Selective Suppression of Undesirable Competitive Oxidation during Selective Catalytic Reduction of Nitrogen Monoxide by Ethene in Excess Oxygen over Metal-Loaded Aluminas

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Calcining cobalt or nickel-loaded alumina at high temperatures suppressed selectively the undesirable oxidation of ethene by oxygen in the selective reduction of nitrogen monoxide by ethene in excess oxygen, while such an effect was not observed over iron-loaded alumina. The reasons were also explained on the basis of the results of XPS studies.

The selective catalytic reduction of nitrogen monoxide by hydrocarbons (SCR-NO) in excess oxygen has been investigated extensively as one of the promising deNO$_x$ processes.[1] In the NO-hydrocarbons-O_2 reaction system, more than two kinds of oxidations of hydrocarbons will generally take place: one is the oxidation by a mixture of NO and O_2 to produce N_2 (the objective reaction), and another is the oxidation by O_2 alone (a major side reaction). One of the crucial problems of designing an effective catalyst for the SCR-NO is to suppress selectively the oxidation of hydrocarbons by O_2. Alumina[2] is known as an excellent oxide catalyst for the SCR-NO, which has much higher selectivity towards N_2 formation. By adding a transition metal on the alumina its activity was enhanced[3-8] but at the same time the activity for the oxidation of hydrocarbons by O_2 was also enhanced. Few studies have been performed on the effective suppression of undesirable competitive oxidation.[9, 10] Hamada et al.[10] reported that raising the calcination temperature of 2 wt% Co-loaded alumina resulted in a decrease in propane conversion and an increase in NO conversion during SCR-NO by propane. This result indirectly indicates that high temperature-calcination brought about the selective suppression of the oxidation of propane by O_2. However, it is not easy to evaluate the contribution of the oxidation of propane by O_2 alone on the basis of the results of the SCR-NO by propane. In the present study, therefore, the oxidation of ethene by O_2 in the absence of NO has been compared with the oxidation in the presence of NO over several metal-loaded aluminas (M/Al_2O_3), because such a comparison can directly give us information about the degree of the selective suppression of the former oxidation.

All M/Al_2O_3 catalysts were prepared by the impregnation of alumina with aqueous solutions of corresponding metal acetates. The solvent evaporation took place while stirring and in a vacuum (water pump) with rotary evaporator at 50 °C until the solid seemed dry, followed by drying at 120 °C for 24 h, and heating at 500 °C for 4 h in air. The alumina used throughout was prepared by hydrolyzing aluminum isopropoxide followed by calcining at 600 °C for 24 h. All the catalyst precursors were ground to powder, and then pressed into pellets followed by crushing, sieving (30-42 mesh), and calcining at 500 or 800 °C for 4 h in air before use. A M/Al_2O_3 catalyst is denoted as follows: M(loading wt%)/Al_2O_3 (calcination temp./ °C). Both NO-C_2H_4-O_2 and C_2H_4-O_2 reactions were carried out with a fixed bed flow reactor at a W/F of 0.18 $g \cdot s \cdot cm^{-3}$ (catalyst, 0.4 g ; total flow rate, 130 $cm^3 \cdot min^{-1}$) at temperatures ranging from 200 to 700 °C. The reactant gas (NO, 1000 or 0 ppm; O_2, 2.0%; C_2H_4, 500 ppm; He, balance) was passed through a catalyst bed. The outflow gas was analyzed by gas chromatography with a Molecular Sieve 5A (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) columns. Catalytic activities for NO reduction were evaluated in terms of percentage conversions of NO to N_2, because N_2O formation was negligible under the present reaction conditions.

In Figure 1a, the oxidation activity curve for the NO-C_2H_4-O_2 reaction was compared with that for the C_2H_4-O_2 reaction over Fe(5 wt%)/Al_2O_3(500). Clearly, a set of the oxidation activity curves was exactly identical. This result means that the NO-C_2H_4-O_2 reaction producing N_2 competes equally with the C_2H_4-O_2 reaction. A similar relationship was also reported for a set of NO-C_3H_8-O_2 and C_3H_8-O_2 reactions over Pt/Al_2O_3 and Cu-ZSM-5.[5] After calcination at 800 °C, a set of the oxidation activity curves shifted to the higher temperature side but still remained identical (Figure 1b); the oxidation activities for the two reactions were reduced equally. Such a calcination effect has not been reported for SCR-NO over Fe/Al_2O_3.[3, 4, 9] Regarding the NO reduction activity of Fe(5 wt%)/Al_2O_3(500), there was no noticeable variation due to the difference in calcination temperature (Figure 1).

With Co(5 wt%)/Al_2O_3(500), a set of the oxidation activity curves was close each other (Figure 2a). However, on calcination at 800 °C (Figure 2b), a set of the oxidation activity curves became evidently separated; favorably, the curve for the C_2H_4-O_2 reaction shifted farther to a higher temperature side than that for the NO-C_2H_4-O_2. In other words, calcination at 800 °C caused the selective suppression of the C_2H_4-O_2 reaction. This situation ought to

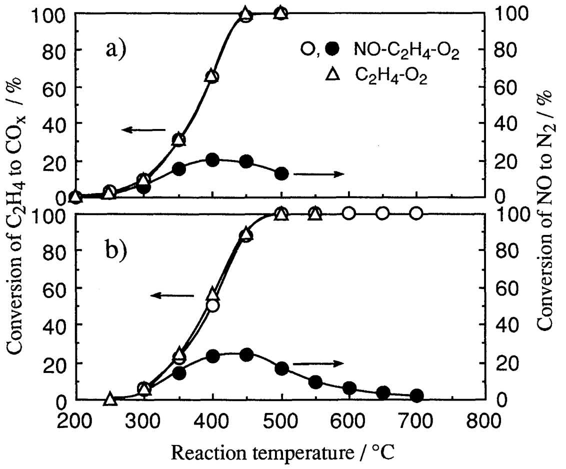

Figure 1. Temperature dependence of the catalytic activities of Fe(5 wt%)/Al_2O_3 catalyst calcined at (a) 500 °C and (b) 800 °C. Conditions: NO = 1000 or 0 ppm, C_2H_4 = 500 ppm, O_2 = 2.0%, catalyst = 0.4 g, total flow rate = 130 $ml \cdot min^{-1}$, W/F = 0.18 $g \cdot s \cdot cm^{-3}$.

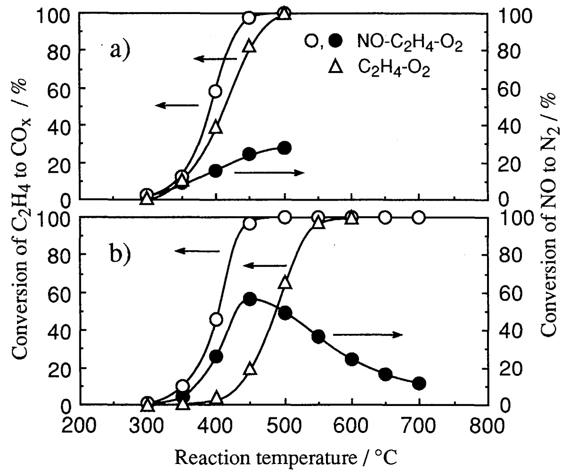

Figure 2. Temperature dependence of the catalytic activities of Co(5 wt%)/Al_2O_3 catalyst calcined at (a) 500 °C and (b) 800 °C. Conditions: the same as those in Figure 1.

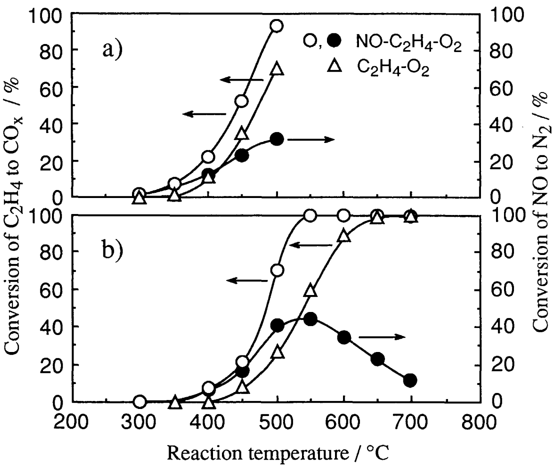

Figure 3. Temperature dependence of the catalytic activities of Ni(5 wt%)/Al_2O_3 catalyst calcined at (a) 500 °C and (b) 800 °C. Conditions: the same as those in Figure 1.

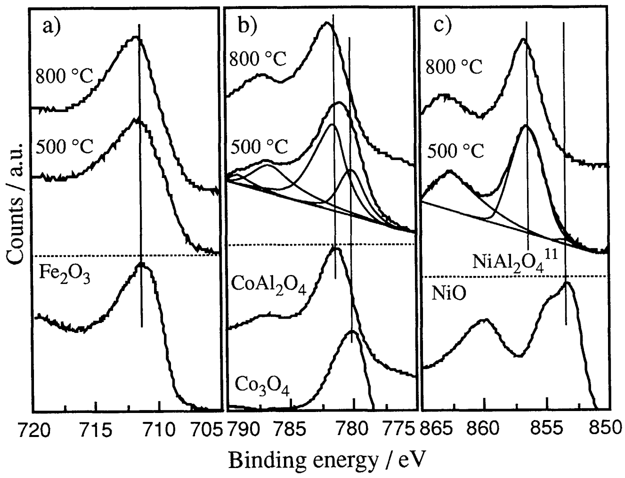

Figure 4. XPS spectra of (a) Fe(5 wt%)/Al_2O_3, (b) Co(5 wt%)/Al_2O_3, and (c) Ni(5 wt%)/Al_2O_3 in the region of $2p_{3/2}$.

enhance the NO-C_2H_4-O_2 reaction producing N_2. Actually the NO conversion to N_2 became much higher than that over Co(5 wt%)/Al_2O_3(500) (Figure 2b).

Again with Ni(5 wt%)/Al_2O_3 (Figure 3), a set of the oxidation activity curves became separated with increasing calcination temperature as in the situation of the Co(5 wt%)/Al_2O_3.

As can be seen in Figure 4, the XPS spectra indicate that Fe(5 wt%)/Al_2O_3(500) contained only MO_x while Co(5 wt%)/Al_2O_3(500) and Ni(5 wt%)/Al_2O_3(500) contained MAl_2O_4 and MO_x (NiO: very little). On calcination at 800 °C, however, the peaks due to Co_3O_4 and NiO almost disappeared indicating that those particles were highly dispersed, while the peak due to Fe_2O_3 remained. The results on the Co/Al_2O_3 and Fe/Al_2O_3 catalysts agree with those on corresponding catalysts (2 wt% loading).[9] It was reported that large Fe_2O_3 particles on Fe(2 wt%)/Al_2O_3 prepared by the impregnation method catalyzed the C_3H_6-O_2 reaction in NO-C_3H_6-O_2.[9] A similar situation could arise for the Fe(5 wt%)/Al_2O_3(500 and 800), since those were prepared by the impregnation method and also contained Fe_2O_3 particles. The above results suggest that the active metal species of Co(5 wt%)/Al_2O_3(800) and Ni(5 wt%)/Al_2O_3(800) are the corresponding metal aluminates, but at present we can not rule out the possibility that trace amounts of the finely divided metal oxides will act as another active metal species.

By reducing the Co loading from 5 wt% to 0.2 wt%, the selective suppression of the C_2H_4-O_2 reaction was successfully achieved over Co/Al_2O_3(500), being in accord with expectations based on the result of the C_3H_6-O_2 reaction in NO-C_3H_6-O_2 over Co/Al_2O_3(500) catalysts having Co loadings between 0.1 and 5 wt%,[9] while over Fe(0.6 wt%)/Al_2O_3(500) no selective suppression of the C_2H_4-O_2 reaction was observed (not shown).

In conclusion, it has been directly confirmed that over Co/Al_2O_3 calcined at high temperatures, the oxidation of ethene by O_2 in the absence of NO was more strongly suppressed than the oxidation in the presence of NO, and has been newly found that Ni/Al_2O_3 exhibited a similar phenomenon too.

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