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Role of supported metals in the selective reduction of nitrogen monoxide with hydrocarbons over metal/alumina catalysts

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Abstract

The promoting effect of supported metals on alumina catalyst was investigated for the reduction of nitrogen monoxide in oxygen-rich atmospheres. For NO reduction with propene over impregnated CoO/Al_2O_3, the first reaction step was found to be the oxidation of NO to NO_2 probably catalyzed by dispersed cobalt species. The next reaction step, which is the reaction of NO_2 with propene to form N_2, was considered to take place on the alumina surface. Although the activity of impregnated FeO/Al_2O_3 was low because of the presence of large iron oxide particles catalyzing propene oxidation with dioxygen, FeO/Al_2O_3 prepared with sol-gel method showed excellent deNO$_x$ activity.

Keywords: NO$_x$ reduction; CoO/Al_2O_3 catalyst; FeO/Al_2O_3 catalyst

1. Introduction

The selective reduction of NO with hydrocarbons in oxygen-rich atmospheres has been reported over various catalysts such as zeolites [1], metal oxides [2] and noble metals [3]. We reported that alumina showed good activity for this reaction among metal oxide catalysts [4] and that supporting metals such as cobalt, iron, copper, etc. promoted the activity of alumina at low temperatures and at high space velocity [5]. The favorable effects of gold and silver were also reported [6,7].

In this paper, we investigated the effect of cobalt and iron addition on the performance of alumina and discussed the role of the supported metals in terms of the state of surface metal species.

2. Experimental

Alumina used in this study was obtained from Sumitomo Chemicals (NK324, 189 m^2 g^{-1}, calcined at 600°C). Alumina-supported cobalt and iron catalysts were prepared by impregnating the alumina with aqueous cobalt acetate and nitric acid-dissolved iron oxalate solutions, followed by drying and calcination in air streams. The catalyst samples are abbreviated as CoO/ or FeO/Al_2O_3 (calc. temp./°C). We also prepared alumina-supported iron catalysts with sol-gel method in which hexyleneglycol

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was used as the solvent. The samples are denoted as FeO/Al_2O_3 (SG, calc. temp./°C).

Catalytic activities were measured with a fixed bed flow reactor. The reaction gas contained NO, NO_2, O_2 and C_3H_6 diluted in helium. Standard experiments were performed by using 0.2 g of catalyst with a total gas flow rate of 62 cm^3 min^{-1}. Steady state measurements were made by decreasing the temperature down from the catalyst calcination temperature. The effluent gas was analyzed by gas chromatography and the catalytic activities were expressed by the conversion of NO to N_2 and that of propene to CO_x. For catalyst characterization, XPS, NO chemisorption, TEM measurements were made. NO chemisorption was done with a pulse technique at room temperature.

3. Results and discussion

3.1. Activity of impregnated cobalt / and iron / alumina

Fig. 1 shows the catalytic activity of CoO/Al_2O_3 (500) with different cobalt loading and 2% FeO/Al_2O_3 (500) for NO reduction with propene in the presence of 10% dioxygen. Alumina gave maximum NO conversion to N_2 at 550°C. When cobalt was added to alumina by impregnation, the effective temperature for NO reduction became lower with an increase of propene oxidation. The highest NO conversion was obtained on 0.1% and 0.5% CoO/Al_2O_3. Higher cobalt loading resulted in a decrease of NO conversion. On the other hand, the addition of iron did not promote the deNO_x activity of alumina, although a shift of the effective temperature range for NO reduction was observed.

The effect of calcination temperature on the activity of 2% CoO/Al_2O_3 is shown in Fig. 2. The deNO_x activity increased with the calcination temperature. This tendency was similar to the effect of cobalt loading. The low activity of 2% FeO/Al_2O_3, on the other hand, was not influenced by calcination temperature.

In order to get information on the role of supported metals, the catalytic activity for propene oxidation with dioxygen in the absence of NO was examined. The results are shown in Fig. 3. Obviously, loading of 0.1%–0.5% CoO did not change the activity of alumina much. More than 2% CoO loading enhanced the oxidation activity. It should be noted that the activity of 2% FeO/Al_2O_3 was quite high compared to CoO/Al_2O_3 catalysts.

It can be seen by comparing Figs. 1 and 3 that the conversion of propene to CO_x on 0.1–2% CoO/Al_2O_3 was much higher for the reaction of $NO–C_3H_6–O_2$ than that for $C_3H_6–O_2$.

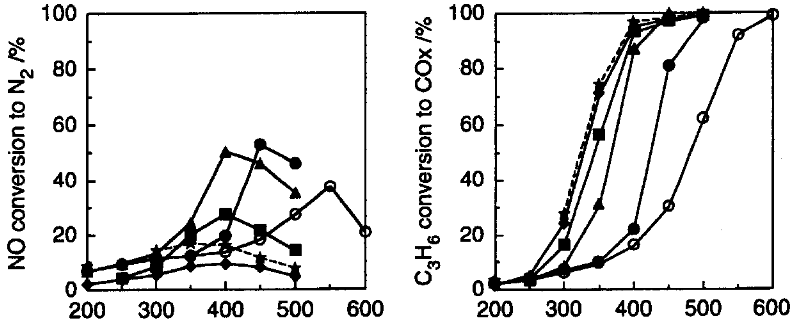

Fig. 1. Activity of CoO/ and FeO/Al_2O_3 (500) for the selective reduction of NO with C_3H_6. (NO = 962 ppm, O_2 = 9.9%, C_3H_6 = 326 ppm, $W/F = 0.19$ g s cm^{-3}). ○ Al_2O_3, ● 0.1% CoO, ▲ 0.5% CoO, ■ 2% CoO, ◆ 5% CoO, ★ 2% FeO.

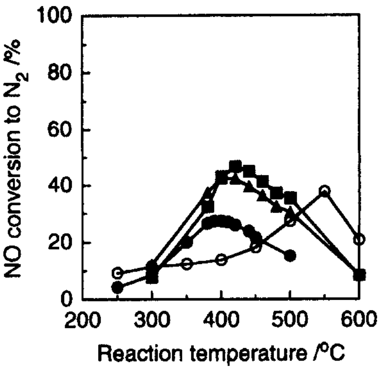

Fig. 2. Effect of the calcination temperature on the activity of 2% CoO/Al_2O_3. ($NO = 962$ ppm, $O_2 = 9.9\%$, $C_3H_6 = 326$ ppm, $W/F = 0.19$ g s cm^{-3}) ○ Al_2O_3, ● 500°C, ▲ 600°C, ■ 800°C.

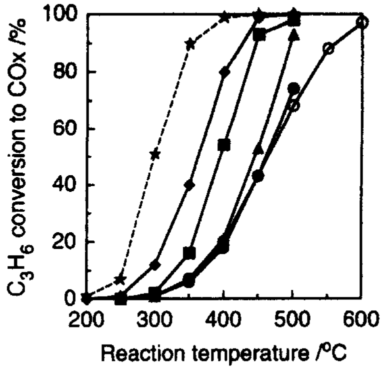

Fig. 3. Activity of CoO/ and FeO/Al_2O_3 (500) for the oxidation of C_3H_6. ($O_2 = 9.9\%$, $C_3H_6 = 326$ ppm, $W/F = 0.19$ g s cm^{-3}) ○ Al_2O_3, ● 0.1% CoO, ▲ 0.5% CoO, ■ 2% CoO, ◆ 5% CoO, ★ 2% FeO.

This fact suggests that the first reaction step for the reaction of $NO–C_3H_6–O_2$ is the oxidation of NO to NO_2 because NO does not react with propene at the present temperature range. Accordingly, the next step is the reaction of NO_2 with propene.

The reactivity of NO_2 was investigated next. Fig. 4 shows the catalytic activity for the reduction of NO_2 with propene in the presence of dioxygen. It is quite interesting that the most active catalyst for NO_2 reduction was not CoO/Al_2O_3 but Al_2O_3. The addition of cobalt decreased NO_2 conversion to N_2. The activity of FeO/Al_2O_3 was not good, either.

It was also found that direct reduction of NO_2 with propene over CoO/Al_2O_3 catalysts in the absence of dioxygen gave almost the same results as of Fig. 4 with regard to NO_2 conversion to N_2. In the case of FeO/Al_2O_3-catalyzed NO_2 reduction with propene, however, two reduction peaks were observed. The peak at higher temperature was found to correspond to the direct reduction of NO with propene.

The above-described results suggest that the reaction of $NO–C_3H_6–O_2$ over CoO/Al_2O_3 proceed via the following steps.

$$NO + O_2 \rightarrow NO_2 \quad (1)$$

$$NO_2 + C_3H_6 \rightarrow N_2 + CO_x + H_2O \quad (2)$$

$$NO_2 + C_3H_6 \rightarrow NO + CO_x + H_2O \quad (3)$$

Although the rate of reaction (1) is low on alumina, impregnated cobalt species promotes

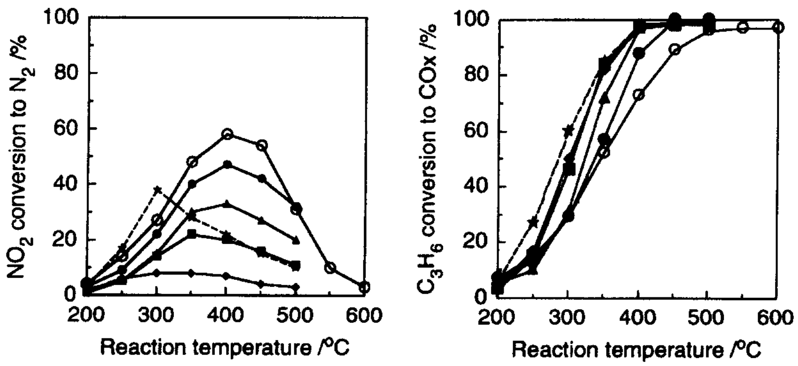

Fig. 4. Activity of CoO/ and FeO/Al_2O_3 (500) for the selective reduction of NO_2 with C_3H_6. ($NO_2 = 939$ ppm, $O_2 = 9.9\%$, $C_3H_6 = 326$ ppm, $W/F = 0.19$ g s cm^{-3}) ○ Al_2O_3, ● 0.1% CoO, ▲ 0.5% CoO, ■ 2% CoO, ◆ 5% CoO, ★ 2% FeO.

this reaction step. The formation of N_2 results from reaction (2) which probably takes place on the alumina surface. The supported cobalt species is not responsible for the second step but causes a side reaction (3) leading to the oxidation of propene to CO_x without reducing NO_2. The low deNO_x activity of FeO/Al_2O_3 can be ascribed to its high activity for propene oxidation with dioxygen.

Table 1
Amount of chemisorbed NO

Sample	NO chem./mol g^{-1}
Al_2O_3	0
0.1% Co/Al_2O_3 (500)	0.31×10^{-6}
0.5% CoO/Al_2O_3 (500)	3.00×10^{-6}
2% CoO/Al_2O_3 (500)	6.07×10^{-6}
5% CoO/Al_2O_3 (500)	19.1×10^{-6}
2% CoO/Al_2O_3 (600)	6.31×10^{-6}
2% CoO/Al_2O_3 (800)	4.11×10^{-6}
2% FeO/Al_2O_3 (500)	4.93×10^{-6}
2% FeO/Al_2O_3 (SG)	10.1×10^{-6}

3.2. Catalyst characterization

The status of the supported metals was analyzed by various techniques. XPS given in Fig. 5 showed that the electronic state of the cobalt species in 2–5% CoO/Al_2O_3 was very close to cobalt acetate or cobalt aluminate ($CoAl_2O_4$). Transmission electron microscope analysis indicated that there were no large particles on the surface of 2% CoO/Al_2O_3 while particles with diameters of 10–30 nm were observed on 2% FeO/Al_2O_3. The particles were found to contain iron by elemental analysis. Taking all XPS into account, it was suggested that they are particles of Fe_2O_3.

In order to know the metal ion dispersion on alumina, NO chemisorption measurements were performed. The results are shown in Table 1. For CoO/Al_2O_3, the amount of chemisorbed NO increased with cobalt loading, suggesting increasing surface cobalt ions. Since it was re-

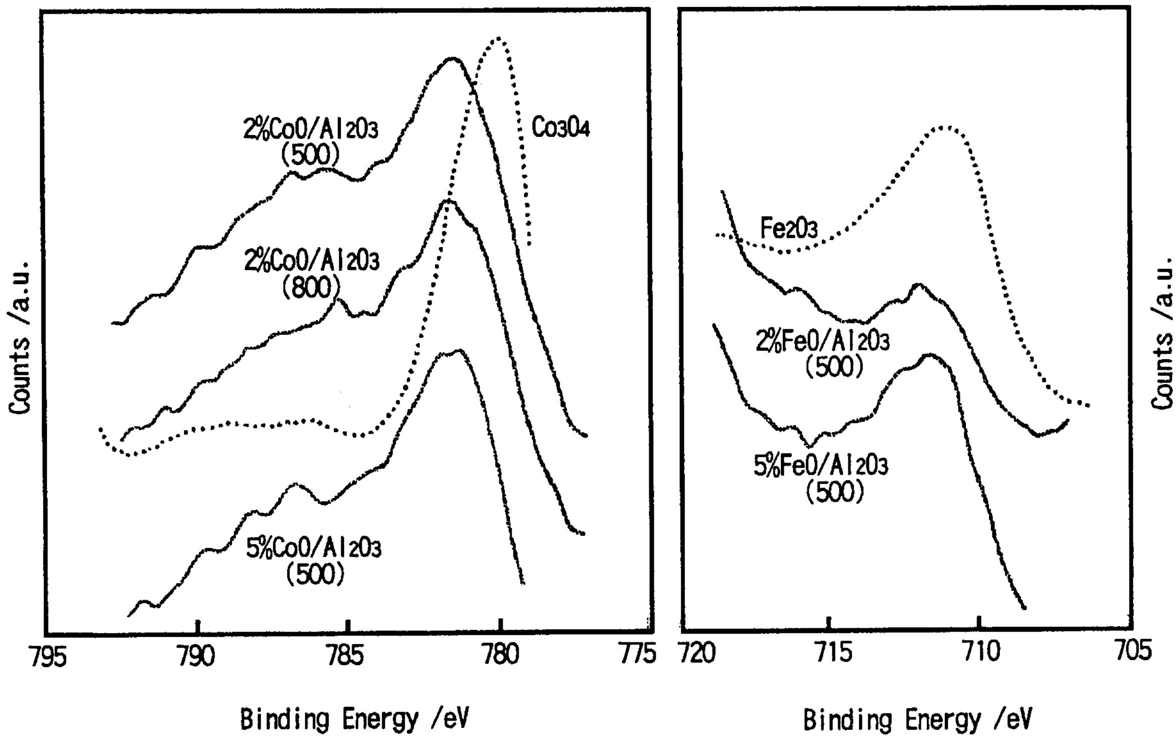

Fig. 5. XPS spectra of CoO/Al_2O_3 and FeO/Al_2O_3 in the region of $2p_{3/2}$.

ported that NO is not chemisorbed on Co/Al_2O_4 because the cobalt ions are shielded from the surface [8], the possibility cannot be ruled out that some surface cobalt species are not as in cobalt aluminate. Calcination of 2% CoO/Al_2O_3 at higher temperatures decreased the amount of chemisorbed NO. At the moment, the true active species for the $deNO_x$ activity is not clear. However, too much surface cobalt ions seem to decrease the activity probably because of the promotion of unfavorable side reactions such as reaction (3). The loss of $deNO_x$ activity for FeO/Al_2O_3 is due to the presence of large Fe_2O_3 particles catalyzing propene oxidation by dioxygen.

3.3. Activity of cobalt / and iron / alumina prepared with sol-gel method

Since highly dispersed surface metal species appears responsible for the promotion of $deNO_x$ activity, we investigated the activity of CoO/ and FeO/Al_2O_3 prepared with sol-gel method. There was not large difference between the activity of CoO/Al_2O_3(SG) and CoO/Al_2O_3. On the other hand, FeO/Al_2O_3 (SG) showed much higher activity for NO reduction than FeO/Al_2O_3, as demonstrated by Fig. 6. FeO/Al_2O_3 (SG) with 0.5% FeO was quite active for NO reduction at 300–400°C in contrast to the impregnated FeO/Al_2O_3. The large amount of chemisorbed NO on 2% FeO/Al_2O_3 (SG) given in Table 1 indicated high dispersion of iron ions on the surface.

The difference in the property of cobalt and iron for the impregnated catalysts is considered partly due to the difference of starting salts for catalyst preparation. But also the stability of metal/aluminate seems responsible for the difference. In fact, thermodynamic calculation showed that cobalt/aluminate species are much more stable than iron/aluminate in the presence of 10% dioxygen.

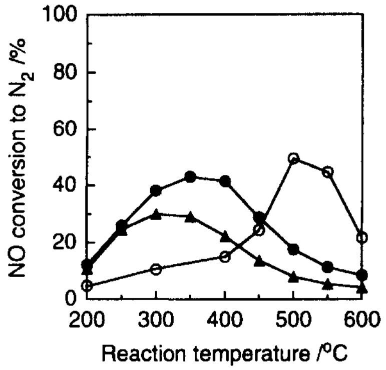

Fig. 6. Activity of FeO/Al_2O_3 (600) prepared with the sol-gel method. (NO = 962 ppm, O_2 = 9.9%, C_3H_6 = 326 ppm, W/F = 0.19 g s cm^{-3}) ○ Al_2O_3, ● 0.5% FeO/Al_2O_3 (SG), ▲ 2% FeO/Al_2O_3 (SG).

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