# Selective Removal of Cobalt Oxide from Cobalt-loaded Alumina Catalysts and Its Effect on the Activity for Selective Catalytic Reduction of Nitrogen Monoxide by Ethene in Excess Oxygen

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The selective removal of $Co_3O_4$ from a cobalt-loaded alumina catalyst resulted in increased activity for the title reaction, indicating that $Co_3O_4$ inhibited the reaction but that the residual $CoAl_2O_4$-like species acted as catalytically active species. $CoAl_2O_4$-like species were sufficiently active for the oxidation of NO to $NO_2$ but much less active for the oxidation of ethene (a side reaction).

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Among $NO_x$ removal processes, most of the research interest has been focused on the selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen.[1] After the reports of Iwamoto et al.[2, 3] and Held et al.[4] on copper ion-exchanged ZSM-5 zeolites, many effective catalysts such as zeolites, metal oxides, and noble metals have been proposed.[5] Among metal oxides, alumina[6] is probably a promising catalyst candidate for practical use because of its excellent activity and thermal stability. Alumina is also used as a catalytic material or support for transition-metals.[7-12] By the analogy with $NO+C_3H_8+O_2$ reaction over alumina and H-zeolites,[8, 9] $NO+C_2H_4+O_2$ over cobalt-loaded alumina catalysts ($Co/Al_2O_3$) is considered to occur via the following mechanism.

$$NO + O_2 \rightarrow NO_2 \tag{1}$$

$$NO_2 + C_2H_4 \rightarrow (C_xH_yO_z) \rightarrow N_2 + CO_x + H_2O \tag{2}$$

$$C_2H_4 + O_2 \rightarrow CO_x + H_2O \tag{3}$$

Recently, it has been reported that the cobalt species and alumina of $Co/Al_2O_3$ function cooperatively in $NO+C_2H_4+O_2$; the cobalt species accelerate step (1) and the alumina catalyzes step (2).[13] Although many studies[8, 13-15] have been made on the role of $Co_3O_4$ and $CoAl_2O_4$, there is still controversy about it. That is partly due to the difficulty in eliminating the catalytic function of one of the two cobalt species. Therefore, we attempted to prepare a special $Co/Al_2O_3$, in which $Co_3O_4$ was selectively removed, and investigated the activities for $NO+C_2H_4+O_2$ and steps (1) and (3).

A $Co/Al_2O_3$ was prepared by impregnating $Al_2O_3$(ALOA) with a cobalt acetate solution, followed by drying the resulting slurries at 120 °C for 18 h and by calcining at 500 °C or 800 °C for 4 h in air. Alumina(ALOA) was produced by heating its precursor at 600 °C for 24 h, which was prepared by the controlled hydrolysis of aluminum tri-isopropoxide. The removal of $Co_3O_4$ in $Co/Al_2O_3$ was performed first by converting it to metallic cobalt and then by dissolving the resulting metallic cobalt in a nitric acid solution (1 M). The metallization was done by heating the original catalysts at 500 °C for 3 h in hydrogen stream. The dissolution was carried out as follows: the reduced samples were immersed in the nitric acid solution at 60 °C for 2 h, and the resulting precipitate was filtered, washed with the nitric acid solution and a distilled water, dried at 120 °C for 18 h. All the catalysts were further calcined at 500 °C or 800 °C for 4 h in air before use. A $Co/Al_2O_3$ catalyst was denoted as follows: Co(loading/wt%)/$Al_2O_3$(calcination temp./°C, MD), where MD stands for the metallization-dissolution treatment. With a Rigaku XPS-7000 spectrometer, X-ray photoelectron spectroscopy (XPS) analysis was performed using a Al$K\alpha$ 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 values thus obtained were within ± 0.2 eV. Experiments of $NO+C_2H_4+O_2$, $NO+O_2$, and $C_2H_4+O_2$ reactions were performed using a fixed-bed flow tubular reactor at a W/F of 0.18 $g{\cdot}s{\cdot}cm^{-3}$ (catalyst, 0.4 g; total flow rate, 130 $cm^3{\cdot}min^{-1}$). The formation of $N_2O$ in $NO+C_2H_4+O_2$ was negligible.

When Co(5)/$Al_2O_3$(500), which is known to have both $Co_3O_4$ and $CoAl_2O_4$,[15] was heated at 500 °C for 3 h in hydrogen stream, the color of the sample changed to black from dark green. Figure 1a indicates that by this process its $Co_3O_4$ was converted to metallic cobalt. Subsequently the obtained sample was treated with the nitric acid solution, then the color changed to blue, suggesting the presence of $CoAl_2O_4$. Actually metallic cobalt was dissolved retaining $CoAl_2O_4$ (Figure 1b). Such $CoAl_2O_4$-like species will be designated as cobalt aluminate hereinafter. By the MD treatment, 45% of the total Co species was removed, while by the dissolution alone 20% was removed and the color was green.

Surprisingly, Co(5)/$Al_2O_3$(500, MD) was more active than Co(5)/$Al_2O_3$(500)[15] for $NO+C_2H_4+O_2$ (Figure 2). The effect of the MD treatment suggests that removed $Co_3O_4$ acted as an undesirable cobalt species and at the same time the residual cobalt aluminate acted as an effective cobalt species. Although CO was formed along with $CO_2$ over Co(5)/$Al_2O_3$(500, MD) but only $CO_2$ was observed over Co(5)/$Al_2O_3$(500). The temperature window of Co(5)/$Al_2O_3$(500, MD) located at the lower temperature side than that of alumina alone. These indicate that its cobalt aluminate evidently promoted $NO+C_2H_4+O_2$. This seems to be a new direct evidence for the fact that cobalt aluminate acts as an active cobalt species in $Co/Al_2O_3$. In addition, by the MD treatment, the activity of $Al_2O_3$(800) alone for $NO+C_2H_4+O_2$ was not changed (Figure 2). On the other hand, in the case of Co(5)/$Al_2O_3$(800), which is

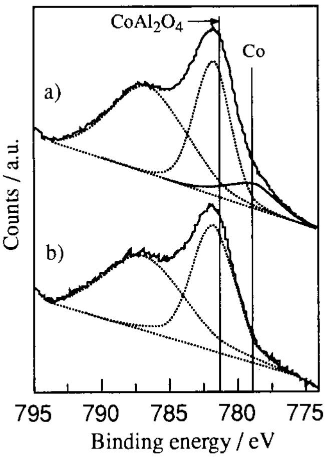

**Figure 1.** XPS spectra of Co(5)/$Al_2O_3$ calcined at 500 °C. a) reduced with hydrogen at 500 °C for 3 h, b) treated with a nitric acid solution (1 M) at 60 °C for 2h after hydrogen reduction.

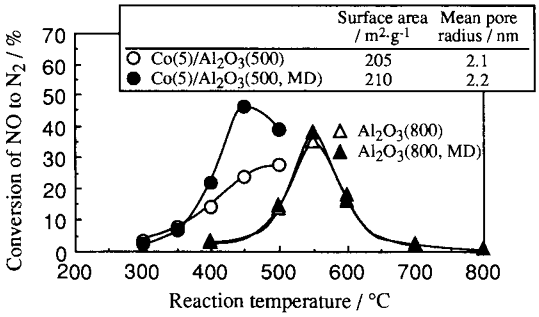

**Figure 2.** Temperature dependence of the catalytic activity of various catalysts for $NO+C_2H_4+O_2$. NO = 1000 ppm, $C_2H_4$ = 500 ppm, $O_2$ = 2.0%, He = balance.

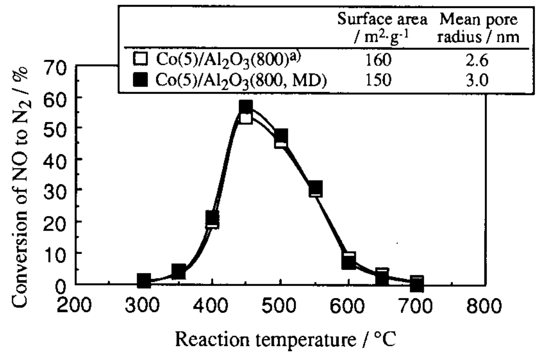

**Figure 3.** Temperature dependence of the catalytic activity of $Co(5)/Al_2O_3$ catalysts for $NO+C_2H_4+O_2$. Composition: the same as that in Figure 2. a) Ref. 15.

known to have only $CoAl_2O_4$[15], the MD treatment caused no change in activity for $NO+C_2H_4+O_2$ (Figure 3). This supports that cobalt aluminate is an active cobalt species. Over $Co(5)/Al_2O_3(800)$ and $Co(5)/Al_2O_3(800, MD)$, CO was formed along with $CO_2$. As shown in Figures 2 and 3, the MD treatment did not result in distinct change in specific surface area and mean pore radius.

Figure 4 shows the activity of various catalysts for $NO+O_2$. Clearly, the activity of $Co(5)/Al_2O_3(500, MD)$ was higher than that of $Al_2O_3(800)$, indicating that cobalt aluminate is active for step (1). The activity of $Co(5)/Al_2O_3(500)$ was much higher than that of $Co(5)/Al_2O_3(500, MD)$. This will be due to the presence of $Co_3O_4$, a catalyst for oxidation, in $Co(5)/Al_2O_3(500)$.

As can be seen in Figure 5, the activity of $Co(5)/Al_2O_3(500, MD)$ for $C_2H_4+O_2$ was remarkably lower than $Co(5)/Al_2O_3(500)$; the activity of $Co(5)/Al_2O_3(500, MD)$ was similar to that of $Co(5)/Al_2O_3(800)$. These suggest that in the case of $Co(5)/Al_2O_3(500)$, $Co_3O_4$ is allowed to catalyze step (3). On the other hand, in the case of $Co(5)/Al_2O_3(500, MD)$, step (3) seems to be suppressed to a minimum level, indicating that cobalt aluminate is much less active for step (3).

In conclusion, the MD treatment was confirmed to be an useful technique to remove selectively $Co_3O_4$ from $Co/Al_2O_3$, and by using $Co_3O_4$-free $Co(5)/Al_2O_3$ it was revealed that cobalt aluminate has sufficient activity for step (1), but nevertheless quite low activity for step (3).

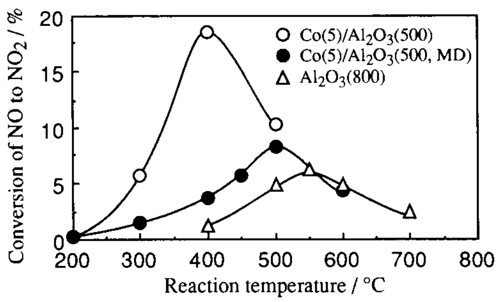

**Figure 4.** Temperature dependence of the catalytic activity of various catalysts for $NO+O_2$. NO = 1000 ppm, $O_2$ = 2.0%, He = balance.

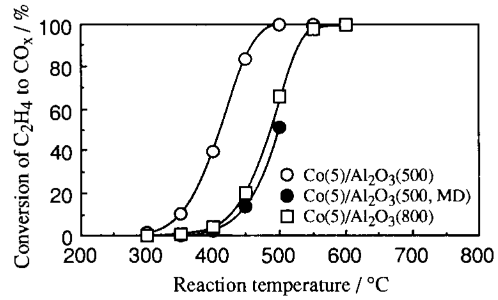

**Figure 5.** Temperature dependence of the catalytic activity of various catalysts for $C_2H_4+O_2$. $C_2H_4$ = 500 ppm, $O_2$ = 2.0%, He = balance.

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