Low Temperature Catalytic Ammonia Synthesis in Electric Field

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Abstract: Ammonia synthesis activities of supported Ru catalysts were investigated. CeO_2-Ru/$La_2Zr_2O_7$ calcined in a high temperature and reducing atmosphere showed not only a high reaction promoting effect in an electric field but also the same activity as the conventional Cs-Ru/MgO catalyst under the condition without electric field. High catalytic activity under electric field can be achieved by using a proton conductive complex oxide support and self-dispersing effect of Ru which is obtained after the calcination at high temperature and reducing atmosphere with co-presence of CeO_2.

Keywords: Ammonia synthesis, Electric field.

1. Introduction

Ammonia has been considered as an excellent hydrogen carrier because of its high hydrogen content (17.6 wt%).[1] At present, the Haber-Bosch process is the main method for ammonia synthesis. This process is conducted at high pressures and high reaction temperatures due to its thermodynamic and kinetic limitations, so it is unsuitable for storage of renewable energy. 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 high ammonia synthesizing activity is exhibited by promoting N_2 cleavage 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, ammonia synthesis activities of various supported Ru catalysts were examined to find suitable catalyst.

2. Experimental

Ru and promoter-loaded catalysts were prepared using an impregnation method. As a catalyst support, proton conductive complex oxides ($La_{10}Si_6O_{27}$, $La_2Zr_2O_7$) or MgO (as a reference) were investigated. These complex oxides were prepared using a solid state reaction. $Ru(acac)_3$ was used as the metal precursor. First the metal precursor was dissolved in acetone with dispersed support oxide powder. Then the aqueous solution of CsOH or cerium acetate was added and evaporated to dryness. The obtained sample was calcined under air atmosphere at 773 K for 2 h or 4%H_2/N_2 balanced gas flow at 973 K for 2 h. Details of the catalyst preparation are shown in Table 1.

In the catalyst screening experiments, a quartz tube (6.0 mm i.d.) fixed-bed flow-type reactor was used. Two stainless steel rods with porous disc electrodes were inserted into the reactors. The upper electrode was set on the top of the catalyst bed. The ground electrode was set on the bottom of the catalyst bed. Activity tests were conducted using 200 mg of catalyst under N_2 (120 SCCM) and H_2 (120 SCCM) flow, 0.9 MPa pressurized and 0 mA(w/o electric field) or 2 mA current condition at various furnace temperatures. The catalyst was pre-treated at 723 K under pure H_2 flow (120 SCCM) for 0.5 h. The catalyst bed temperature was measured using a thermocouple installed at the center of the catalyst layer on the outer periphery of the reaction tube. Produced ammonia was trapped in 0.1 M boric acid aqueous solution, and then analyzed quantitatively with an ion chromatograph.

3. Results and discussion

Figure 1 shows ammonia synthesis activities for various supported Ru catalysts. In the case of conventional Cs-Ru/MgO catalyst, reaction results in an electric field omitted because electric field did not formed but discharged. The catalysts which contains $La_{10}Si_6O_{27}$ (LSO) or $La_2Zr_2O_7$ (LZO) as a substrate showed particularly high catalytic activity under application of the electric field. These results support the mechanism that the surface protonics on the catalyst contributes to the reaction promotion in the ammonia synthesis using the electric field. Especially, CeO_2-Ru/LZO catalyst calcined at 973 K under 4%H_2/N_2 balanced gas (#5) indicated good performance at low temperature in the electric field, in addition to showing the same activity as conventional Cs-Ru/MgO catalyst under thermal conditions (without electric field). On the other hand, even with the same composition, catalyst #4 indicated low activity.

XRD and TEM(-EDS) analyses of catalysts #4 and #5 were carried out in order to confirm the cause of change in the activity due to the difference in the calcination conditions. As a result of the XRD measurement, a peak derived from Ru metal was observed in the catalyst #4 after the pretreatment, but was not observed in the catalyst #5. From TEM Images, fine particles of <10 nm can be seen in the catalyst #5 while coarse particles are supported in the catalyst #4. Particle sizes were measured for 228 (catalyst # 4) or 123 (catalyst # 5) supported particles. The mode diameter was 13.8 nm for catalyst #4 and 7.1 nm for catalyst #5. The dispersion of Ru should be improved by high temperature calcination under reducing atmosphere. In addition, highly dispersed CeO_2 was also confirmed in the catalyst #5 by TEM-EDS analysis. From these results, it is considered that the catalyst #5 indicated high activity due to its high dispersion of Ru by calcinations in a high temperature and reducing atmosphere. Self-dispersion of Ru particles near CeO_2 should occur by calcination under such conditions, since the interaction between Ru and CeO_2 is strong.

Table 1. Catalysts evaluated in this work; superior figures in composition indicates weight ratio.

Entry	Composition	Calcination condition
#1	^{12}CsOH-^{7}Ru/^{100}MgO	773 K, 2 h, Air
#2	^{12}CsOH-^{7}Ru/$^{100}La_{10}Si_6O_{27}$	773 K, 2 h, Air
#3	^{12}CsOH-^{7}Ru/$^{100}La_2Zr_2O_7$	773 K, 2 h, Air
#4	$^{8}CeO_2$-^{7}Ru/$^{100}La_2Zr_2O_7$	773 K, 2 h, Air
#5	$^{8}CeO_2$-^{7}Ru/$^{100}La_2Zr_2O_7$	973 K, 2 h, 4%H_2/N_2 balance

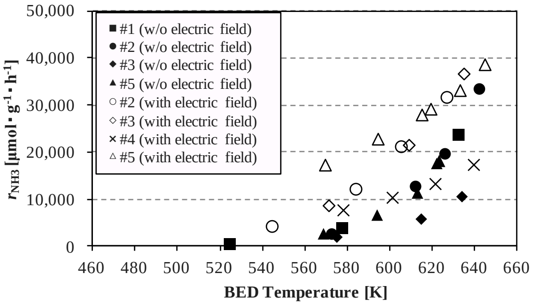

Figure 1. Temperature dependence of ammonia synthesis rate (r_{NH3}) at 0.9 MPa

4. Conclusions

Supported Ru catalysts which contain proton conductive complex oxides ($La_{10}Si_6O_{27}$, $La_2Zr_2O_7$) showed excellent activity in the ammonia synthesis using electric field. Especially, CeO_2-Ru/$La_2Zr_2O_7$ catalyst calcined under 4%H_2/N_2 balanced gas flow at 973 K showed high catalytic activity, that is, an ammonia production rate of >20 mmol・g^{-1}・h^{-1} at 608 K. Such high catalytic activity is achieved due to self-dispersing of Ru by calcinating in a high temperature and reducing atmosphere with coexisting Ru and CeO_2.

References

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