Ammonia Synthesis via Non-Equilibrium Reaction of Lithium Nitride in Hydrogen Flow Condition*1

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Lithium nitride Li3N is hydrogenated below 300°C under 0.5 MPa of H2, and then LiNH2 and LiH are formed as products. Furthermore, the reaction between LiNH2 and H2 proceeds below 250°C under 0.5 MPa of H2 flow condition, which forms NH3 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 H2 flow condition, where a gas circuit system and a larger scale NH3 synthesis system were designed and assembled for the experiments. [doi:10.2320/matertrans.M2014382]

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1. Introduction

Ammonia (NH3) has been produced on massive scale in the world and used as various feedstock of nitrogenous chemical products. Recently, NH3 is regarded as hydrogen carrier for sustainable society, which potentially leads to strong demands for large-scale synthesis of NH3 with high efficiency and moreover laboratory-scale synthesis of high purity NH3 or deuterated ammonia (ND3) for fundamental researches on NH3 utilization as energy carrier.1,2) Haber-Bosch process is a well-known ammonia synthesis technique for industrialized mass production. The annual production of NH3 in the world by this Haber-Bosch process reached as much as 1.3 hundred million tons in 2010.2) Although this process is recognized as the most efficient method for large scale NH3 production, it needs high temperature of 400–600°C and high pressure of 20–40 MPa even in the presence of iron oxide catalyst.3,4) Therefore, it should be difficult to adopt the process for the synthesis of high purity NH3 or ND3 in laboratory-scale.

The reason that the production of NH3 from H2 and N2 needs such high temperature and pressure even though the reaction is exothermic (ΔH = 46 kJ/mol NH3), is due to the strong triple bond between N atoms in N2 molecule.5) Therefore, it is an important issue how to dissociate N2 efficiently for NH3 synthesis under mild condition. In this view, the reaction of lithium (Li) with N2 attracts attention, described by the following reaction (1),

\[6Li + N_2 \rightarrow 2Li_3N. \tag{1}\]

Only Li is potential material to react with N2 below 100°C, forming lithium nitride (Li3N).6) In other words, it is one of the simplest way to dissociate the nitrogen triple bond (N≡N), which possibly realizes the NH3 synthesis under milder condition by reaction between Li3N and H2.

Therefore, we proposed NH3 synthesis process applying reactions of the amide-imide hydrogen storage system7-15) and metal hydride-ammonia system12-15) respectively described by the following reactions,

\[Li_3N + 2H_2 \rightarrow 2LiH + LiNH_2, \tag{2}\]
\[LiNH_2 + H_2 \rightarrow NH_3 + LiH. \tag{3}\]

Since each reaction proceeds below 300°C and 0.5 MPa, it is expected that the NH3 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.16)

In this study, the reaction conditions of the proposed NH3 synthesis process from Li3N 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.
2. Experimental Procedure

2.1 Investigation of NH₃ production from Li₃N by DSC and MS

Commercial lithium nitride (Li₃N) (99.5%, Aldrich) was used for the experiments in this work. The reaction of Li₃N with H₂ for NH₃ 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 H₂ flow is regarded as thermodynamic non-equilibrium state because the gaseous product, NH₃, 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, CuKa radiation), where the samples were covered by a polyimide sheet (Du Pont-Toray Co., LTD., Kapton®) to protect the samples from oxidation during XRD measurements.

2.2 Investigation of NH₃ production from LiNH₂ 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 circuiting 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 NH₃ trap chamber. A reaction cell loading a weighed amount (42 mg) of commercial LiNH₂ (95%, Aldrich) was connected to the gas circuit system and 0.5 MPa H₂ with a molar ratio of H₂/LiNH₂ = 100 was introduced. After that, the experiments were carried out under gas circulated condition with 16 and 88 sccm (= cc min⁻¹ at 0.1 MPa, 0°C) of flow rates at 300°C. NH₃ trap using liquid N₂ was used to reduce the partial pressure of NH₃ in the circuit system. In order to estimate the reaction yield, the amount of NH₃ 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 NH₃ and ND₃ synthesis

Mixture of LiD and LiND₂ were synthesized as starting materials for this experiments by reaction between Li₃N (99.5%, Aldrich) and high purity D₂ gas (> 99.8%) instead of the reaction (2). In order to realize a certain amount of D₂ flow condition for the reaction (3), gas collecting system by hydrogen storage alloys without waste of D₂ was designed and assembled. Figure 2 shows the schematic image of the closed H₂ flow system used for scale up test. This system is composed of reaction cell, hydrogen storage tanks, heaters, pressure gauge, flow meter, and NH₃ 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 LiND₂ loaded in the reaction cell and heated under D₂ flow condition (1.0 MPa, 1.0 L min⁻¹) at 300°C with ND₃ trap.

After the reaction, the amount of generated ND₃ in the trap was weighted.

3. Result and Discussions

3.1 Investigation of NH₃ production from Li₃N by DSC and MS

Hydrogenation of Li₃N under H₂ flow was investigated by DSC and MS. Since the NH₃ production reaction of LiH-NH₃ 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 ΔG on this reaction is expressed as follows,

\[ \Delta G = \Delta H - T(\Delta S^0 + R \ln(P_{H_2}/P_{NH_3})) \]  

where ΔH, ΔS⁰, R, P_H₂, and P_NH₃ are, respectively, the enthalpy change, the standard entropy change, the gas constant, partial pressure of H₂, and partial pressure of NH₃. 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 H₂ flow condition in an open system, suggesting that the value of the entropy is increased by reducing P_NH₃. Figure 3 shows the DSC-MS profile of Li₃N under 0.5 MPa of the H₂ 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 Li₃N described by the reaction (2). The temperature for this reaction is consistent with the results reported before. It is also possible that the reaction (3) proceeds 200°C in this condition. 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 NH₃ gas was clearly observed above 230°C. It was expected that the NH₃ generation originated in hydrogenation of LiNH₂. The onset temperature for NH₃ desorption was about 230°C, which was closed to that reported before. The NH₃ desorption intensity was increased with during the heating, indicating that the reaction (3) gradually proceeds from 230°C after the LiNH₂ formation by the reaction (2) around 200°C. Here, the MS detection of our experimental system is slightly delayed.
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 Li3N and LiNH2. This indicates that the LiNH2 generated by the prior hydrogenation of Li3N gradually reacted with H2 to form NH3 and LiH. Here, Li2O 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 Li2O 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 Li2O phase, suggesting that any effects of the impurity into the essential reaction could be negligible. From the above results, it was confirmed that the objective two-step process for NH3 production proceeded under relatively lower temperature and pressure in the H2 flow condition. In thermodynamic analyses based on the experimental results and equation (4), the partial pressure of NH3 is reduced to be 4~12 Pa as an overestimation under the experimental conditions, where the $\Delta H^\circ$ and $S^\circ$ were calculated by combining reported $\Delta H^\circ$ and $S^\circ$ 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 J mol$^{-1}$ K$^{-1}$ for NH3, 130.7 J mol$^{-1}$ K$^{-1}$ for H2, $-179.5 \text{kJ mol}^{-1}$ for LiNH2, and approximate $S^\circ$ values of LiNH2, 80~90 J mol$^{-1}$ K$^{-1}$ which is similar to the $S^\circ$ value of complex hydrides such as LiBH4 and LiAlH4.20
3.2 Investigation of NH₃ production from LiNH₂ in gas circuit system

From the above DSC experiments, the feasibility of NH₃ generation from Li₃N under H₂ 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 NH₃ production process, the most important issue is how to control the reaction (3). Thus, the hydrogenation property of LiNH₂ 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 H₂ for NH₃ under a certain pressure and gas flow rate in the circulating system. Additionally, NH₃ trap by using liquid N₂ is equipped into the circulating line, thus the generated NH₃ can be removed from the circulated gases. It is expected that the partial pressure of NH₃ is reduced to a sufficient level to realize the progress of reaction (3) because the temperature of liquid N₂ is low enough compared with the freezing point of NH₃. Here, the inner volume of the trap part is sufficiently-large. Thus, almost all the generated NH₃ can be trapped even if the experiments are performed by a maximum circuit rate, in other words, the generated NH₃ is not reached to sample part again during the circulation. As described above, it is essential to control the entropy change by reducing NH₃ partial pressure for the hydrogenation of LiNH₂. Therefore, the investigation for hydrogenation reaction of Li₃N was performed under H₂ flow condition in open system by DSC-MS in section 3.1. However, such flow condition, which exhausts unreacted H₂ and generated NH₃ 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 H₂ loss, which would be more practical condition than that of DSC experiments. Figure 5 shows XRD pattern of the product after the LiNH₂ 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 LiNH₂ 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 NH₃ gas in the solid sample part, indicating that NH₃ 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, where the circulating rate was 88 sccm. Although diffraction peaks corresponding to LiNH₂ observed after the experiments with 16 sccm totally disappeared. Here, in these experiments, although a small amount of Li₂O derived from impurity in the reagent was observed by XRD, it would

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Enthalpy of formation $\Delta H^o$ (kJ·mol⁻¹)</th>
<th>Entropy $S^o$ (J·K⁻¹·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH (s)</td>
<td>−90.5</td>
<td>20</td>
</tr>
<tr>
<td>LiNH₂ (s)</td>
<td>−179.5</td>
<td>80−90*</td>
</tr>
<tr>
<td>H₂ (g)</td>
<td>0</td>
<td>130.7</td>
</tr>
<tr>
<td>NH₃ (g)</td>
<td>−45.9</td>
<td>192.8</td>
</tr>
</tbody>
</table>

*Assumed $S^o$ value for LiNH₂.

![Fig. 5 XRD patterns of LiNH₂ before: (a) and after: (b) the treatment under 16 sccm H₂ flow condition for 8 h at 300°C. XRD pattern of LiNH₂ (PDF#75-0049), LiH (PDF#78-0838), and Li₂O (PDF#65-2972) are referred from databases.](image1)

![Fig. 6 XRD patterns of LiNH₂ before: (a) and after: (b) the treatment under 88 sccm H₂ flow condition for 4 h: (b) and 6 h: (c) at 300°C. XRD pattern of LiNH₂ (PDF#75-0049), LiH (PDF#78-0838), and Li₂O (PDF#65-2972) are referred from databases.](image2)
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 NH3 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 NH3 by diffusing NH3 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 NH3 was trapped. As the results, sufficiently low $P_{\text{NH3}}$ and highly efficient condition for NH3 production can be realized when the faster circulating rate.

3.3 Scale up test for ND3 synthesis

The scale up test of the reaction (3) for the ND3 synthesis was performed. As described above, a certain diffusion rate of generated NH3 from reaction field is important for efficient NH3 production from LiNH2. Therefore, it is necessary to make the higher H2 flow rate for larger scale NH3 production. Thus, the gas flow system with higher H2 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 H2 equilibrium pressure of the hydrogen storage alloy. By this pressure difference, it was expected that the sufficient H2 flow condition through reaction cell is realized. In this process, the unreacted H2 is collected into the alloys controlled at lower temperature, and H2 can be reused by exchanging the flow direction with temperature control of tanks. As a result, the H2 loss except the NH3 generation reaction is suppressed, where this would be advantage point as productive NH3 synthesis. In the actual experiment, we used D2 gas instead of H2 gas. Then the pressure and flow rate of inside gas were monitored, and the generated ND3 was collected in the trap. It was clarified that flow rate prepared by this reaction system was 1.0 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 g ND3 was successfully produced by heating the mixture of LiD and LiND2 in 1.0 MPa of D2 flow condition with 1.0 L min⁻¹ of flow rate at 300°C for 4 h, resulting in 0.25 g h⁻¹ of production rate. Whereas Haber-Bosch process needs high temperature of 400–600°C and high pressure of 20–40 MPa, the result in this study indicates that the NH3 production by the reactions (1) and (2) can be operated under comparatively mild condition and is remarkably useful as efficient ND3 synthesis method in laboratory-scale.

4. Conclusions

In this work, NH3 production by the hydrogenation Li3N and the reaction of LiNH2 and H2 were investigated to propose a novel NH3 synthesis method in laboratory-scale. As a result, the NH3 generation from Li3N in 0.5 MPa of H2 flow condition below 300°C was confirmed by DSC-MS and XRD, indicating that the NH3 production from Li3N can proceed in milder condition than conventional method by using the objective two step reactions. For the investigation of NH3 generation from LiNH2 in the closed system, a gas circuit system was designed and used for the experiment. The system can circulate mixture gas of NH3 and H2 with enough flow rate and reduce the partial pressure of NH3 by the trap using liquid N2. As a result, it was clarified that NH3 generation proceeded even in the closed system, which would be considered as more practical condition. Furthermore, NH3 synthesis test on a larger scale was conducted, where the higher D2 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 ND3 production at realistic reaction rate (0.25 g h⁻¹) was demonstrated in 1.0 L min⁻¹ of D2 flow condition below 300°C and 1.0 MPa.

REFERENCES