

# Ammonia Synthesis via Non-Equilibrium Reaction of Lithium Nitride in Hydrogen Flow Condition\*<sup>1</sup>

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Lithium nitride Li<sub>3</sub>N is hydrogenated below 300°C under 0.5 MPa of H<sub>2</sub>, and then LiNH<sub>2</sub> and LiH are formed as products. Furthermore, the reaction between LiNH<sub>2</sub> and H<sub>2</sub> proceeds below 250°C under 0.5 MPa of H<sub>2</sub> flow condition, which forms NH<sub>3</sub> and LiH. In this study, we proposed and investigated another synthesis method of ammonia by combining these two reactions, which proceed in laboratory-scale under more moderate conditions than those of Haber–Bosch process. As a result, it was experimentally clarified that the ammonia synthesis were able to be operated below 300°C with realistic reactions rate by non-equilibrium reaction field under 0.5 MPa H<sub>2</sub> flow condition, where a gas circuit system and a larger scale NH<sub>3</sub> synthesis system were designed and assembled for the experiments. [doi:10.2320/matertrans.M2014382]

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## 1. Introduction

Ammonia (NH<sub>3</sub>) has been produced on massive scale in the world and used as various feedstock of nitrogenous chemical products. Recently, NH<sub>3</sub> is regarded as hydrogen carrier for sustainable society, which potentially leads to strong demands for large-scale synthesis of NH<sub>3</sub> with high efficiency and moreover laboratory-scale synthesis of high purity NH<sub>3</sub> or deuterated ammonia (ND<sub>3</sub>) for fundamental researches on NH<sub>3</sub> utilization as energy carrier.<sup>1)</sup> Haber-Bosch process is a well-known ammonia synthesis technique for industrialized mass production. The annual production of NH<sub>3</sub> in the world by this Haber-Bosch process reached as much as 1.3 hundred million tons in 2010.<sup>2)</sup> Although this process is recognized as the most efficient method for large scale NH<sub>3</sub> production, it needs high temperature of 400–600°C and high pressure of 20–40 MPa even in the presence of iron oxide catalyst.<sup>3,4)</sup> Therefore, it should be difficult to adopt the process for the synthesis of high purity NH<sub>3</sub> or ND<sub>3</sub> in laboratory-scale.

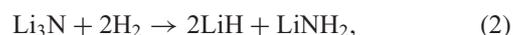
The reason that the production of NH<sub>3</sub> from H<sub>2</sub> and N<sub>2</sub> needs such high temperature and pressure even though the reaction is exothermic ( $\Delta H = 46$  kJ/mol NH<sub>3</sub>), is due to the strong triple bond between N atoms in N<sub>2</sub> molecule.<sup>5)</sup>

Therefore, it is an important issue how to dissociate N<sub>2</sub> efficiently for NH<sub>3</sub> synthesis under mild condition. In this view, the reaction of lithium (Li) with N<sub>2</sub> attracts attention, described by the following reaction (1),



Only Li is potential material to react with N<sub>2</sub> below 100°C, forming lithium nitride (Li<sub>3</sub>N).<sup>6)</sup> In other words, it is one of the simplest way to dissociate the nitrogen triple bond (N≡N), which possibly realizes the NH<sub>3</sub> synthesis under milder condition by reaction between Li<sub>3</sub>N and H<sub>2</sub>.

Therefore, we proposed NH<sub>3</sub> synthesis process applying reactions of the amide-imide hydrogen storage system<sup>7–11)</sup> and metal hydride-ammonia system,<sup>12–15)</sup> respectively described by the following reactions,



Since each reaction proceeds below 300°C and 0.5 MPa, it is expected that the NH<sub>3</sub> synthesis process under moderate condition becomes possible by optimizing the reaction condition. Regarding the cycle of materials, Li should be regenerated from LiH as the final product in reaction (3). However, the thermal decomposition of LiH requires more than 500°C. The effective regeneration process of Li metal below 300°C differently from simple decomposition is necessary, e.g. the metallic Li can be obtained below 500°C by using a reaction between crystalline graphite and LiH.<sup>16)</sup>

In this study, the reaction conditions of the proposed NH<sub>3</sub> synthesis process from Li<sub>3</sub>N were investigated by preparing various types of reaction systems, which were open system, closed gas circuit system, and closed system with gas exchange using hydrogen storage alloys, and the feasibility of the proposed process was discussed from the experimental results.

\*<sup>1</sup>This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. 77 (2013) 580–584. In order to more precisely explain the background, the experimental procedures, and the results, some parts of the contents were revised as follows. X ray diffraction profile of lithium nitride powder and the corresponding patterns in database ( $\alpha$ -Li<sub>3</sub>N; PDF#75-8952 and  $\beta$ -Li<sub>3</sub>N; PDF#76-0821) were added in Fig. 4. The sentence of the abstract was slightly modified. References of 2–7), 15–19), and 20) were added and the reference of the Japanese website was removed from this paper.

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\*<sup>3</sup>Hikaru Yamamoto who contributed to the development for the gas circuit apparatus is added as a coauthor in this paper on reconsidering the matter.

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## 2. Experimental Procedure

### 2.1 Investigation of NH<sub>3</sub> production from Li<sub>3</sub>N by DSC and MS

Commercial lithium nitride (Li<sub>3</sub>N) (99.5%, Aldrich) was used for the experiments in this work. The reaction of Li<sub>3</sub>N with H<sub>2</sub> for NH<sub>3</sub> production was investigated by using differential scanning calorimetry (DSC) (TA Instruments, Q10 PDSC), which is installed into a glove box (Miwa MFG, MP-P60 W) filled with purified Ar (> 99.9999%). The generated gases during the DSC measurements is *in-situ* monitored by using mass spectrometry (MS) (Canon Anelva Corporation, M-100QA), which is connected to the reactor of DSC apparatus. The reaction condition using H<sub>2</sub> flow is regarded as thermodynamic non-equilibrium state because the gaseous product, NH<sub>3</sub>, is immediately removed from the reaction field. The solid samples before and after the reaction were identified by X-ray diffraction (XRD) measurement (Rigaku, RINT-2100, CuK $\alpha$  radiation), where the samples were covered by a polyimide sheet (Du Pont-Toray Co., LTD., Kapton<sup>®</sup>) to protect the samples from oxidation during XRD measurements.

### 2.2 Investigation of NH<sub>3</sub> production from LiNH<sub>2</sub> in gas circuit system

In order to realize the reaction (3) in closed system, a gas circuit system was designed. Figure 1 shows the schematic image of the gas circulating system designed for this experiment. This apparatus includes a gas densimeter (Yokogawa Electric Corporation, GD400), circulation pump (Nittou kouatsu), gas flow meter (ACE Inc., AFM-150), pressure gauge, and NH<sub>3</sub> trap chamber. A reaction cell loading a weighed amount (42 mg) of commercial LiNH<sub>2</sub> (LiNH<sub>2</sub>) (95%, Aldrich) was connected to the gas circuit system and 0.5 MPa H<sub>2</sub> with a molar ratio of H<sub>2</sub>/LiNH<sub>2</sub> = 100 was introduced. After that, the experiments were carried out under gas circulated condition with 16 and 88 sccm (= cc min<sup>-1</sup> at 0.1 MPa, 0°C) of flow rates at 300°C. NH<sub>3</sub> trap using liquid N<sub>2</sub> was used to reduce the partial pressure of NH<sub>3</sub> in the circuit system. In order to estimate the reaction yield, the amount of NH<sub>3</sub> trapped during the reaction was measured by using a gas densimeter. The solid materials were identified by XRD before and after the reaction.

### 2.3 Scale up test for NH<sub>3</sub> and ND<sub>3</sub> synthesis

Mixture of LiD and LiND<sub>2</sub> were synthesized as starting materials for this experiments by reaction between Li<sub>3</sub>N (99.5%, Aldrich) and high purity D<sub>2</sub> gas (> 99.8%) instead of the reaction (2). In order to realize a certain amount of D<sub>2</sub> flow condition for the reaction (3), gas collecting system by hydrogen storage alloys without waste of D<sub>2</sub> was designed and assembled. Figure 2 shows the schematic image of the closed H<sub>2</sub> flow system used for scale up test. This system is composed of reaction cell, hydrogen storage tanks, heaters, pressure gauge, flow meter, and NH<sub>3</sub> trap. The couple of tanks loaded by the same hydrogen storage alloy were connected to both ends of reaction cell and thermally controlled. Then, a sufficient amount of mixture of LiD and LiND<sub>2</sub> loaded in the reaction cell and heated under D<sub>2</sub> flow condition (1.0 MPa, 1.0 L min<sup>-1</sup>) at 300°C with ND<sub>3</sub> trap.

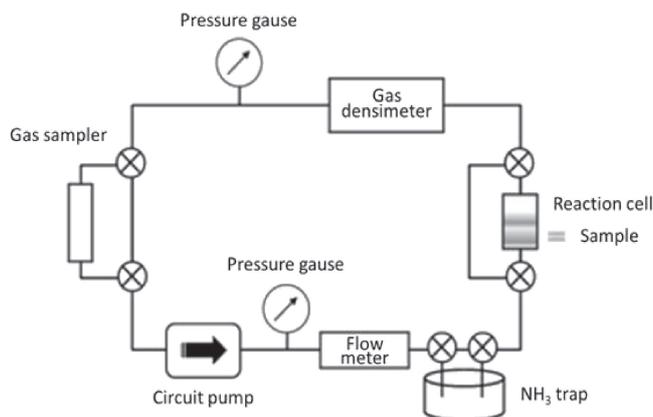


Fig. 1 Schematic view of gas circuit system.

After the reaction, the amount of generated ND<sub>3</sub> in the trap was weighted.

## 3. Result and Discussions

### 3.1 Investigation of NH<sub>3</sub> production from Li<sub>3</sub>N by DSC and MS

Hydrogenation of Li<sub>3</sub>N under H<sub>2</sub> flow was investigated by DSC and MS. Since the NH<sub>3</sub> production reaction of LiH-NH<sub>3</sub> system described by reaction (3) is endothermic reaction, the thermodynamics should be considered to control the reaction process at a moderate temperature. Gibbs free energy change  $\Delta G$  on this reaction is expressed as follows,

$$\Delta G = \Delta H - T(\Delta S^0 + R \ln(P_{\text{H}_2}/P_{\text{NH}_3})) \quad (4)$$

where  $\Delta H$ ,  $\Delta S^0$ ,  $R$ ,  $P_{\text{H}_2}$ , and  $P_{\text{NH}_3}$  are, respectively, the enthalpy change, the standard entropy change, the gas constant, partial pressure of H<sub>2</sub>, and partial pressure of NH<sub>3</sub>. In order to manage the reaction progress at lower temperature, it is essential to decrease the value of the last entropy term in the equation (4). In the DSC-MS experiments, the reaction was investigated under the H<sub>2</sub> flow condition in an open system, suggesting that the value of the entropy is increased by reducing  $P_{\text{NH}_3}$ . Figure 3 shows the DSC-MS profile of Li<sub>3</sub>N under 0.5 MPa of the H<sub>2</sub> flow condition. As shown in this DSC profile, exothermic peak was observed from 200°C during heating, which would be originated in the hydrogenation of Li<sub>3</sub>N described by the reaction (2). The temperature for this reaction is consistent with the results reported before.<sup>8)</sup> It is also possible that the reaction (3) proceeds 200°C in this condition.<sup>14)</sup> However, it is difficult to distinguish the reaction temperature because the smaller endothermic peak due to the reaction (3) would be overlapped with the larger exothermic peak due to the reaction (2). In the mass spectra, generation of NH<sub>3</sub> gas was clearly observed above 230°C. It was expected that the NH<sub>3</sub> generation originated in hydrogenation of LiNH<sub>2</sub>. The onset temperature for NH<sub>3</sub> desorption was about 230°C, which was closed to that reported before.<sup>14)</sup> The NH<sub>3</sub> desorption intensity was increased with during the heating, indicating that the reaction (3) gradually proceeds from 230°C after the LiNH<sub>2</sub> formation by the reaction (2) around 200°C. Here, the MS detection of our experimental system is slightly delayed

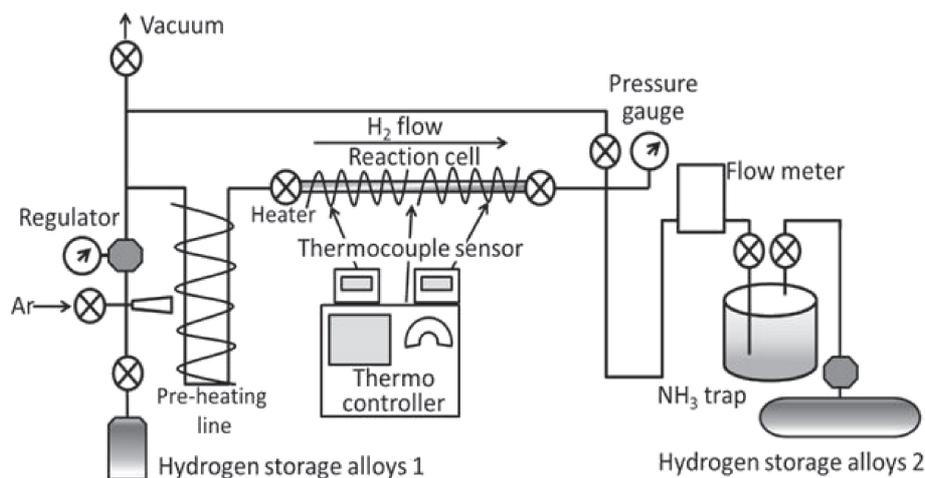


Fig. 2 Schematic view of D<sub>2</sub> flow system for ND<sub>3</sub> synthesis.

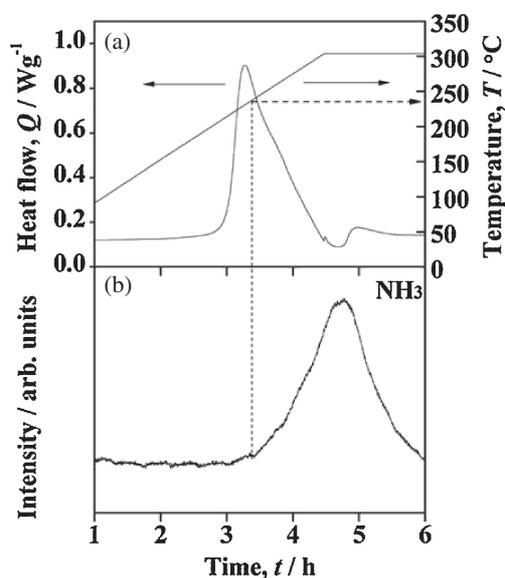


Fig. 3 DSC (a)-MS (b) profiles of Li<sub>3</sub>N under 0.5MPa of H<sub>2</sub> flow condition at 1.0°C min<sup>-1</sup> heating rate. NH<sub>3</sub> generation temperature is indicated with the auxiliary line (---).

from the DSC signal with fast response, and the reaction kinetics of the light elements based materials are generally slow. From the above facts, it is suggested that the accurate reaction temperature of (3) is difficult to be distinguished. Figure 4 shows XRD pattern of the product after the DSC-MS measurement. The X-ray diffraction peaks of LiH was observed as the reaction product without any traces for the diffraction peaks of Li<sub>3</sub>N and LiNH<sub>2</sub>. This indicates that the LiNH<sub>2</sub> generated by the prior hydrogenation of Li<sub>3</sub>N gradually reacted with H<sub>2</sub> to form NH<sub>3</sub> and LiH. Here, Li<sub>2</sub>O phase observed in XRD profile would be derived from impurity in the reagent. Generally, X-ray diffraction intensity is strongly related to electron number of atoms in the material. If the amount of Li<sub>2</sub>O is considerable in the samples, the diffraction intensity has to be much stronger than that of LiH. Thus, it is considered that the amount of the impurity was small by taking account of the intensity of LiH phase and Li<sub>2</sub>O phase, suggesting that any effects of the impurity into the essential reaction could be negligible. From

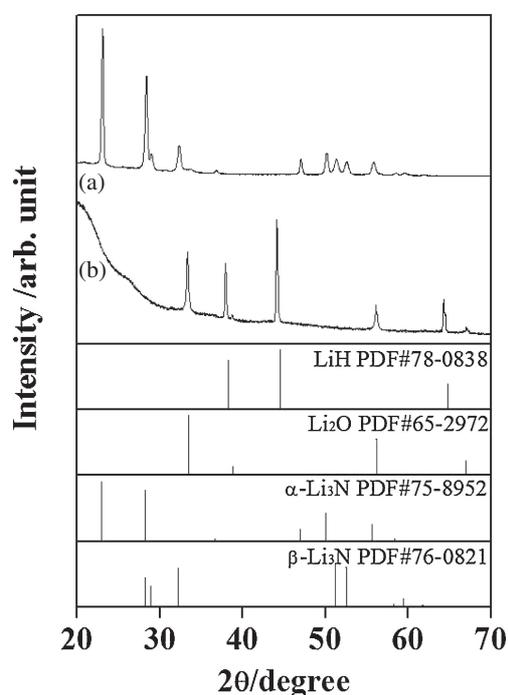


Fig. 4 XRD patterns of Li<sub>3</sub>N before: (a) and after: (b) the treatment under H<sub>2</sub> flow condition for 4 h at 300°C. XRD pattern of LiH (PDF#78-0838), Li<sub>2</sub>O (PDF#65-2972), α-Li<sub>3</sub>N (PDF#75-8952) β-Li<sub>3</sub>N (PDF#76-0821) are referred from databases.

the above results, it was confirmed that the objective two-step process for NH<sub>3</sub> production proceeded under relatively lower temperature and pressure in the H<sub>2</sub> flow condition. In thermodynamic analyses based on the experimental results and equation (4), the partial pressure of NH<sub>3</sub> is reduced to be 4~12 Pa as an overestimation under the experimental conditions, where the  $\Delta H$  and  $\Delta S^0$  were calculated by combining reported  $\Delta^f H^0$  and  $S^0$  values as shown in Table 1,  $-90.5 \text{ kJ mol}^{-1}$  and  $20.0 \text{ J mol}^{-1} \text{ K}^{-1}$  for LiH,  $-45.9 \text{ kJ mol}^{-1}$  and  $192.8 \text{ J mol}^{-1} \text{ K}^{-1}$  for NH<sub>3</sub>,  $130.7 \text{ J mol}^{-1} \text{ K}^{-1}$  for H<sub>2</sub>,  $-179.5 \text{ kJ mol}^{-1}$  for LiNH<sub>2</sub>,<sup>17-19</sup> and approximate  $S^0$  values of LiNH<sub>2</sub>, 80~90 J mol<sup>-1</sup> K<sup>-1</sup> which is similar to the  $S^0$  value of complex hydrides such as LiBH<sub>4</sub> and LiAlH<sub>4</sub>.<sup>20</sup>

Table 1 Standard enthalpy of formation and standard entropy for H<sub>2</sub>, NH<sub>3</sub>, LiH, and LiNH<sub>2</sub>.

Compounds	Enthalpy of formation $\Delta_f H^\circ$ (kJ·mol <sup>-1</sup> )	Entropy $S^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
LiH (s)	-90.5	20
LiNH <sub>2</sub> (s)	-179.5	80-90*
H <sub>2</sub> (g)	0	130.7
NH <sub>3</sub> (g)	-45.9	192.8

\*Assumed  $S^\circ$  value for LiNH<sub>2</sub>.

### 3.2 Investigation of NH<sub>3</sub> production from LiNH<sub>2</sub> in gas circuit system

From the above DSC experiments, the feasibility of NH<sub>3</sub> generation from Li<sub>3</sub>N under H<sub>2</sub> flow was demonstrated. In the process, the reaction (2) is not difficult to be operated because this exothermic reaction proceeds even at closed system. In order to control the proposed NH<sub>3</sub> production process, the most important issue is how to control the reaction (3). Thus, the hydrogenation property of LiNH<sub>2</sub> was further investigated in closed-circuit system. For the experiment, the gas circuit apparatus was used as mentioned in the experimental part. By using the gas circuit system, it becomes possible to *in-situ* measure the concentration of H<sub>2</sub> for NH<sub>3</sub> under a certain pressure and gas flow rate in the circulating system. Additionally, NH<sub>3</sub> trap by using liquid N<sub>2</sub> is equipped into the circulating line, thus the generated NH<sub>3</sub> can be removed from the circulated gases. It is expected that the partial pressure of NH<sub>3</sub> is reduced to a sufficient level to realize the progress of reaction (3) because the temperature of liquid N<sub>2</sub> is low enough compared with the freezing point of NH<sub>3</sub>. Here, the inner volume of the trap part is sufficiently-large. Thus, almost all the generated NH<sub>3</sub> can be trapped even if the experiments are performed by a maximum circuit rate, in other words, the generated NH<sub>3</sub> is not reached to sample part again during the circulation. As described above, it is essential to control the entropy change by reducing NH<sub>3</sub> partial pressure for the hydrogenation of LiNH<sub>2</sub>. Therefore, the investigation for hydrogenation reaction of Li<sub>3</sub>N was performed under H<sub>2</sub> flow condition in open system by DSC-MS in section 3.1. However, such flow condition, which exhausts unreacted H<sub>2</sub> and generated NH<sub>3</sub> gases, is totally different from practical condition, because the hydrogen gas has to be consumed a lot in the open system. On the other hand, in the case of above gas circuit system, it is expected that the hydrogenation reaction proceeds even in closed system without the H<sub>2</sub> loss, which would be more practical condition than that of DSC experiments. Figure 5 shows XRD pattern of the product after the LiNH<sub>2</sub> hydrogenating treatment for 8 h at 300°C, where the circulating rate was 16 sccm. Although diffraction peaks corresponding to LiH was observed, it was confirmed that a trace of LiNH<sub>2</sub> remained in the product. In this case, the reaction yield was 35.6%. These results indicated that the  $P_{\text{NH}_3}$  was reduced to less than 12 Pa and the reaction proceeded by using the circulating system because LiH was clearly generated. However, the 16 sccm of circuit rate was not enough to reach the same level of  $P_{\text{NH}_3}$  as the DSC condition due to slow diffusion rate of NH<sub>3</sub> gas in the solid sample part,

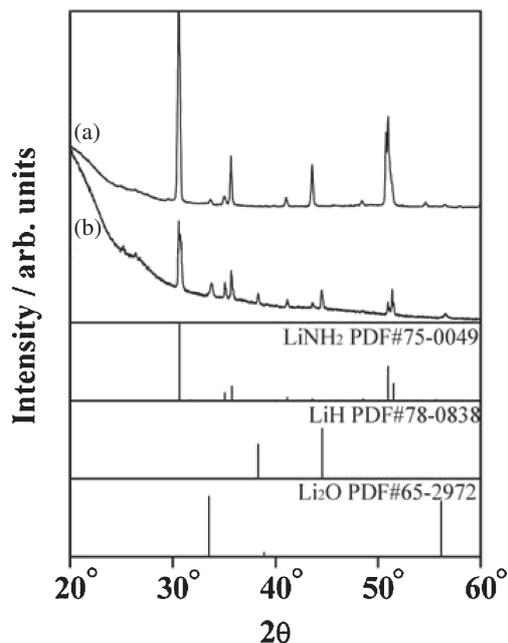


Fig. 5 XRD patterns of LiNH<sub>2</sub> before: (a) and after: (b) the treatment under 16 sccm H<sub>2</sub> flow condition for 8 h at 300°C. XRD pattern of LiNH<sub>2</sub> (PDF#75-0049), LiH (PDF#78-0838), and Li<sub>2</sub>O (PDF#65-2972) are referred from databases.

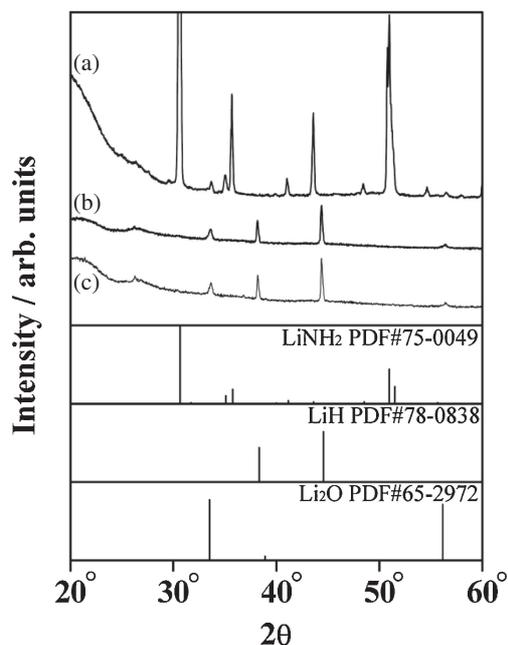


Fig. 6 XRD patterns of LiNH<sub>2</sub> before: (a) and after the treatment under 88 sccm H<sub>2</sub> flow condition for 4 h: (b) and 6 h: (c) at 300°C. XRD pattern of LiNH<sub>2</sub> (PDF#75-0049), LiH (PDF#78-0838), and Li<sub>2</sub>O (PDF#65-2972) are referred from databases.

indicating that NH<sub>3</sub> was not removed enough from reaction field. Therefore, the reaction condition was changed to higher circulating rate of 88 sccm. Figure 6 shows XRD pattern of the product in circulating system for 4 h and 6 h at 300°C. The diffraction peaks corresponding to LiNH<sub>2</sub> observed after the experiments with 16 sccm totally disappeared. Here, in these experiments, although a small amount of Li<sub>2</sub>O derived from impurity in the reagent was observed by XRD, it would

not influence the quantitative discussion because of the same reason as section 3.1. The reaction yields for 4 and 6 h were estimated from  $\text{NH}_3$  concentration by using the gas densimeter, and the values were respectively 75.3% and 91.6%. As described above, it is important to decrease the partial pressure of  $\text{NH}_3$  by diffusing  $\text{NH}_3$  gas effectively from the reaction field for the reaction (3). In this experiment by using gas circulating system, the gas in the closed system was circulated and simultaneously  $\text{NH}_3$  was trapped. As the results, sufficiently low  $P_{\text{NH}_3}$  and highly efficient condition for  $\text{NH}_3$  production can be realized when the faster circulating rate.

### 3.3 Scale up test for $\text{ND}_3$ synthesis

The scale up test of the reaction (3) for the  $\text{ND}_3$  synthesis was performed. As described above, a certain diffusion rate of generated  $\text{NH}_3$  from reaction field is important for efficient  $\text{NH}_3$  production from  $\text{LiNH}_2$ . Therefore, it is necessary to make the higher  $\text{H}_2$  flow rate for larger scale  $\text{NH}_3$  production. Thus, the gas flow system with higher  $\text{H}_2$  flow rate by hydrogen storage alloys was designed and assembled. When the temperatures of the tanks were controlled in high and low temperatures, the pressure gradient was generated because of different  $\text{H}_2$  equilibrium pressure of the hydrogen storage alloy. By this pressure difference, it was expected that the sufficient  $\text{H}_2$  flow condition through reaction cell is realized. In this process, the unreacted  $\text{H}_2$  is collected into the alloys controlled at lower temperature, and  $\text{H}_2$  can be reused by exchanging the flow direction with temperature control of tanks. As a result, the  $\text{H}_2$  loss except the  $\text{NH}_3$  generation reaction is suppressed, where this would be advantage point as productive  $\text{NH}_3$  synthesis. In the actual experiment, we used  $\text{D}_2$  gas instead of  $\text{H}_2$  gas. Then the pressure and flow rate of inside gas were monitored, and the generated  $\text{ND}_3$  was collected in the trap. It was clarified that flow rate prepared by this reaction system was  $1.0 \text{ L min}^{-1}$ , which is approximately ten times faster than that required in the above circulating system to complete the reaction. By using this reaction system,  $1.0 \text{ g ND}_3$  was successfully produced by heating the mixture of  $\text{LiD}$  and  $\text{LiND}_2$  in  $1.0 \text{ MPa}$  of  $\text{D}_2$  flow condition with  $1.0 \text{ L min}^{-1}$  of flow rate at  $300^\circ\text{C}$  for 4 h, resulting in  $0.25 \text{ g h}^{-1}$  of production rate. Whereas Haber-Bosch process needs high temperature of  $400\text{--}600^\circ\text{C}$  and high pressure of  $20\text{--}40 \text{ MPa}$ , the result in this study indicates that the  $\text{NH}_3$  production by the reactions (1) and (2) can be operated under comparatively mild condition and is remarkably useful as efficient  $\text{ND}_3$  synthesis method in laboratory-scale.

## 4. Conclusions

In this work,  $\text{NH}_3$  production by the hydrogenation  $\text{Li}_3\text{N}$  and the reaction of  $\text{LiNH}_2$  and  $\text{H}_2$  were investigated to propose a novel  $\text{NH}_3$  synthesis method in laboratory-scale.

As a result, the  $\text{NH}_3$  generation from  $\text{Li}_3\text{N}$  in  $0.5 \text{ MPa}$  of  $\text{H}_2$  flow condition below  $300^\circ\text{C}$  was confirmed by DSC-MS and XRD, indicating that the  $\text{NH}_3$  production from  $\text{Li}_3\text{N}$  can proceed in milder condition than conventional method by using the objective two step reactions. For the investigation of  $\text{NH}_3$  generation from  $\text{LiNH}_2$  in the closed system, a gas circuit system was designed and used for the experiment. The system can circulate mixture gas of  $\text{NH}_3$  and  $\text{H}_2$  with enough flow rate and reduce the partial pressure of  $\text{NH}_3$  by the trap using liquid  $\text{N}_2$ . As a result, it was clarified that  $\text{NH}_3$  generation proceeded even in the closed system, which would be considered as more practical condition. Furthermore,  $\text{NH}_3$  synthesis test on a larger scale was conducted, where the higher  $\text{D}_2$  flow system by pressure gradient between couple of hydrogen storage alloy tanks was designed for the experiment. By using the system, a certain amount of  $\text{ND}_3$  production at realistic reaction rate ( $0.25 \text{ g h}^{-1}$ ) was demonstrated in  $1.0 \text{ L min}^{-1}$  of  $\text{D}_2$  flow condition below  $300^\circ\text{C}$  and  $1.0 \text{ MPa}$ .

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