Change in Activity of Alumina by Calcination Temperature for Selective Reduction of Nitrogen Monoxide with Ethene in Excess Oxygen

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Mostly, the activities for $NO+C_2H_4+O_2$ and its related reactions decreased with increasing calcination temperature. In $NO_2+C_2H_4$, N_2 was selectively formed over alumina calcined at 800 °C, while over alumina calcined at the other temperatures, not only N_2 but also NO was formed. Taking into account the temperature window as well, the most advantageous calcination temperature of alumina is 800 °C as a catalyst for $NO+C_2H_4+O_2$.

Among NO_x removal processes, most of the research interest has been focused on the selective catalytic reduction of NO with hydrocarbons(HC) 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] Of metal oxides, alumina[6, 7] is a promising catalyst candidate for practical use because of its excellent activity and thermal stability. Alumina is also used as a catalyst material or a catalyst support of some transition-metal loaded catalysts.[8-13] It is well-known that the activity for adsorption and catalytic function of alumina is revealed by partial dehydroxylation of its surface.[14] Probably, the catalytic activity of alumina for $NO+HC+O_2$ reaction could also be affected by the degree of the dehydroxylation, but previous studies have paid little attention to the effect of calcination temperature on its activity. Therefore, we investigated the calcination-temperature dependence of the activity for $NO+C_2H_4+O_2$, and explained the dependence, based on the results of $NO+O_2$, $NO_2+C_2H_4$, and $C_2H_4+O_2$, which are believed to be the elementary reactions and a side reaction of $NO+C_2H_4+O_2$ over alumina, respectively.

Alumina(ALOA) was produced by heating its precursor at 500 °C or 600 °C for 24 h, which was prepared by the controlled hydrolysis of aluminum tri-isopropoxide. Then it was pressed into pellets at 200 $kg{\cdot}m^{-2}$, followed by crushing, sieving (30-42 mesh) and again heating at 500-1200 °C for 4 h in air just before being used for catalytic run. Calcined alumina was denoted as ALOA(calcination temperature/ °C). The specific surface area of alumina samples was determined by the analysis of N_2 sorption data. X-Ray powder diffraction (XRD) patterns were taken with a Rigaku-Electronic diffractometer RINT-1200 using monochromatic Cu$K\alpha$ radiation. Experiments of NO(1000 ppm)+C_2H_4(500 ppm)+O_2(2%), NO(1000 ppm)+O_2(2%), NO_2(1000 ppm)+C_2H_4(500 ppm), and C_2H_4(500 ppm)+O_2(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 $cm^3{\cdot}min^{-1}$) at temperatures ranging from 300 to 800 °C. The outflow gas during $NO+C_2H_4+O_2$ 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). The catalytic activity for NO reduction was evaluated by a term of percentage conversion of NO to N_2, since N_2O formation was negligible under the present reaction conditions. The outflow gas during $NO+O_2$ was analyzed by infrared spectroscopy.

Figure 1 shows the activity of alumina calcined at various temperatures for $NO+C_2H_4+O_2$ as a function of reaction temperature. The activity for the reduction of NO to N_2 decreased with increasing calcination temperature at all reaction temperatures except for 600 °C; at 600 °C the activity of ALOA(600) was lower than that of ALOA(800). The integrated activity of ALOA(800) below 600 °C seems to be equal to that of ALOA(600). ALOA(800) can also be used at 600 - 800 °C. Then, its available temperature window will become nearly twice. In view of these points, 800 °C is considered to be the optimum calcination temperature of alumina. The activity curve for the conversion of ethene to CO_x (CO_2 and CO) also shifted to the higher temperature side with increasing calcination temperature.

The reaction mechanism of $NO+C_2H_4+O_2$ over alumina is reported as follows.[7]

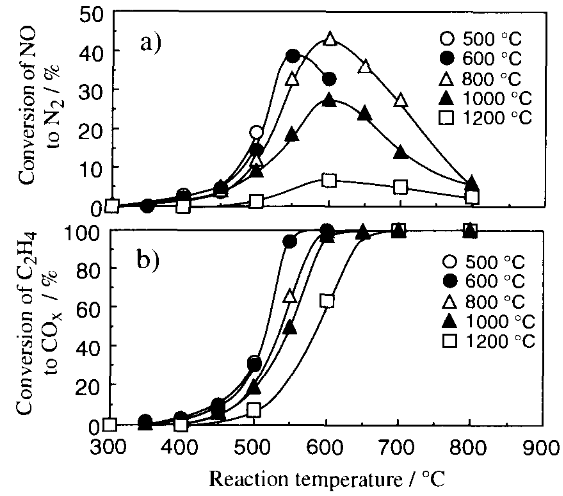

Figure 1. Temperature dependence of the catalytic activity of Al_2O_3 calcined at various temperatures for $NO+C_2H_4+O_2$.

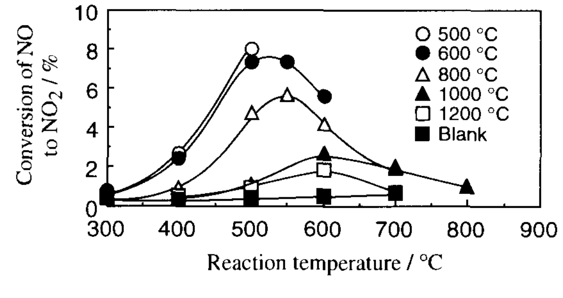

Figure 2. Temperature dependence of the catalytic activity of Al_2O_3 calcined at various temperaturse for $NO+O_2$.

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

$$NO_2 + C_2H_4 \rightarrow N_2 + CO_x + H_2O \quad (2)$$

$$C_2H_4 + O_2 \rightarrow CO_x + H_2O \quad (3)$$

To explain the reasons for the dependence of the activity of alumina on its calcination temperature, first, the activity for step (1) was studied (Figure 2). It was found that the activity curve shifted to the higher temperature side and the maximum conversion decreased with increasing calcination temperature.

Second, the activity for step (2) was studied (Figure 3). In the absence of alumina, no N_2 was formed. As a whole, the activity curve shifted to the higher temperature side and the maximum conversion decreased with increasing calcination temperature. It should be stressed that the activity of ALOA(800) is close to that of ALOA(600), unlike the situation for step (1). In this reaction, NO was also formed over most aluminas (Figure 4), but over ALOA(800), its yield was extraordinarily low. This indicates that over ALOA(800), NO_2 was selectively reduced to N_2, although the reason is not clear at present.

The activity for step (3), a side reaction, was also examined (Figure 5). The activity curve shifted to the higher temperature side with increasing calcination temperature.

Table 1 lists the BET specific surface area and the crystal structure of alumina calcined at various temperatures. The specific surface area decreased with increasing calcination temperature. The crystal structure of alumina heated below 800 °C was γ-type (JCPDS: 10-0425), and those of ALOA(1000) and ALOA(1200) were θ-type and α-type, respectively.

The decreases in activity for all the reactions above with calcination temperature seem to be correlated with that in specific surface area. And the decrease in specific surface area could be caused by the sintering accompanied by the change in crystal structure of alumina.

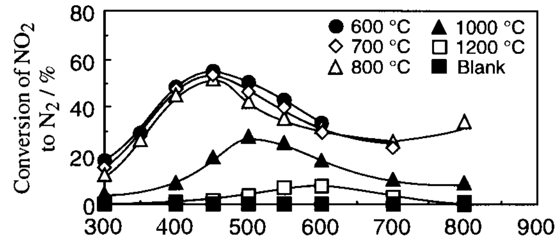

Figure 3. Temperature dependence of the catalytic activity of Al_2O_3 calcined at various temperatures for NO_2+C_2H_4.

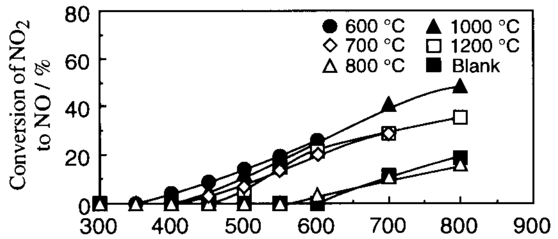

Figure 4. Temperature dependence of the catalytic activity of Al_2O_3 calcined at various temperatures for NO_2+C_2H_4.

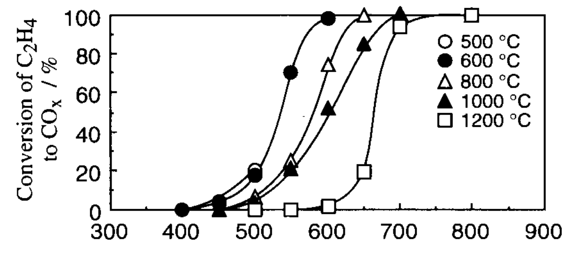

Figure 5. Temperature dependence of the catalytic activity of Al_2O_3 calcined at various temperatures for C_2H_4+O_2.

Table 1. Surface area and crystal phase of Al_2O_3 calcined at various temperatures

Calc. temp. / °C	Surface area / $m^2 \cdot g^{-1}$	Crystal phase
500	264	γ
600	177	γ
800	143	γ
1000	85	θ
1200	7	α

In NO+C_2H_4+O_2(Figure 1), the NO conversion of ALOA(600) was not so higher than that of ALOA(800) at 550 °C considering their difference in ethene conversion, and at 600 °C the NO conversion of ALOA(600) became lower than that of ALOA(800) although their ethene conversions were similar. These will be attributed to the fact that ethene as a reductant of NO can be consumed more fruitlessly over ALOA(600) than over ALOA(800) by C_2H_4+O_2 (Figure 5). In addition, the temperature window of ALOA(600) is significantly narrower than that of ALOA(800). Therefore, the optimum or advantageous calcination temperature of alumina is 800 °C for NO+C_2H_4+O_2.

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