Marked difference in activity of alumina catalysts for selective catalytic reduction of nitrogen monoxide by ethene in excess oxygen

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Alumina is well-known as an effective catalyst for the title reaction. The present study revealed that the activity of an alumina catalyst for the reaction largely depended on its type. A critical factor affecting the activity of an alumina was neither the surface area nor pore structure, but the purity; the higher the purity, the higher the activity. Active alumina catalysts showed high activity for both the oxidation of NO to NO_2 and the reduction of NO_2 by ethene.

Keywords: selective catalytic reduction, nitrogen oxide, nitrogen dioxide, hydrocarbons, Al_2O_3, oxidation of nitrogen oxide to nitrogen dioxide

1. Introduction

In relation to the processes for removing nitrogen oxides (NO_x) in exhaust gases, the selective catalytic reduction of NO_x by hydrocarbons (HC) in the presence of excess oxygen (denoted as $NO_x + HC + O_2$) has recently attracted much attention [1]. This catalytic process was first confirmed over copper ion-exchanged zeolites by Iwamoto et al. [2,3] and Held et al. [4]. Many effective catalysts such as zeolites, metal oxides and supported noble metals have been reported [5]. Of the metal oxides, alumina has been regarded as a promising catalyst candidate because of its excellent activity and durability [6]. Frequently, alumina has been modified by adding a transition metal such as Co, Cu, Fe, Ag and Pt as another active component [7–12].

In general the preparative method of a solid catalyst affects its surface and physical properties and hence the activity of the catalyst mostly depends on its method of preparation. Such a relationship will also be observed for alumina as a catalyst for $NO_x + HC + O_2$. However, most of the research effort has not been directed at such a topic. Some of the authors preliminarily reported that highly pure aluminas showed greater activity for $NO + HC + O_2$ (HC: C_2H_4) [13]. Almost the same result was also obtained for $NO_x + HC + O_2$ (HC: C_3H_8) [14]. Teraoka et al. [15] referred to the preeminence of a commercial alumina, JRC-ALO4, in activity for $NO + HC + O_2$ (HC: C_2H_4). Recently, Radtke et al. [16] have studied the effect of the type of alumina on the formation of the by-products and on the overall catalytic performance in $NO_x + HC + O_2$ (HC: C_2H_4, C_3H_6) using two different commercial γ-aluminas, and reported that the type of alumina played a crucial role in governing the overall catalytic behavior. Therefore, we should pay particular attention to the types of the alumina samples used by other researchers when we compare their activity for $NO_x + HC + O_2$ shown in the literature.

However, the difference in activity of various alumina catalysts for $NO_x + HC + O_2$ has not been studied intensively. In particular, no study has been made on the activities of different aluminas for the NO oxidation by O_2 and the NO_2 reduction by hydrocarbons, which are considered to be the elementary reactions of $NO + HC + O_2$ [17]. Consequently, there is no guiding principle in choosing the best alumina catalyst for $NO_x + HC + O_2$.

The present work focuses on clarifying the differences in activity of five commercial aluminas for $NO + HC + O_2$ (HC: C_2H_4) and on investigating the requirements of the most active alumina on the basis of both mechanistic discussion and catalyst characterization.

2. Experimental

Five alumina samples (denoted as JRC-ALO1–5) were supplied from the Catalysis Society of Japan and the sixth alumina (denoted as ALOA) was produced by heating its precursor at 873 K for 24 h, which was prepared by the controlled hydrolysis of aluminum tri-isopropoxide. Doped alumina catalysts were prepared by

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wet impregnation of ALOA with aqueous solutions of $NaHCO_3$ or $(NH_4)_2SO_4$. All the alumina samples, which were obtained in the form of powder, were pressed into pellets at 200 kg m^{-2}, followed by crushing, sieving (355–500 μm) and again heating at 1073 K for 4 h in air just before being used in catalytic runs.

The specific surface area, mean pore radius and pore volume of the alumina samples were determined by analysis of N_2 sorption data. Elemental analysis of ALOA was performed with X-ray fluorescence spectroscopy (XRF). X-ray powder diffraction (XRD) patterns were taken with a Rigaku diffractometer RINT-1200 using nickel-filtered Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) analyses were performed with a Rigaku XPS-7000 spectrometer.

The experiments of NO(1000 ppm) + C_2H_4(500 ppm) + O_2(2%), NO(1000 ppm) + C_2H_4(500 ppm), NO(1000 ppm) + O_2(2%), NO_2(1000 ppm) + C_2H_4 (500 ppm) + O_2(2%), NO_2(1000 ppm) + C_2H_4(500 ppm) and C_2H_4(500 ppm) + O_2(2%) were performed using a fixed-bed flow tubular reactor at a W/F of 0.18 g s cm^{-3} (catalyst, 0.40 g; total flow rate, 130 cm^3 min^{-1}; balance, He) at temperatures ranging from 573 to 1073 K. The outflow gas of the reactions except for NO + 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), while the outflow gas of NO + O_2 was analyzed by infrared spectroscopy.

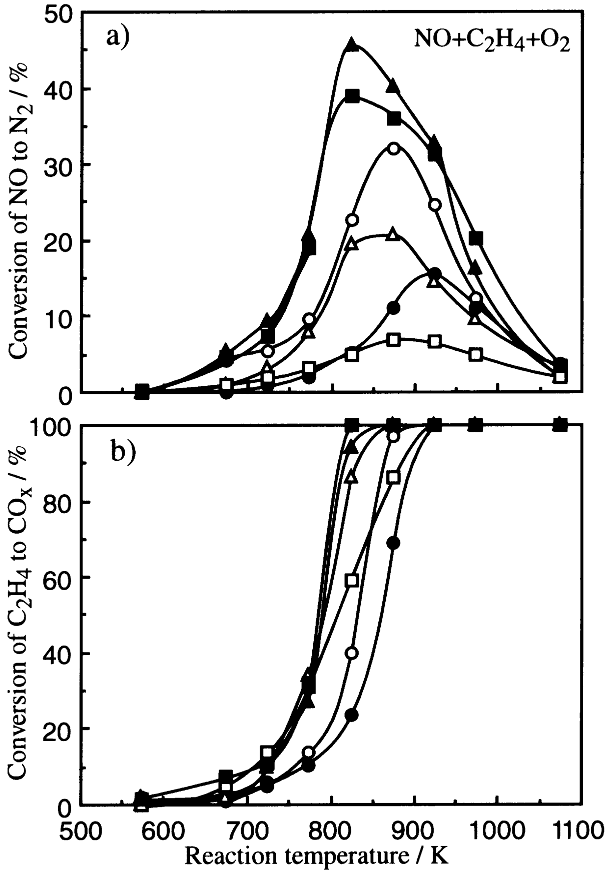

Figure 1. Temperature dependence of the activity of various alumina catalysts for NO + C_2H_4 + O_2. (○) ALO1; (●) ALO2; (△) ALO3; (▲) ALO4; (□) ALO5; (■) ALOA.

3. Results and discussion

3.1. NO + C_2H_4 + O_2 reaction

Figure 1a shows the activity of various alumina catalysts for NO + C_2H_4 + O_2. The formation of N_2O was negligible. Clearly, the activity was quite different in terms of both the maximum NO conversion ($C_{M,NO}$) and the temperature bringing it about ($T_{M,NO}$). The $C_{M,NO}$ values of ALO4 and ALOA were higher and the $T_{M,NO}$ values were lower than for any other aluminas. The $T_{M,NO}$ of ALO2 was the highest and those of ALO1, ALO3 and ALO5 were at around 873 K.

The conversion levels of ethene to CO_x (CO_2 and CO) are plotted in figure 1b. On the basis of the temperature (T_{50}) at which the ethene conversion level reached 50%, the oxidation activity of the alumina catalysts can be ordered as follows: ALO4, ALOA > ALO3 > ALO5 > ALO1 > ALO2.

3.2. NO + C_2H_4 and NO_2 + C_2H_4 + O_2 reactions

As can be seen in figure 2a, the activity of the aluminas for NO + C_2H_4 also depended on their types. Below 783 K, NO + C_2H_4 hardly occurred, while NO + C_2H_4 + O_2 greatly proceeded (figure 1). These results indicate that NO + C_2H_4 scarcely contributes to the NO reduction in NO + C_2H_4 + O_2, and the coexisting O_2 promotes the NO reduction regardless of the type of alumina. Such an oxygen effect was already reported for alumina and H-ZSM-5 and the effect is believed to be due to the formation of NO_2 as an intermediate by the reaction between NO and O_2 [17]. Figure 3a shows the activity of the aluminas for NO_2 + C_2H_4 + O_2. The temperatures (T_{M,NO_2}) giving the maximum NO_2 conversions (C_{M,NO_2}) shifted toward the lower temperature side by 50–150 K compared to the corresponding $T_{M,NO}$ values for NO + C_2H_4 + O_2. The results of figures 1, 2 and 3 suggest that coexisting O_2 reacts with NO to produce NO_2. Similar findings were already reported for NO + C_3H_8 + O_2 over alumina [17]. The order of the activity evaluated from both C_{M,NO_2} and T_{M,NO_2} was similar to that of the activity for NO + C_2H_4 + O_2, although the activity of ALO3 for NO_2 + C_2H_4 + O_2 was much lower unlike the situation in NO + C_2H_4 + O_2.

3.3. NO + O_2, NO_2 + C_2H_4 and C_2H_4 + O_2

For all the aluminas, the NO conversion to N_2 in the

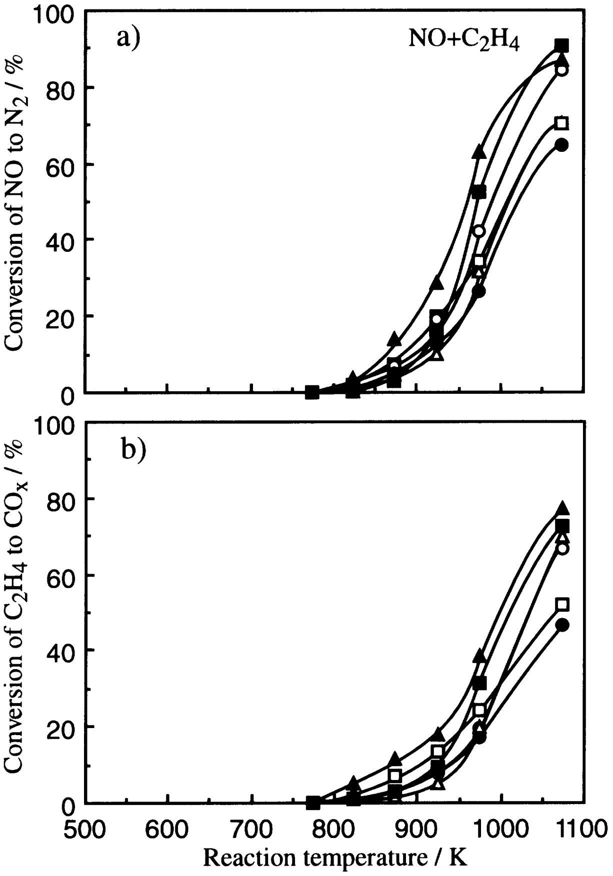

Figure 2. Temperature dependence of the activity of various alumina catalysts for $NO + C_2H_4$. (○) ALO1; (●) ALO2; (△) ALO3; (▲) ALO4; (□) ALO5; (■) ALOA.

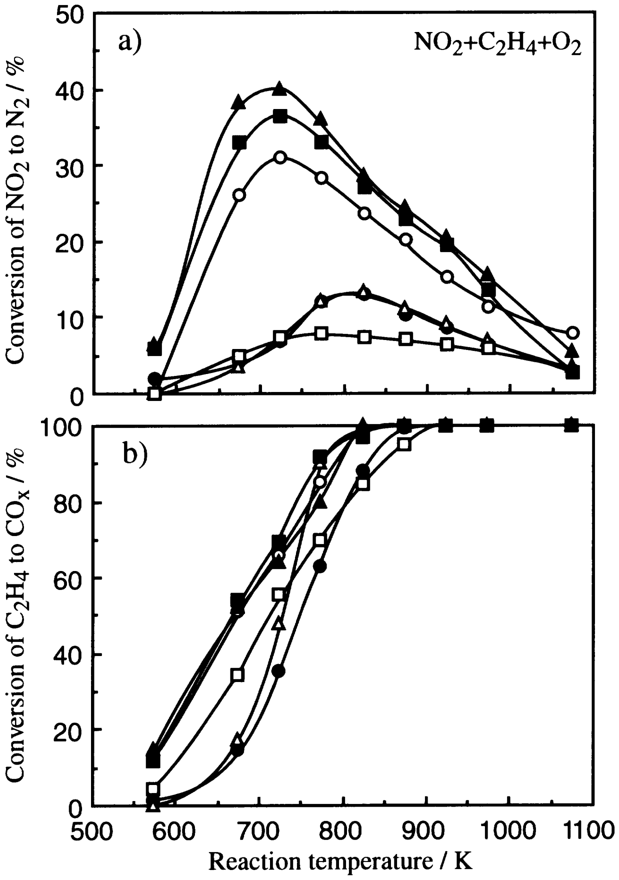

Figure 3. Temperature dependence of the activity of various alumina catalysts for $NO_2 + C_2H_4 + O_2$. (○) ALO1; (●) ALO2; (△) ALO3; (▲) ALO4; (□) ALO5; (■) ALOA.

presence of oxygen ($NO + C_2H_4 + O_2$) was higher than in the absence of oxygen ($NO + C_2H_4$), and, moreover, the NO_2 conversion to N_2 in $NO_2 + C_2H_4 + O_2$ took place at lower temperatures than NO conversion to N_2 in $NO + C_2H_4 + O_2$. These results indicate that $NO + C_2H_4 + O_2$ over the aluminas occur via the following mechanism, which is similar to the mechanism for $NO + C_3H_8 + O_2$ over alumina and H-zeolites [8,9]:

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

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

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

The differences in activity for the elementary reaction steps could result in a variety of activities of the aluminas for $NO + C_2H_4 + O_2$.

Figure 4 illustrates the activity of various aluminas for step (1). The activities at several temperatures are roughly equal to those in the literature [17]. Figure 5a shows the activity of the aluminas for step (2). Judging from the maximum conversions and the temperatures causing them in figures 1, 4 and 5, the activity order for step (1), step (2) and $NO + C_2H_4 + O_2$ can be summarized in table 1. For all the aluminas, there is a good correlation between the $NO_2 + C_2H_4$ reaction rates and the $NO + C_2H_4 + O_2$ reaction rates, but no correlation

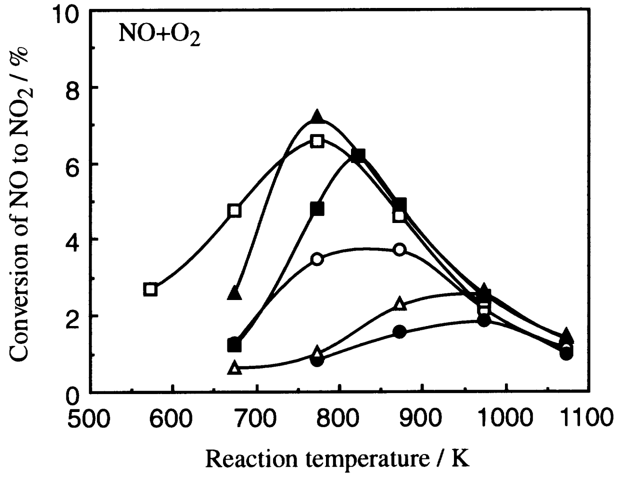

Figure 4. Temperature dependence of the activity of various alumina catalysts for $NO + O_2$. (○) ALO1; (●) ALO2; (△) ALO3; (▲) ALO4; (□) ALO5; (■) ALOA.

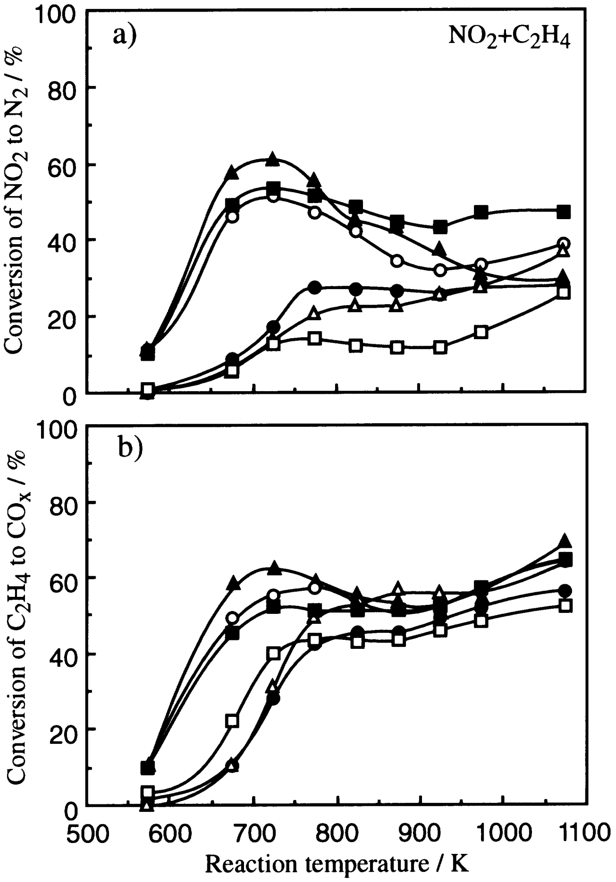

Figure 5. Temperature dependence of the activity over various alumina catalysts for $NO_2 + C_2H_4$. (○) ALO1; (●) ALO2; (△) ALO3; (▲) ALO4; (□) ALO5; (■) ALOA.

between the $NO + O_2$ rates and the $NO + C_2H_4 + O_2$ reaction rates. These relationships might be explained by assuming that step (2) is dominant. On the other hand, except for ALO5, there is a good correlation between the $NO + O_2$ and $NO_2 + C_2H_4$ reaction rates and the $NO + C_2H_4 + O_2$ reaction rates (see the order shown in parentheses), giving no clue for considering the rate-determining step. As to whether ALO5 is an exceptional alumina for $NO + C_2H_4 + O_2$, however, a further study is necessary.

If step (3) competes with step (2) in $NO + C_2H_4 + O_2$, the selectivity toward NO reduction must be decreased. The conversion levels of ethene to CO_x in $C_2H_4 + O_2$ are plotted in figure 6. Below 873 K, the activity of ALO1, ALO3 and ALO5 was higher, but above 873 K, the activity of ALO4 and ALOA was higher than that of the others. A comparison of figure 1b with figure 6 indicates that the ethene conversion level in $NO + C_2H_4 + O_2$ over ALO1 is lower than that in $C_2H_4 + O_2$ below 823 K, and the ethene conversion levels in $NO + C_2H_4 + O_2$ over ALO3 and ALO5 were comparable to that in $C_2H_4 + O_2$ below 723 K. Therefore, over ALO1, ALO3 and ALO5, step (3) will considerably compete with step (2) in these temperature regions. On the other hand, over ALO4 and ALOA step (3) will only slightly compete with step (2). Interestingly, both ALO4 and ALOA, having high NO-oxidation activity, showed moderate ethene-oxidation activity, although ALO2 having the lowest NO-oxidation activity showed the lowest ethene-oxidation activity. For all the aluminas, there was no correlation found between the activities for the two kinds of oxidations. These results suggest that a good alumina catalyst for $NO + C_2H_4 + O_2$ requires moderate ethene-oxidation activity too.

Table 1
The activity order[a] of various aluminas for $NO + O_2$, $NO_2 + C_2H_4$ and $NO + C_2H_4 + O_2$

Alumina	$NO + O_2$	$NO_2 + C_2H_4$	$NO + C_2H_4 + O_2$
ALO1	4th (3rd)	3rd (3rd)	3rd (3rd)
ALO2	6th (5th)	4th (4th)	5th (5th)
ALO3	5th (4th)	5th (5th)	4th (4th)
ALO4	1st (1st)	1st (1st)	1st (1st)
ALO5	2nd	6th	6th
ALOA	3rd (2nd)	2nd (2nd)	2nd (2nd)

[a] The ordinal numbers in the parentheses indicate the order in the activity of the aluminas except for ALO5.

The above consideration leads to the following general conclusion: an effective alumina catalyst for $NO + C_2H_4 + O_2$ should be active for both $NO + O_2$ and $NO_2 + C_2H_4$, and moderately active for $C_2H_4 + O_2$. ALO4 and ALOA, which were most active for $NO + C_2H_4 + O_2$, are thought to meet these crucial conditions.

3.4. *Characterization of aluminas and the factors affecting the activity for $NO + C_2H_4 + O_2$*

Next we will discuss the reason why the activity of alumina for $NO + C_2H_4 + O_2$ is dependent on its type. X-

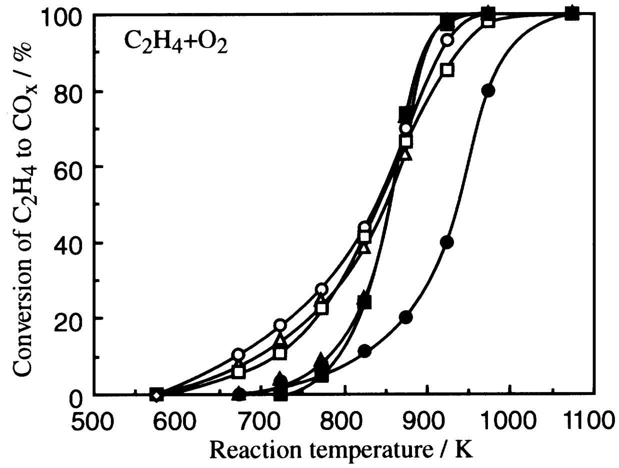

Figure 6. Temperature dependence of the activity of various alumina catalysts for $C_2H_4 + O_2$. (○) ALO1; (●) ALO2; (△) ALO3; (▲) ALO4; (□) ALO5; (■) ALOA.

Table 2
The specific surface area, mean pore radius, pore volume and composition of various alumina catalysts

Catalyst	Surface area ($m^2\ g^{-1}$)	Mean pore radius (nm)	Pore volume ($cm^3\ g^{-1}$)	Composition [a] (wt%)			
				Fe_2O_3	SiO_2	Na_2O	S
ALO1	158	7.9	0.62	0.03	0.03	0.03	0.05
ALO2	234	4.3	0.64	0.03	0.22	0.04	2.00
ALO3	120	5.8	0.47	0.01	0.01	0.3	n.d.
ALO4	149	7.2	0.73	0.01	0.01	0.01	n.d.
ALO5	204	3.5	0.42	0.68		0.02	0.57
ALOA	145	3.5	0.38	n.d. [b)]	n.d. [b)]	n.d. [b)]	n.d. [b)]

[a] Toshio Uchijima, Catalytic Science and Technology, 1, Kodansha (1991), p. 393.
[b] This work. n.d.: not detected.

ray diffraction analysis indicated that the crystal structure of all the aluminas heated at 1073 K was γ-type (JCPDS: 10-0425). Therefore, the difference in activity for $NO + C_2H_4 + O_2$ should be explained by factors other than crystal structure. Table 2 lists the BET specific surface area, pore radius and volume, and the composition of various aluminas. If the surface area is a critical factor determining the activity of an alumina for $NO + C_2H_4 + O_2$, ALO2 and ALO5, which have large surface area, should be more active than ALO4 or ALOA, but this is contrary to the facts (figure 1a and table 2). In addition, ALO4 and ALOA did not rank high in surface area, but they showed very high activity. Therefore, the surface area is not the critical factor. With regard to the pore structure, ALO1 was superior to ALOA, but the activity of the former was lower than that of the latter. Thus, the pore radius and volume are not critical factors either. It was also found that there was no significant difference in the XPS Al 2p spectrum of any of the alumina samples (not shown).

As can be seen in table 2, ALO4 contained the fewest impurities of the five commercial aluminas, and in ALOA the four kinds of impurities were not detected by XRF. A comparison of table 2 and figure 1 indicates that relatively pure aluminas show higher activity according to any measure than those containing impurities. Conversely, the impurities seem to strongly influence the NO reduction activity, especially in ALO2 and ALO5. Figure 7 shows the activity of some doped-ALOA catalysts for $NO + C_2H_4 + O_2$. Clearly, the additives altered the intrinsic activity of ALOA; Na and S species acted as inhibitors for $NO + C_2H_4 + O_2$, although the specific surface area of the doped-ALOA catalysts was almost the same as that of ALOA. The effects of the impurities on $NO + C_2H_4 + O_2$ as well as its elementary steps will be published separately.

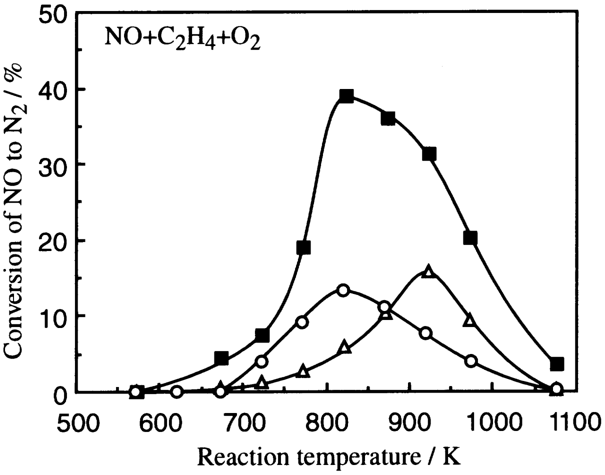

Figure 7. Temperature dependence of the activity of doped alumina catalysts for $NO + C_2H_4 + O_2$. (■) ALOA; (○) Na(0.9 wt%)/ALOA; (△) S(1 wt%)/ALOA.

4. Conclusion

(1) The catalytic activity of alumina for $NO + C_2H_4 + O_2$ depends strongly on the type used.

(2) The excellent performance of pure aluminas for $NO + C_2H_4 + O_2$ is attributed to their high activity for both $NO + O_2$ and $NO_2 + C_2H_4$.

(3) A critical factor affecting the activity of alumina for $NO + C_2H_4 + O_2$ seems to be neither the surface area nor pore structure, but the impurities; the higher the purity, the higher the activity.

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