[Regular Paper]

Roles of CoAl_2O_4 , Co_3O_4 , and Alumina for Selective Catalytic Reduction of NO with Ethene in Excess Oxygen

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The catalytic activities of pure CoAl_2O_4 , Co_3O_4 , physical mixture of CoAl_2O_4 and Al_2O_3 , and Co_3O_4 free $\text{Co}/\text{Al}_2\text{O}_3$ for the reduction of NO with ethene in excess oxygen, the oxidation of NO, and the oxidation of ethene were investigated to elucidate the activities of CoAl_2O_4 , Co_3O_4 and Al_2O_3 . Pure CoAl_2O_4 was more active than Al_2O_3 for oxidation of NO, the initiation step of the selective reduction of NO over $\text{Co}/\text{Al}_2\text{O}_3$, but was less active than Co_3O_4 for oxidation of ethene. Well-mixed CoAl_2O_4 – Al_2O_3 catalyst calcined at 800°C had higher activity for selective catalytic reduction of NO with ethene in excess oxygen than catalyst calcined at 500°C as well as roughly-mixed CoAl_2O_4 – Al_2O_3 catalyst. The high activity of CoAl_2O_4 – Al_2O_3 catalyst depends on the synergy of CoAl_2O_4 and Al_2O_3 particles at their interfaces. Selective removal of Co_3O_4 from cobalt-loaded alumina, Co_3O_4 -free $\text{Co}/\text{Al}_2\text{O}_3$, enhanced the activity for selective catalytic reduction of NO with ethene in excess oxygen, indicating that Co_3O_4 inhibited the reaction, and that the residual CoAl_2O_4 -like species was catalytically active. High activity of $\text{Co}/\text{Al}_2\text{O}_3$ calcined at 800°C for the selective reduction of NO with ethene in excess oxygen is due to the formation of CoAl_2O_4 on the surface layer of γ - Al_2O_3 .

Keywords

Cobalt aluminate, Cobalt oxide, Nitrogen monoxide, Ethene, Selective catalytic reduction

1. Introduction

Selective catalytic reduction of nitrogen monoxide in the presence of hydrocarbons and excess oxygen is one of the most promising methods to remove nitrogen oxides in exhaust gases^{1)–20)}. The selective catalytic reduction of NO proceeds by the successive reactions of (1) $\text{NO} + 1/2\text{O}_2 \rightarrow \text{NO}_2$ and (2) $\text{NO}_2 + \text{HC}$ (hydrocarbon) $\rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$ ³⁾. In addition to the reactions (1) and (2), the undesirable reaction (3) $\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ occurs^{3),10),18)}.

Hamada *et al.* reported that Al_2O_3 is the most active catalyst for the selective reduction of nitrogen monoxide among the single-component metal oxides^{2),3)}. We have also confirmed the high activity of Al_2O_3 and investigated the characteristic features of Al_2O_3 as compared to the other metal oxide catalysts²¹⁾. Although both reactions (1) and (3) involve oxidation with oxygen, Al_2O_3 is very selective for reaction (1). Modification of Al_2O_3 with a second component may increase the activity by promoting reactions (1) and (2) as well as suppressing reaction (3). In order to find an effi-

cient modification of Al_2O_3 , addition of a second component to Al_2O_3 was examined. Torikai *et al.* reported that Co is the most effective among 11 species added to Al_2O_3 ^{6),10)} as a second component. Hamada *et al.* also reported that Co is the most effective species to be added to Al_2O_3 . In our previous, we compared the effectiveness of the addition of Ni, Fe, and Co to Al_2O_3 , and found that Co is the most effective¹⁷⁾.

Although Co is recognized as the most effective species to be added to Al_2O_3 , there still exists controversy about the active species of Co, and roles of surface species present on the catalyst in the reduction of NO with ethene. Hamada *et al.* initially proposed that reaction (1) is probably catalyzed by dispersed cobalt species³⁾ and not by CoAl_2O_4 ¹⁵⁾, and reaction (2) by the surface of the Al_2O_3 . However, they revised their proposal later: the active species of $\text{Co}/\text{Al}_2\text{O}_3$ are tiny CoAl_2O_4 crystallites dispersed on Al_2O_3 ¹⁶⁾.

In the preceding paper, we examined the effects of Co loading, starting material of Co, and calcination temperature in catalyst preparation on the activity of $\text{Co}/\text{Al}_2\text{O}_3$ catalyst²²⁾. The results showed that the catalytic activity is due to CoAl_2O_4 formed during the catalyst preparation. The Co species in $\text{Co}/\text{Al}_2\text{O}_3$ catalyst varies with the preparation conditions. Cobalt species

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in different states should show different catalytic activities. Both Co_3O_4 and CoAl_2O_4 are present in $\text{Co}/\text{Al}_2\text{O}_3$ catalysts. Co_3O_4 is highly active for reaction (3), so that Co_3O_4 is an undesirable component. Therefore, preparation of a $\text{Co}/\text{Al}_2\text{O}_3$ catalyst containing no Co_3O_4 would be helpful to suppress the undesirable reaction (3) and for the elucidation of the roles of each Co species.

In the present study, a method to remove Co_3O_4 selectively from a mixture of Co_3O_4 and CoAl_2O_4 was developed, and the reactions (1), (2), and (3) were carried out over pure CoAl_2O_4 , Co_3O_4 , physical mixture of CoAl_2O_4 and Al_2O_3 , and $\text{Co}/\text{Al}_2\text{O}_3$ free of Co_3O_4 to elucidate the involvement of CoAl_2O_4 , Co_3O_4 , and Al_2O_3 in the reduction of nitrogen monoxide with ethene. A model for the formation of active surface sites in $\text{Co}/\text{Al}_2\text{O}_3$ during calcination is proposed.

2. Experimental

2.1. Preparation of Catalysts

Cobalt oxide, Co_3O_4 , was prepared by heating cobalt hydroxide at 500°C for 4 h and then at 800°C for 4 h in air. Cobalt hydroxide was prepared from an aqueous solution of cobalt nitrate by hydrolysis with 10% aqueous ammonia to a final pH of 7. The precipitate was filtered, washed with deionized water, and dried at 120°C for 18 h.

CoAl_2O_4 was prepared from stoichiometric amounts of Co and Al metal powders which were dissolved in nitric acid (0.5 M) at 60°C , then urea added as a precipitant, and the mixture heated at 95°C to form the precipitate, which was filtered, washed with deionized water, filtered again, dried at 120°C for 24 h, calcined at 500°C for 4 h, and finally calcined at 1000°C for 4 h.

$\text{Co}/\text{Al}_2\text{O}_3$ catalyst was prepared by impregnating Al_2O_3 with cobalt acetate solution, followed by drying the resultant slurry at 120°C for 18 h and calcining at 500°C or 800°C for 4 h in air. Al_2O_3 was prepared from aluminum tri-isopropoxide by hydrolysis with deionized water. Aluminum tri-isopropoxide was purchased from Kojundo Chemical Lab. Co., Ltd. and purified by repeated distillation three times, then poured dropwise into deionized water maintained at 0°C with vigorous stirring to precipitate aluminum hydroxide. The precipitate was filtered and washed thoroughly with deionized water. The resultant material was dried at 120°C for 24 h, and then calcined at 600°C for 24 h in air.

$\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalyst was prepared by grinding a mixture of CoAl_2O_4 and Al_2O_3 with a Co content of 5 wt% for 10 min with a FRITSCH planetary micro mill pulverisette 10 using an agate pot and balls, followed by pelletizing, crushing, sieving (30-42 mesh), and finally calcining at 500°C or 800°C for 4 h in air. This type of $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalyst is named here in

the form WMC-temperature of calcination/ $^\circ\text{C}$; where WMC indicates "well-mixed and calcined." For comparison, a roughly-mixed $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalyst with the same Co content as WMC-500, but consisting of the components in the form of pellets (30-42 mesh), was also prepared and used as a catalyst without further calcination. This type of $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalyst is named here RM; where RM indicates "roughly-mixed."

The removal of Co_3O_4 in $\text{Co}/\text{Al}_2\text{O}_3$ was performed by converting the Co_3O_4 component to metallic cobalt and then dissolving the resulting metallic cobalt in nitric acid (1 M). Metallization was achieved by heating the catalyst at 500°C for 3 h in a hydrogen stream. Dissolution was carried out by immersing the reduced catalyst in nitric acid at 60°C for 2 h, and the remaining solid was filtered, washed with nitric acid and distilled water, and dried at 120°C for 18 h. All catalysts were further calcined at 500°C or 800°C for 4 h in air before use. $\text{Co}/\text{Al}_2\text{O}_3$ catalyst was named here in the form: Co (loading/wt%)/ Al_2O_3 (calcination temp./ $^\circ\text{C}$, MD), where MD indicates the metallization-dissolution treatment.

2.2. Characterization of Catalyst

X-Ray photoelectron spectroscopy (XPS) analysis was performed with a Rigaku XPS-7000 spectrometer using an $\text{AlK}\alpha$ X-ray source operated at 10 kV and 30 mA. The binding energies were corrected by using the value of 285.0 eV for the C 1s level resulting from the contaminated carbon. The reproducibilities of the obtained values were within ± 0.2 eV.

2.3. Reaction Procedures

Reduction of NO with ethene in excess oxygen, oxidation of NO and oxidation of ethene were carried out in a fixed bed flow reactor with W/F of $0.18 \text{ g}\cdot\text{s}\cdot\text{cm}^{-3}$ at temperatures ranging from 200 to 800°C . All catalysts were packed with quartz wool plugs in a U-shaped quartz tube reactor (inner diameter, 6 mm) and then heated *in situ* at 300°C . The reactant gas (NO, 1000 ppm or 0 ppm; O_2 , 2.0%; C_2H_4 , 500 ppm or 0 ppm; He, balance) was passed at a total flow rate of $130 \text{ cm}^3\cdot\text{min}^{-1}$ through the catalyst bed (0.40 g). The outflow gas was analyzed by gas chromatography using two columns packed with 5A molecular sieves (3 m; separation for N_2 , O_2 , CO, and NO) and Porapak Q (3 m; separation for CO_2 , C_2H_4 , and N_2O). Sampling was carried out twice at every temperature to check the reproducibility of the activity. N_2O formation was negligible under the present reaction conditions in the reduction of NO with ethene in excess oxygen.

3. Results

Figure 1 illustrates the activity of the Co_3O_4 catalyst for the reduction of NO with ethene in excess oxygen, the oxidation of NO and the oxidation of ethene. Co_3O_4 was very active for the oxidation of NO and the

Fig. 1 Temperature Dependence of the Catalytic Activity of Co_3O_4

Fig. 2 Temperature Dependence of the Catalytic Activity of CoAl_2O_4

oxidation of ethene, but no nitrogen was formed in the reduction of NO with ethene in excess oxygen.

Figure 2 shows the activity of the CoAl_2O_4 catalyst for the three reactions. Clearly, the activities of CoAl_2O_4 for the oxidation of NO and the oxidation of ethene were lower than those of Co_3O_4 , but nitrogen was formed in the reduction of NO with ethene in excess oxygen.

Figure 3 shows the activities of three types of $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalysts for the reduction of NO with ethene in excess oxygen as a function of reaction temperature. RM catalyst showed higher activity than Al_2O_3 below *ca.* 500°C, although the activity of pure CoAl_2O_4 (0.06 g, weight of Co in RM) was quite low (max conv. = 2%). These results indicate that the CoAl_2O_4 in RM catalyst promoted the reaction in cooperation with Al_2O_3 . WMC-500 catalyst showed higher activity than RM catalyst, implying the degree of contact between CoAl_2O_4 and Al_2O_3 particles is correlated with the activity. The activity was enhanced by raising the calcination temperature to 800°C. The activities of the three types of $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ catalysts

Fig. 3 Temperature Dependence of the Catalytic Activity of Various Catalysts for Reduction of NO

Fig. 4 XPS Spectra of Various Catalysts

for the reduction of NO with ethene in excess oxygen decreased in the order $\text{WMC-800} > \text{WMC-500} > \text{RM}$. The activity for the formation of CO_x was also in the order $\text{WMC-800} > \text{WMC-500} > \text{RM}$.

Figure 4 shows the binding energy of Co 2p was

Table 1 Ratio of Cobalt and Aluminum in the Mixture of CoAl_2O_4 and Al_2O_3

Catalyst	Co/Al
RM	0.26
WMC-500	0.27
WMC-800	0.32
$\text{Co(5)/Al}_2\text{O}_3$	0.38

a) calcined at 500°C in air, b) reduced with hydrogen at 500°C for 3 h, c) treated with nitric acid (1 M) at 60°C for 2 h after hydrogen reduction.

Fig. 5 XPS Spectra of $\text{Co(5)/Al}_2\text{O}_3$

higher for WMC-800 than for WMC-500. Since shift of the binding energy to higher energy is generally ascribed to more positively-charged metal species, the Co species of WMC-800 must be positively charged due to the strong interaction between the Co species of CoAl_2O_4 and Al_2O_3 . The binding energy of Co 2p was also higher for WMC-800 than for $\text{Co(5)/Al}_2\text{O}_3$ (800, MD). In addition, the binding energy of Co 2p was higher for WMC-500 than for RM and CoAl_2O_4 . These results suggest that the interaction between the Co species of CoAl_2O_4 and Al_2O_3 also occurs in WMC-500.

Table 1 shows the ratio of Co/Al in the physical mixture of CoAl_2O_4 and Al_2O_3 calculated from the XPS peak intensity. The ratio of Co/Al increased with

Fig. 6 Temperature Dependence of the Catalytic Activity of Various Catalysts for a) Oxidation of NO and b) Oxidation of Ethene

higher calcination temperature, indicating that the surface concentration of Co increases with higher calcination temperature.

Heating of $\text{Co(5)/Al}_2\text{O}_3(500)$, which is known to contain both Co_3O_4 and CoAl_2O_4 ¹⁸⁾, at 500°C for 3 h in a hydrogen stream caused the color of the sample to change from dark green to black. Figure 5 shows the XPS spectra of $\text{Co(5)/Al}_2\text{O}_3$ calcined at 500°C (spectrum a), then reduced by hydrogen at 500°C (spectrum b) and finally treated with nitric acid (spectrum c). The peak ascribed to metallic Co replaced the peak of Co_3O_4 in spectrum b), but the peak of metallic Co had vanished in spectrum c). These results indicate that the Co_3O_4 component is converted to metallic Co by hydrogen treatment at 500°C, and that the metallic Co is removed by the treatment with nitric acid, whereas the CoAl_2O_4 component remained unchanged. The catalyst appeared blue after the treatment with nitric acid. The CoAl_2O_4 -like species will be designated as cobalt aluminate in this study.

Figure 6 a) shows the activity of various catalysts for the oxidation of NO. The activity of $\text{Co(5)/Al}_2\text{O}_3(500)$ was much higher than that of $\text{Co(5)/Al}_2\text{O}_3(500, \text{MD})$ due to the presence of Co_3O_4 in $\text{Co(5)/Al}_2\text{O}_3(500)$. Figure 6 b) shows the activity of $\text{Co(5)/Al}_2\text{O}_3(500, \text{MD})$ for the oxidation of ethene was remarkably lower than $\text{Co(5)/Al}_2\text{O}_3(500)$ suggesting that the Co_3O_4 component was present in $\text{Co(5)/Al}_2\text{O}_3(500)$, and cat-

Fig. 7 Temperature Dependence of the Catalytic Activity of Various Catalysts for Reduction of NO

analyzes the oxidation of ethene. On the other hand, Co₃O₄ was absent in Co(5)/Al₂O₃(500, MD), so the oxidation of ethene was minimum, indicating that cobalt aluminate is much less active for the oxidation of ethene.

Figure 7 a) shows that Co(5)/Al₂O₃(500, MD) was much more active than Co(5)/Al₂O₃(500) for the reduction of NO with ethene in excess oxygen. The effect of the MD treatment suggests that the removed Co₃O₄ acted as an undesirable cobalt species and the preserved cobalt aluminate acted as an effective cobalt species. Although CO and CO₂ are not distinguished in **Fig. 7 b)**, CO was formed together with CO₂ over Co(5)/Al₂O₃(500, MD), but only CO₂ was observed over Co(5)/Al₂O₃(500). This result also suggests that Co(5)/Al₂O₃(500) had higher oxidation activity than Co(5)/Al₂O₃(500, MD), probably because the former catalyst contains more Co₃O₄.

Figure 7 b) also shows the conversion of ethene to CO_x during the reduction of NO with ethene in excess oxygen. The conversion of ethene to CO_x was slightly higher for Co(5)/Al₂O₃(500) than for Co(5)/Al₂O₃(500, MD). Conversion of ethene reached 97% at the reaction temperature of 450°C, indicating that almost all ethene was consumed. This is slightly different to the case of WMC-800, for which the conversion of ethene was 79% at 450°C, as shown in **Fig. 3**.

4. Discussion

The present results obtained can be interpreted in terms of the different roles of Co₃O₄, CoAl₂O₄ and Al₂O₃ in the reduction of NO with ethene to form N₂.

Reduction of nitrogen monoxide with ethene proceeds by the successive reactions of (1) $\text{NO} + 1/2\text{O}_2 \rightarrow \text{NO}_2$ and (2) $\text{NO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$, so the catalyst should promote reactions (1) and (2), but not reaction (3) $\text{C}_2\text{H}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$, which consumes ethene unproductively.

As shown in **Fig. 1**, Co₃O₄ was very active for both reaction (1) and undesirable reaction (3). In the presence of Co₃O₄, ethene was quickly consumed by oxidation to form carbon dioxide and water, and little reactant remains for the reduction of NO₂ by reaction (2). Therefore, the selective reduction of NO will not proceed efficiently in the presence of Co₃O₄.

The catalytic activities of CoAl₂O₄ were quite different from those of Co₃O₄. As shown in **Fig. 2**, CoAl₂O₄ had lower oxidation activity than Co₃O₄ for both ethene and NO. In particular, the ethene oxidation activity was far lower for CoAl₂O₄ than for Co₃O₄. The NO oxidation activity of CoAl₂O₄ was not as high as that of Co₃O₄, but was significantly higher than that of Al₂O₃. The low activity for ethene oxidation and the high activity for NO oxidation are favorable for the reduction of NO with ethene. However, the catalytic activity of CoAl₂O₄ for the reduction of NO with ethene is lower than that of Al₂O₃, and far less than that of Co/Al₂O₃. Al₂O₃ is the most active single-component metal oxide for reaction (2) $\text{NO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$ ²⁰. Al₂O₃ may be a required component for a highly active catalyst for the reduction of NO with ethene, and thus the combination of CoAl₂O₄ with Al₂O₃ is the optimum catalyst for the reduction of NO with ethene. This study found that a physical mixture of CoAl₂O₄ and Al₂O₃ had a higher activity than only CoAl₂O₄ or only Al₂O₃.

The catalytic activity of Co/Al₂O₃ varies with the preparation conditions. Our previous study showed that the optimum calcination temperature of Co/Al₂O₃ is 800°C, at which the formation of CoAl₂O₄ is maximized and the formation of Co₃O₄ is minimized, but retaining the γ -type structure of Al₂O₃. The presence of Co₃O₄ is not favorable for the reduction of NO with ethene as mentioned above. Therefore, removal of the Co₃O₄ component from Co/Al₂O₃ should improve the catalytic activity of Co/Al₂O₃ for the reduction of NO with ethene. As shown in **Fig. 7**, the catalytic activity of Co/Al₂O₃ was improved by removal of Co₃O₄ from Co/Al₂O₃ by MD treatment.

Co(5)/Al₂O₃(500, MD) and WMC-800 were expected to show similar catalytic activities, but this study found slight differences. The maximum activity for the reduction of NO with ethene in excess oxygen was

Fig. 8 Change in the Morphology of Co/Al₂O₃ with Calcination Temperature

observed at the reaction temperatures of 450°C and 500°C for Co(5)/Al₂O₃(500, MD) and WMC-800 as shown in **Figs. 3** and **7**, possibly due to the difference in the calcination temperature of Al₂O₃. Al₂O₃ in Co(5)/Al₂O₃(500, MD) was calcined at 500°C, whereas Al₂O₃ in WMC-800 was calcined at 800°C. Our previous study showed that the catalytic activity of Al₂O₃ for the oxidation of ethene with oxygen is higher for Al₂O₃ calcined at 500°C than for Al₂O₃ calcined at 800°C. Al₂O₃ in Co(5)/Al₂O₃(500) possessed the properties of Al₂O₃ calcined at 500°C, whereas Al₂O₃ in WMC-800 possessed the properties of Al₂O₃ calcined at 800°C. Therefore, Co(5)/Al₂O₃(500, MD) consumed much more ethene than WMC-800 at 450°C, because the Al₂O₃ in Co(5)/Al₂O₃(500, MD) seems to consume more ethene than that in WMC-800.

The change in the state of Co with calcination temperature is illustrated in **Fig. 8**. Co in Co/Al₂O₃ is mostly in the form of Co₃O₄ after calcination at 300°C²¹⁾. Co₃O₄ gradually converted into CoAl₂O₄ at higher calcination temperatures, and the conversion becomes almost complete at a calcination temperature of 800°C. The XPS peak intensity ratio of Co/Al for the physical mixture of CoAl₂O₄ increased with higher calcination temperature as listed in **Table 1**. Calcination of the mixture at 800°C obtained a Co/Al ratio close to the value for Co/Al₂O₃ calcined at 800°C. Since XPS is more sensitive to the surface composition than to the bulk composition, the increase in the ratio of Co/Al with higher calcination temperature suggests that the Co containing species becomes extended over the surface at higher calcination temperature. At calcination temperatures between 500°C and 800°C, the Co₃O₄ species persisted in Co/Al₂O₃ to some extent. The remaining Co₃O₄ hinders the selective reduction of NO with ethene. After calcination at 800°C, the Co species was mostly in the form of CoAl₂O₄, and Al₂O₃ remained as the γ -type. Therefore, Co/Al₂O₃ catalyst calcined at 800°C catalyzed reaction (1) $\text{NO} + \text{O}_2 \rightarrow$

NO_2 over the CoAl₂O₄ component and reaction (2) $\text{NO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$ over the γ -Al₂O₃ component. For the successive reactions (1) and (2), the two active components should preferably be close to each other. Calcination above 800°C results in the transformation of γ -Al₂O₃ into α -Al₂O₃, which had no activity for reaction (2).

Changes in the morphology of Co/Al₂O₃ with increasing calcination temperature as suggested above are illustrated in **Fig. 8**.

5. Conclusions

- (1) Cobalt-loaded alumina (Co/Al₂O₃) calcined at 800°C has high activity for the selective reduction of NO with ethene in excess oxygen due to the formation of CoAl₂O₄ on the surface layer of γ -Al₂O₃.
- (2) CoAl₂O₄ catalyzes the oxidation of NO with oxygen to form NO₂ but not the oxidation of ethene.
- (3) γ -Al₂O₃ catalyzes the reaction of NO₂ with ethene to form N₂.
- (4) Co₃O₄ formed on the surface of Al₂O₃ after calcination at temperatures lower than 800°C catalyzes the oxidation of ethene with oxygen, which is unfavorable for the selective reduction of NO.
- (5) Co₃O₄ can be successfully removed by selective reduction of Co₃O₄ with H₂ to form metallic Co which is then dissolved in nitric acid (MD treatment).
- (6) Co changes state with the calcination temperature and MD treatment.

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要 旨

酸素過剰雰囲気下におけるエチレンによる NO 選択還元反応 —コバルトアルミネート、酸化コバルトとアルミナの役割—

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酸素過剰雰囲気下でのエチレンを還元剤に用いた NO 選択接触還元反応 ($\text{C}_2\text{H}_4\text{-SCR}$) 中で CoAl_2O_4 , Co_3O_4 とアルミナの役割を明確にするために, CoAl_2O_4 , Co_3O_4 , $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ 触媒, および Co_3O_4 を含まない $\text{Co/Al}_2\text{O}_3$ の 4 種類の触媒を用いて, $\text{C}_2\text{H}_4\text{-SCR}$, $\text{NO} + \text{O}_2$ 反応および $\text{C}_2\text{H}_4 + \text{O}_2$ 反応を行った。 CoAl_2O_4 は Al_2O_3 より $\text{NO} + \text{O}_2$ 反応 ($\text{Co/Al}_2\text{O}_3$ 上の $\text{C}_2\text{H}_4\text{-SCR}$ の開始反応) に対して高活性を示し, Co_3O_4 より $\text{C}_2\text{H}_4 + \text{O}_2$ 反応 ($\text{C}_2\text{H}_4\text{-SCR}$ の副反応) に対して低活性であった。800℃ で焼成した $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ 触媒は, $\text{C}_2\text{H}_4\text{-SCR}$ において CoAl_2O_4

と Al_2O_3 の物理混合触媒, および 500℃ で焼成した $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ 触媒より高い活性を示した。これは $\text{CoAl}_2\text{O}_4\text{-Al}_2\text{O}_3$ 触媒中の CoAl_2O_4 粒子と Al_2O_3 粒子の接触界面でのお互いの協力作用が大きな要因であることを示唆する。 $\text{Co/Al}_2\text{O}_3$ 上にある Co_3O_4 を選択的に除去した結果, その $\text{C}_2\text{H}_4\text{-SCR}$ 活性は向上した。これは Co_3O_4 が $\text{C}_2\text{H}_4\text{-SCR}$ を抑制していたこと, $\text{Co/Al}_2\text{O}_3$ 上に残った CoAl_2O_4 が活性種として働くことを示唆する。したがって, 800℃ で焼成した $\text{Co/Al}_2\text{O}_3$ の高い活性は $\gamma\text{-Al}_2\text{O}_3$ 表面での CoAl_2O_4 の生成に起因すると考えられる。