Ammonia synthesis over Ru-supported Ca-N-H materials

Masaaki Kitano,[a] **Yasunori Inoue,**[b] **Masato Sasase,**[b] **Tomofumi Tada,**[a] **Toshiharu Yokoyama,**[b] **Michikazu Hara,**[b] **Hideo Hosono** [a,b,*]

[a] *Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

[b] *Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

**Corresponding author: 81-45-924-5009, E-mail address: hosono@msl.titech.ac.jp*

Abstract: Ca_2NH, which consists of Ca^{2+}, N^{3-}, and H^- ions, is formed from Ca_2N electride during ammonia synthesis and effectively promotes the cleavage of N_2 to form NH_3 on Ru catalyst although Ca_2NH is not intrinsically low work function material. The high catalytic performance of Ru/Ca_2NH is attributed to the formation of $[Ca_2N]^+\cdot e^-_{1-x}H^-_x$ with a low work function of 2.3 eV. In addition, Ru/$Ca(NH_2)_2$ catalyst exhibit an extremely high activity for ammonia synthesis at low reaction temperatures.

Keywords: Ammonia synthesis, Ruthenium, hydride.

1. Introduction

Catalytic ammonia synthesis is vital for production of fertilizer, which is needed to produce food for the world's expanding population. The rate-determining step of ammonia synthesis is cleavage of the N≡N bond, because the bond energy is extremely large. In the reaction, a N_2 molecule adsorbs on surface of transition metal catalyst such as Fe and Ru by donating electrons from its bonding orbitals and accepting electrons to the antibonding π orbitals (back-donation). This back-donation produces weakening N≡N bond resulting in enhancement of efficiency of cleavage of N_2. Electron donation from appropriate promoters is therefore a key to enhancing the efficiency of NH_3 synthesis using Fe or Ru-catalysts. Recently, we have found that Ru-loaded $12CaO\cdot 7Al_2O_3$ electride (Ru/C12A7:e^-) with low work function exhibits high catalytic activity for ammonia synthesis.[1] However, the activity of Ru/C12A7:e^- significantly decreases at low reaction temperatures (320°C), which is strongly correlated with the weak hydrogen desorption properties at low temperatures. In the present study, we report that Ca-N-H compounds such as Ca_2NH and $Ca(NH_2)_2$ strongly promote the cleavage of N_2 to form NH_3 on Ru nanoparticles under low temperature conditions. In addition, the effect of H^- ion on the ammonia synthesis activity is revealed by experimental and theoretical investigation.

2. Experimental (or Theoretical)

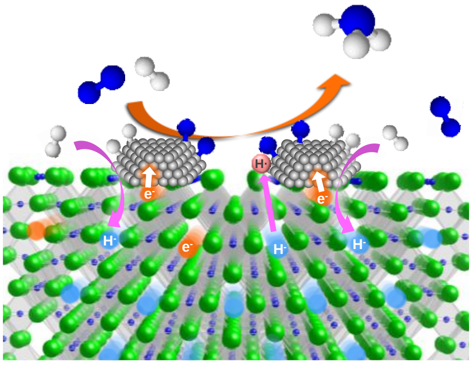
Ca_2N was prepared by solid-state reaction of Ca_3N_2 and Ca metal shot at 800ºC for 50 h in a vacuum. $Ca(NH_2)_2$ was synthesized by heating a Ca metal in liquid NH_3. $Ru_3(CO)_{12}$ was used as a Ru precursor. XRD, FT-IR, HAADF-STEM, XPS, XAFS, Raman, H_2 and CO pulse chemisorption, N_2 adsorption-desorption were used to characterize the catalysts.

Ammonia synthesis reactions were conducted in a fixed bed flow system with an ultrapure mixture of $N_2/H_2 = 1/3$. The concentration of ammonia in the stream that left the catalyst bed (0.1 g catalyst) was monitored under steady-state conditions of temperature (400°C), gas flow rate (60 $mL\cdot min^{-1}$) and pressure (0.1 MPa). The produced ammonia was trapped in 5 mM sulfuric acid solution and the amount of NH_4^+ generated in the solution was determined using ion chromatography.

3. Results and discussion

Ca_2N phase was converted completely into Ca_2NH during ammonia synthesis, when Ru-loaded Ca_2N was used as a catalyst.[2] Ru/Ca_2NH exhibits higher catalytic activity than Cs-Ru/MgO and Ru/C12A7:e^-, especially below 300°C, and ammonia formation can be distinctly observed even at 200°C. The apparent activation energy of Ru/Ca_2NH for ammonia synthesis is 60 kJ mol^{-1}, which is one-half that of Cs-Ru/MgO (120 kJ mol^{-1}). Furthermore, Ru/Ca_2NH functions as a stable catalyst for ammonia synthesis over long periods without degradation in activity. The total amount of produced ammonia for the reaction of 54 h reached 27 mmol, which is more than 25 times the total nitrogen content in Ca_2NH (1.06 mmol). This result indicates that the ammonia produced is not derived from the decomposition of the Ca_2NH support. The catalytic activity of Ru/CaNH, which consists of Ca^{2+} and NH^{2-} ions (the formal charge of hydrogen is +1) was also investigated for comparison. Although CaNH is composed of same elements as Ca_2NH, Ru/CaNH has much lower catalytic activity and a higher activation energy (110 kJ mol^{-1}) than Ru/Ca_2NH. This result clearly indicates that H^- ions play an important role in ammonia synthesis.

To understand the reactivity of these materials with hydrogen, H_2-TPA and TPD on the catalysts were examined. Ru/Ca_2N:e^- can absorb hydrogen above 150°C, which means that the hydrogen storage reaction ($H^0 + e^- \rightarrow H^-$) takes place to form Ca_2NH. On the other hand, H_2 is released ($H^- \rightarrow H^0 + e^-$) from Ru/$Ca_2NH$ above 200°C. Furthermore, the onset temperature for H_2 desorption from Ru/Ca_2NH is much lower than that for Ru/CaNH (*ca*. 500°C). These results show that hydrogen incorporation and desorption reactions proceed above 200°C over Ru/Ca_2NH. It should be noted that the work function of hydrogen deficient Ca_2NH (i.e., $[Ca_2N]^+\cdot e^-_{1-x}H^-_x$) is determined to be 2.3 eV by DFT calculation. In addition, the DFT calculation revealed that the hydrogen vacancy can be readily formed by the combination of Ca_2NH and Ru nanoparticles. These computational results support the idea that anionic electrons with a low WF are formed in nonstoichiometric hydrides, $[Ca_2N]^+\cdot e^-_{1-x}H^-_x$, by Ru catalysts during the reaction, which facilitates N_2 cleavage on the hydride via electron donation from the anionic electrons to the loaded Ru nanoparticles. A possible reaction mechanism of ammonia synthesis over Ru/Ca_2NH is shown in Figure 1.



① $H_2 \rightarrow H_{(ad)} \rightarrow H^-$ ($[Ca_2N]^+\cdot e^- + H \rightarrow [Ca_2N]^+\cdot H^-$)

② $[Ca_2N]^+\cdot H^- \leftrightarrow [Ca_2N]^+\cdot e^-_{1-x}H^-_x + H\cdot$

③ $H\cdot + N_{(ad)} \rightarrow NH_3$

Figure 1. Schematic illustration of ammonia synthesis over Ru/Ca_2NH.

$Ca(NH_2)_2$ was also demonstrated to function as efficient electronic promoter of Ru catalyst in ammonia synthesis. During ammonia synthesis, Ru nanoparticles are distinctly anchored on the surface of $Ca(NH_2)_2$ by strong Ru─N interaction, which leads to the epitaxial growth of Ru on the support surface. The high catalytic performance is due to the formation of high-density Ru nanoparticles and high electron donor ability at the Ru/$Ca(NH_2)_2$ interface.

4. Conclusions

Ru/Ca_2NH and Ru/$Ca(NH_2)_2$ exhibit much higher catalytic performance for ammonia synthesis at low temperatures than conventional Ru catalysts reported to date, including Ru/C12A7:e^-. The formation of anionic electrons in these materials results in a small work function, which accounts for the strong electron donation ability that facilitates efficient N_2 cleavage on Ru. N adatoms on Ru preferentially react with H atoms derived from the hydride to form NH species. These reactions proceed even at ca. 200°C, so that ammonia synthesis is catalyzed above 200°C. The present results demonstrate that the strong electron-donating ability and the reversible exchangeability between H^- ions in the lattice and anionic electrons at low temperatures are requisite for the Ru catalyst support in low-temperature ammonia synthesis.

References

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