Activation of N-N bond by surface protonics on Ru-support interface for ammonia synthesis at low temperature

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Abstract: The mechanism of catalytic ammonia synthesis in an electric field was investigated. The temperature dependency of ammonia synthesis rate showed that the ammonia synthesis in the electric field became advantageous at lower temperature owing to surface protonics. The Ru particle size dependency on turn over frequency indicated that proton conducting over the catalyst surface reacted with N_2 at Ru-CeO_2 interface and assisted the cleavage of N-N bond in the electric field.
Keywords: Ammonia synthesis, Electric field, proton hopping.

1. Introduction

Ammonia has been considered as an excellent hydrogen carrier for sustainable energy thanks to its high hydrogen density (17.6 wt%).[1] On the other hand, because of rigid triple bond of nitrogen, ammonia synthesis requires high temperatures. Many researchers have tried to activate nitrogen bond and synthesize ammonia under mild conditions. As a novel approach for overcoming the difficulties, we adopted a catalytic reaction in an electric field. [2] In our previous studies, we have found that N_2 cleavage was promoted in the electric field over 9.9wt%Cs/5wt%Ru/$SrZrO_3$ (Cs/Ru/SZO).[3,] It is suggested that proton hopping over the catalyst surface is a dominant factor for activation of N-N bond.[3, 4] In this work, 5wt%Ru/CeO_2 was used as a catalyst for the ammonia synthesis in the electric field. The temperature dependency of the catalytic activity with the electric field was investigated. To elucidate the active site, the Ru particle size dependency on the turn over frequency (TOF) was investigated.

2. Experimental

As a catalyst support, CeO_2 (JRC-CEO-1) was used. Ru supported catalyst (Ru/CeO_2) was synthesized with an impregnation method. $(C_5H_7O_2)_3Ru$ was used as a metal precursor.

A fixed-bed flow-type reactor was used for all activity tests. For application of the electric field, stainless steel rods were inserted into a catalyst bed and 6 mA direct current was imposed. The imposed current and response voltages were detected with an oscilloscope. Activity tests were conducted using 100 mg of catalyst under N_2 (60 SCCM) and H_2 (180 SCCM) flow at various preset temperatures. The catalyst was pre-treated at 723 K under N_2 (60 SCCM) and H_2 (180 SCCM) for 2 h. The catalyst bed temperature during application of the electric field was detected with a thermocouple inserted into the catalyst bed. Produced ammonia was trapped in distilled water, then analyzed quantitatively with an ion chromatograph.

The particle diameters of Ru catalysts were characterized by CO adsorption. Before the measurements, the catalyst was pre-treated under H_2 flow at 723 K for 2 h and evacuated at 723 K for 1 h. After the pre-treatment, the temperature was decreased to 323 K and 10 % CO was dosed.

3. Results and discussion

The activity tests of 5wt%Ru/CeO_2 were conducted at various temperatures (Figure 1). Results revealed that ammonia synthesis in the electric field becomes advantageous as the decrease in the catalyst bed temperature in a low temperature region. The conversion of N_2 was still not in an equilibrium, and is kinetic. In our previous studies, we have reported that the proton hopping on the catalyst surface is a dominant factor for the N_2 activation.[3, 4] The adsorption of conductive species like proton is advantageous at lower temperatures. Therefore, it is suggested that the activation of ammonia synthesis with protons attributed to the specific trend of Arrhenius plot in the electric field.

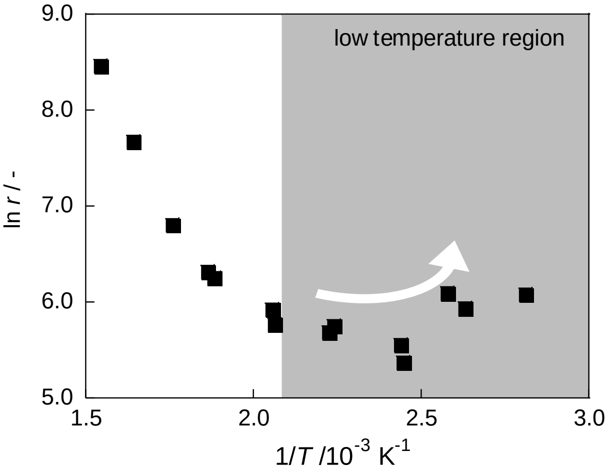

Figure 1. Arrhenius plots for ammonia synthesis in the electric field.

Generally, it is regarded that protons hop over the catalyst support (CeO_2). Therefore, ammonia synthesis in the electric field is likely to occur at the Ru-CeO_2 interface. To elucidate the reaction site for ammonia synthesis in the electric field, the turn over frequency of various amounts of Ru loaded catalyst was evaluated. Figure 2 presents the Ru particle size dependency on turn over frequency with the electric field (443 K) and without the electric field (573 K), as determined by the Ru specific surface area (TOF-s) or Ru perimeter (TOF-p). Generally, the Ru B_5-type site is clarified to be the active site for ammonia synthesis. It is regarded that the optimum size of Ru particle size to give the maximum amount of B_5 site is about 2 nm.[5] Regarding the ammonia synthesis without the electric field, TOF-s increased at around 2 nm corresponding to general trends. However, the trends differed extremely in the electric field. The activities in the electric field strongly depended on the Ru perimeter (Figure 2b), which suggests that the ammonia synthesis in the electric field proceeded mainly at the Ru-CeO_2 interface.

These two results suggest that ammonia synthesis with the electric field is promoted by surface protonics on the catalyst support. The hoping proton reacts with N_2 at Ru-CeO_2 interface.

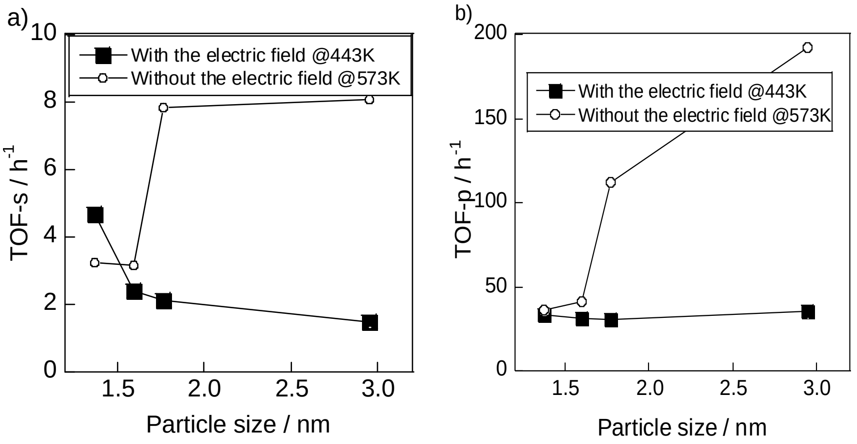

Figure 2. Ru particle size dependency on turnover frequency, a) TOF-s, b) TOF-p.

4. Conclusions

5wt%Ru/CeO_2 showed high catalytic activities for ammonia synthesis in the electric field. The specific trend of Arrhenius plots indicated that the amount of proton species on catalyst surface is a main factor for activation of N_2 dissociation in the electric field. Furthermore, the TOF-p dependency on Ru particle size suggested that protons react with N_2 at Ru-CeO_2 interface.

References

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