Ammonia synthesis reactions over inorganic-organic hybrid catalysts of metal hydride-conjugated macromolecule composites

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Abstract: The catalytic synthesis of ammonia from molecular nitrogen and hydrogen over the inorganic-organic composite catalyst of LiH-poly(*p*-phenylene) was demonstrated. Production amount of ammonia drastically increased by composing LiH with conjugated macromolecule of poly(*p*-phenylene). At the reaction conditions of 400°C and 1.0 MPa, the production amount of ammonia was 3.4 times larger than the stoichiometric amount, indicating that this system is truly catalytic.

Keywords: inorganic-organic hybrid catalyst, ammonia synthesis, hydrogen storage.

1. Introduction

Ammonia is a compound that is used as a raw material for producing fertilizer but also for chemical industry. The artificial synthesis of ammonia from N_2 and H_2 is of great importance for sustaining food production on the earth. Moreover, its utilization as an energy carrier has received growing attention. The ammonia production has been conducted with the Haber-Bosch process to date using iron-based catalysts typically at the reaction conditions of 500°C and 20 MPa. However, in the view point of energy efficiency and plant construction, the process at lower pressure and temperature is desired. Although, Ru is known as an active element for the ammonia synthesis working at the moderate conditions[1], application of precious metal catalysts to large scale industrial processes such as the ammonia production should be avoided from both the economical and the element strategic view. Therefore, development of highly active catalysts composed with abundant elements has been desired for a long time.

Meanwhile, metallic Li is known as one of a few materials which enables to activate N_2 molecule at room temperature (Fig. 1, step 1). Li_3N, which is the product of the reaction between Li and N_2, is known to convert into $LiNH_2$ in the presence of hydrogen (step 2)[2]. Furthermore, $LiNH_2$ gradually transforms into LiH with releasing NH_3 in the hydrogen atmosphere (step 3)[3]. By combining these known reactions, a novel ammonia synthesis system is proposed as shown in Fig. 1. However, the conversion of LiH to metallic Li requires quite harsh conditions so that it is difficult to let the cycle proceed. Therefore, it would be possible to complete the proposed catalyst cycle if LiH can be easily converted into metallic Li or its equivalent material at the similar reaction conditions. Recently, we have found that the inorganic-organic composites of metal hydrides and conjugated macromolecules can reversibly store/release hydrogen at a much lower temperature of 300°C than that of pure LiH (700~800°C)[4]. From the results of isotopic tracer experiment, Raman spectroscopy, and electrical conductivity measurement, it is found that the hydrogen release reaction can be facilitated by transferring the electron on H^- to vacant π-orbitals of conjugated macromolecule. In this work, the catalytic ammonia production on this inorganic-organic composite of metal hydride and conjugated macromolecules are demonstrated.

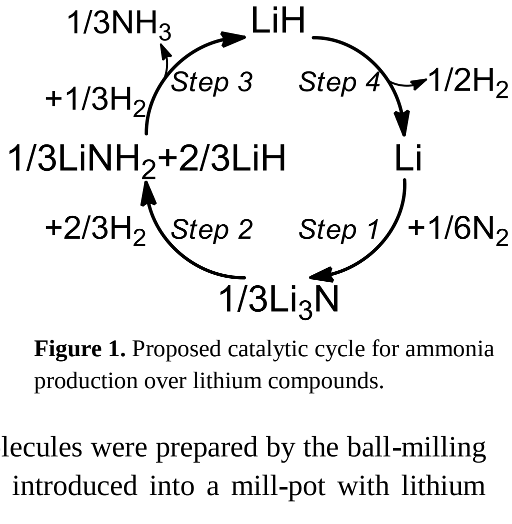

Figure 1. Proposed catalytic cycle for ammonia production over lithium compounds.

2. Experimental

The composites of lithium hydride with conjugated macromolecules were prepared by the ball-milling technique. Conjugated macromolecules of poly(*p*-phenylene) was introduced into a mill-pot with lithium hydride and zirconia balls, and the pot was rotated using a planetary ball-milling-machine for a certain period. The molar ratio of macromolecules and lithium hydride was adjusted to Li:C = 1:1 or 1:2. The ammonia synthesis experiments were conducted with a fixed bed reactor as follows: the mixed gas of N_2 and H_2 with a flow ratio of 1:3 was passed through the LiH-conjugated macromolecule composites (Li: 6 mmol) at the temperature ranging from 300 to 500^{o}C. The outlet gas was passed through a diluted aqueous HCl solution and the solution was analyzed by ion-chromatography. The produced amount of ammonia was determined based on the concentration of NH_4^+ detected in the HCl solution.

3. Results and discussion

When the mixed gas of N_2 and H_2 was passed through the bed of the composite of lithium hydride and poly(*p*-phenylene) (LiH-PPP) at 350^{o}C, ammonia was produced with the rate of 0.038 μmol/min. On the other hand, the production rate of ammonia was lower than the detection level when the pure LiH was used as the catalyst in the same condition. These results clearly indicate that the composing of LiH with the conjugated macromolecule enhanced the ammonia production. Although the ammonia production rate over LiH-PPP was increased by increasing the reaction temperature to 400 and 450^{o}C, a gradual decrease of ammonia production rate with the reaction time was observed at 450^{o}C. Moreover, the ammonia production rate decreased significantly at the further increased temperature of 500^{o}C. The strange temperature dependency of the ammonia production over LiH-PPP was investigated by the XRD analysis of the spent catalysts (Fig. 2). It is found that lithium cyanamide ($Li_2(NCN)$) was mainly formed on the catalysts tested at 450 and 500^{o}C, while LiH was mainly detected on the catalysts tested at 350 and 400^{o}C. Therefore, the formation of inactive $Li_2(NCN)$ probably due to the reaction between $LiNH_2$ and decomposed polymer species is suggested to be a reason for the degraded catalytic activity at a high temperature over 450^{o}C.

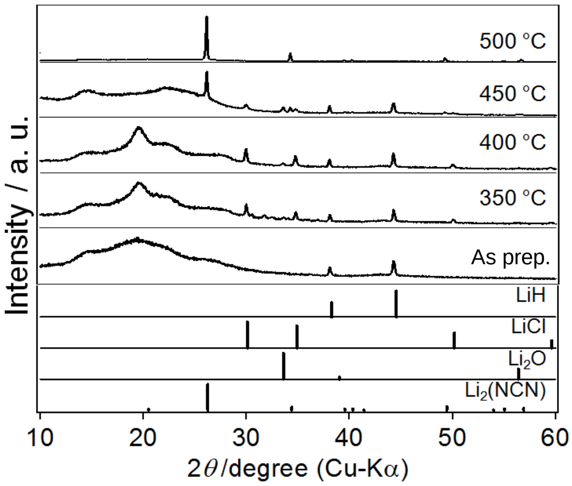

Figure 2. XRD patterns of LiH-PPP after the ammonia synthesis reaction at the varying temperature.

The durability test of the catalyst was also conducted. At the reaction conditions of 400^{o}C and 1.0 MPa, the constant ammonia production rate of 0.23 μmol/min did not change significantly during 20 days of the reaction, and the total ammonia production amount reached to 6.7 mmol. This ammonia production amount is larger than the molar of lithium in the introduced catalyst and corresponds to 3.4 times larger amount than the expected ammonia production amount in one catalytic cycle shown in Fig. 1. Therefore, it is concluded that LiH-PPP catalytically produces ammonia from N_2 and H_2.

4. Conclusions

The catalytic ammonia synthesis from molecular nitrogen and hydrogen proceeded over the inorganic-organic composite catalyst of LiH-poly(*p*-phenylene). The catalyst was stable at the reaction conditions of 400^{o}C and 1.0 MPa for at least 20 days, while inactive lithium cyanamide was formed at the higher temperature.

References

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