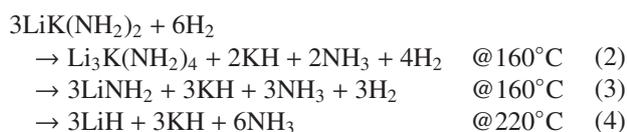


Fig. 5 XRD patterns of complex  $\text{LiK}(\text{NH}_2)_2$  synthesized from  $\text{LiNH}_2$  and  $\text{KNH}_2$  by ball-milling process before: (a) and after the hydrogenation reaction under 100 sccm  $\text{H}_2$  flow condition at  $160^\circ\text{C}$  for 3 h: (b), 14 h: (c), and at  $220^\circ\text{C}$  for 10 h: (d). The inset shows the enlarged figure for the profile of the product after the hydrogenation at  $220^\circ\text{C}$  for 10 h to find the peaks of  $\text{LiH}$ ; XRD pattern of  $\text{LiNH}_2$  (PDF#75-0049),  $\text{KH}$  (PDF#65-9244), and  $\text{Li}_3\text{K}(\text{NH}_2)_4$  (PDF#75-2490) are referred from databases.

product after the ball-milling process was also composed of the several phases, however, the ratio of the components would be slightly different from that of the ammonolysis product. Meanwhile, in the comparison between the IR spectra in Fig. 4 (c) and Fig. 4 (d), the observed two infrared absorption peaks corresponding to the  $-\text{NH}_2$  group of the product after the ball-milling process were located in the same energy range with that of complex  $\text{LiK}(\text{NH}_2)_2$  formed by the ammonolysis of  $\text{LiH-KH}$  composite. Thus, the amide compound synthesized by ball-milling process is also represented as “complex  $\text{LiK}(\text{NH}_2)_2$ ” as well as the ammonolysis product for convenience in the following discussion.

Figure 5 shows XRD pattern of the products after the hydrogenation reaction for each reaction time at  $160^\circ\text{C}$  and  $220^\circ\text{C}$ , where XRD pattern of complex  $\text{LiK}(\text{NH}_2)_2$  before hydrogenation reaction is also shown in Fig. 5 (a). In the XRD profile of the product after the hydrogenation reaction for 3 h at  $160^\circ\text{C}$  as shown in Fig. 5 (b), diffraction pattern corresponding to  $\text{KH}$  phase was clearly observed, indicating that hydrogenation reaction proceeds in the condition. Besides, diffraction pattern corresponding to  $\text{Li}_3\text{K}(\text{NH}_2)_4$  was observed, suggesting that complex  $\text{LiK}(\text{NH}_2)_2$  is hydrogenated in the initial stage to form  $\text{Li}_3\text{K}(\text{NH}_2)_4$  and  $\text{KH}$  as the first hydrogenation products. Then, the product was further hydrogenated at the same condition. As a result, it was confirmed that all of  $\text{Li}_3\text{K}(\text{NH}_2)_4$  was hydrogenated to form  $\text{LiNH}_2$  and  $\text{KH}$  at  $160^\circ\text{C}$  for 14 h as shown in Fig. 5 (c). Finally, it was

confirmed that the peaks corresponding to  $\text{LiNH}_2$  was not observed and only KH and LiH phases were found as shown in Fig. 5 (d) and its enlarged figure to find the peaks of LiH, indicating that complex  $\text{LiK}(\text{NH}_2)_2$  was almost fully hydrogenated at this temperature. Herein, Dong *et al.* reported that hydrogenation of  $\text{LiNH}_2$  can be improved by introducing small amount of KH or  $\text{KNH}_2$ . They claimed that a binary amide of  $\text{Li}_3\text{K}(\text{NH}_2)_4$  as an intermediate has an important role for the reactivity with  $\text{H}_2$ <sup>18,19</sup>, which might be applied to our experiment because  $\text{LiNH}_2$  was hydrogenated in the presence of abundant KH in this study. Thus, it was demonstrated that the hydrogenation reaction of complex  $\text{LiK}(\text{NH}_2)_2$  can proceed by following reaction (eqs. (2), (3), (4)) in closed circuit system under 220°C.



#### 4. Conclusions

In this study, ammonolysis and hydrogenation reactions of the LiH-KH composite -  $\text{NH}_3$  system were investigated. For the ammonolysis reaction at room temperature, it was clarified that reaction of the LiH-KH composite prepared by ball-milling and heat-treatment with  $\text{NH}_3$  showed much higher reaction rate than that expected from the reaction rate of LiH and KH with  $\text{NH}_3$  and then the reaction yield reached almost 100% after 1 h. The enhancement of the reaction rate could be caused by forming novel material complex  $\text{LiK}(\text{NH}_2)_2$  as the reaction product. The unknown phase in the XRD profile was characterized by IR spectroscopy and would be complex  $\text{LiK}(\text{NH}_2)_2$ , which might possibly possess similar properties such as high solubility and/or diffusivity of  $\text{NH}_3$  with that of  $\text{KNH}_2$ . The gravimetric hydrogen generation capacity for the LiH-KH composite -  $\text{NH}_3$  system was estimated to be 4.87 mass% from the composition, and the utilizable capacity was 4.72 mass%, which was obtained by the reaction yield of 96.9% for 1 h in this study. This value is higher than that of the KH system, 3.39 mass%, and LiH system, 3.19 mass%, estimated by using the experimental reaction yield for 1 h.

Hydrogenation reaction of complex  $\text{LiK}(\text{NH}_2)_2$  synthesized by ball-milling process from  $\text{LiNH}_2$  and  $\text{KNH}_2$  was investigated in the closed system by a gas circuit apparatus. As

a result, it was confirmed that the hydrogenation process of complex  $\text{LiK}(\text{NH}_2)_2$  proceeds by several steps. At 160°C, complex  $\text{LiK}(\text{NH}_2)_2$  reacts with  $\text{H}_2$  to form  $\text{Li}_3\text{K}(\text{NH}_2)_4$  and KH as the first product, and then the  $\text{Li}_3\text{K}(\text{NH}_2)_4$  is hydrogenated at the same temperature to form  $\text{LiNH}_2$  and KH. Finally, the remaining  $\text{LiNH}_2$  is totally hydrogenated at 220°C to form LiH.

From the above results, it is concluded that the LiH-KH composite -  $\text{NH}_3$  system reversibly generates and absorbs hydrogen with high capacity and reactivity, which are realized by combining the advantageous properties of LiH (high capacity) and KH (high reactivity) as a synergetic effect. Therefore, the system is recognized as one of the most promising way to realize a practical conversion technique between  $\text{NH}_3$  and  $\text{H}_2$ .

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