Ammonia synthesis using Co supported catalysts in an electric field

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Abstract:

Catalytic ammonia synthesis in an electric field over 5wt%Co/$Ce_{0.5}Zr_{0.5}O_2$ catalyst was investigated. Catalyst of 5wt%Co/$Ce_{0.5}Zr_{0.5}O_2$ showed high activity at low temperatures in the electric field compared to the catalytic reaction without it. We found reduction conditions of Co had an important role on ammonia synthesis, and the reduction at 973 K for 0.5 h was the most suitable condition for ammonia synthesis with the electric field. Moreover, the activity for ammonia synthesis drastically increased with application of the electric field. The apparent activation energy decreased with the electric field, indicating the reaction path changed with its application.

Keywords: Ammonia synthesis, Electric field, Cobalt supported catalyst

1. Introduction

The demand of ammonia is increasing as a fertilizer or chemical productions. Recently, ammonia is also attracting an attention as a hydrogen career. Ammonia is mainly synthesized via Haber-Bosch process, which consumes a lot of energy as it needs high pressure and high temperature conditions. On the other hand, for ammonia synthesis as hydrogen career, a small scale and distributed type of plant are more convenient. The development of ammonia synthesis which can be operated under mild conditions is anticipated. We have already discovered that an application of electric field makes it possible to produce ammonia even under mild conditions. Moreover, we have already discovered Ru supported catalyst has high activity for the synthesis. However, Ru is known for its high cost and is not suitable for practical use. Then, we focused on Co, which holds the ability for N_2 dissociation, as it is relatively cheaper than Ru. In this study, we developed Co supported catalysts which has high activity for ammonia synthesis in the electric field.

2. Experimental

$Ce_{0.5}Zr_{0.5}O_2$ was prepared using a complex polymerization method with ethylenediamine tetraacetic acid and citrate ions. Co was supported by an impregnation method using $Co(NO_3)_2 \cdot 6H_2O$. Catalytic activity tests were conducted with a fixed bed flow type reactor equipped with a quartz tube (6.0 mm i.d.). The catalyst was crushed into 355-500 μm and 200 mg of the catalyst was charged in the reactor. Reactant feed gases were nitrogen and hydrogen (N_2: H_2 = 1: 3, total flow rate: 60 or 240 SCCM). For the reaction in the electric field, two stainless steel electrodes (2.0 mm o.d.) were inserted contiguously to the catalyst bed in the reactor. The electric field was imposed using a constant current (6.0 mA) with a DC power supply. Product gases were analyzed using a GC-TCD, and the amount of NH_3 were analyzed by an ion-chromatograph.

3. Results and discussion

As a catalyst, 5wt%Co/$Ce_{0.5}Zr_{0.5}O_2$ was prepared and activity tests were conducted with changing the reduction conditions. Results are shown in Table 1. In this case, the reduction time was constant: 2 h. From these tests, we found that the best reduction temperature was 973 K. The effect of pre-reduction on the catalytic activity was considered as follows: the reduction of cobalt, sintering, and structural change of the support. However, from the results of XRD measurements, it was revealed that the structure of the support was almost the same under these conditions.

Table 1. The dependence of reduction temperature on catalytic activity

	Reduction temperature / K	Average ammonia synthesis rate / μmol g^{-1} h^{-1}
Without electric field	723	2.6
With electric field	723	174.6
	773	184.8
	873	184.9
	973	221.4
	1073	207.7

Moreover, CO pulse measurement was conducted to calculate the metallic surface area. It was indicated that the higher the reduction temperature was, the larger its area became. From the fact that the activity decreased at over 973 K, we concluded that the most appropriate temperature for reduction was 973 K.

Table 2. The dependence of reduction time on catalytic activity

	Reduction time / h	Average ammonia synthesis rate / μmol g^{-1} h^{-1}
Without electric field	0.5	87.9
With electric field	0.25	211.6
	0.5	293.5
	1	247.8
	2	221.4

Next, we conducted the activity tests with changing retention time of reduction treatment. Results are shown in Table 2. The activity was the highest when catalyst was reduced at 973 K for 0.5 h. These results suggested that the balance between electronic state of cobalt and particle size of supported cobalt is significant.

Figure 1 presents Arrhenius plots for both cases with and without electric field. As shown in Figure 1, the activity increased drastically with application of the electric field. The apparent activation energies were calculated as 38 kJ mol^{-1} for the reaction without electric field and as 16.2 kJ mol^{-1} for the reaction with electric field. The activation energy decreased in half, indicating that the reaction path changed upon applying the electric field.

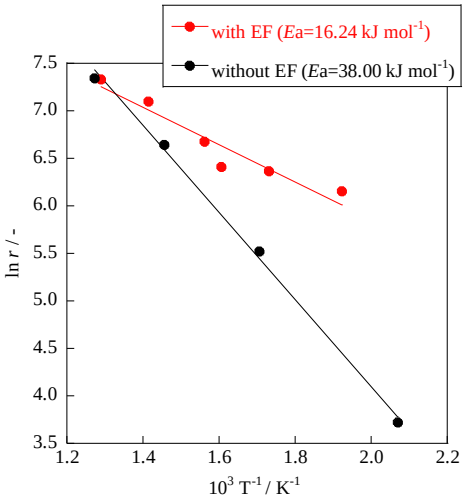

Figure 1. Arrhenius plots for both reactions with/without electric field

4. Conclusions

The reduction treatment condition was optimized over 5wt%Co/$Ce_{0.5}Zr_{0.5}O_2$ catalyst for ammonia synthesis in an electric field. It was found that the reduction treatment at 973 K for 0.5 h showed the highest activity. From these results, we elucidated that there were mainly 2 factors for the activity; 1: the electronic conditions of Co metal. 2: the particle size of Co metal. When we have conducted temperature changing test, the activity increased significantly with electric field even at lower temperatures. The apparent activation energy of the activity with electric field was almost as half as that of the activity without electric field.

References

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