Selective catalytic reduction of nitrogen oxides with hydrocarbons over Zn–Al–Ga complex oxides

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Selective reduction of NO with hydrocarbons was studied using metal oxide catalysts having a spinel structure. A Zn–Al–Ga complex oxide was found to be very active and selective for the catalytic reduction of NO with both C_3H_6 and CH_4. It was revealed that the role of oxygen at the initial stage of the reaction strongly depends on the reductants; oxygen is mainly used for NO oxidation to NO_2 in the reduction with CH_4, whereas it is used both for NO oxidation to NO_2 and oxidation of C_3H_6 to an active intermediate in the reduction with C_3H_6.

Keywords: nitrogen oxide, selective reduction, hydrocarbon, spinel

1. Introduction

Removal of nitrogen oxides (NO_x) in the exhaust gases from industrial boilers and vehicle engines is necessary to protect our environment. Selective catalytic reduction of NO_x with hydrocarbon reductants in excess of oxygen is an attractive means for purification of the exhaust gases, especially for purification of the gases containing excess oxygen emitted from lean-burn engines and diesel engines [1,2]. As a candidate of the catalyst for the NO_x selective reduction, ion-exchanged zeolites and metal oxides have been extensively studied [3–8]. In these studies, various light paraffins and olefins were used as a reductant. In terms of the activity of the NO_x selective reduction depending on the kinds of hydrocarbon, it has been reported that Cu-ZSM5 is more active with olefins than with paraffins such as CH_4 and C_3H_8, whereas a supported Ga catalyst is more active with paraffins than with olefins [3]. From the viewpoint of the NO_x removal from real exhaust, the catalyst is desired to be active with any kind of reductant.

In the present study, we examined complex oxides as the catalyst for the NO_x selective reduction because they had high thermal stability. As a result of many examinations, we found that Zn–Al–Ga complex oxide having a spinel structure was very active for the NO_x selective reduction with hydrocarbons. We focused on the catalytic behavior of the Zn–Al–Ga complex oxide catalyst in various gas compositions; the catalytic activity was measured for the selective reduction of NO and NO_2 with either CH_4 or C_3H_6 as a reductant. The influence of oxygen on the catalytic activities was also evaluated, and the role of oxygen in the NO_x selective reduction over the Zn–Al–Ga complex oxide catalyst was discussed.

2. Experimental

The Zn–Al–Ga complex oxide catalyst was prepared by coprecipitation of zinc, aluminum, and gallium nitrates followed by filtration and drying. Then, the dry material was calcined at 1073 K. The mole fraction in oxide basis of Zn, Al and Ga was 30, 35, and 35 mol%, respectively. Also, Al_2O_3 (γ; referred to as Al hereafter), Ga_2O_3 (β; Ga), $ZnAl_2O_4$ (Zn–Al), and $ZnGa_2O_4$ (Zn–Ga) were prepared in the same manner.

The crystal phases of the samples were confirmed by X-ray analysis. Their specific surface areas were measured with the BET method. Catalytic reaction experiments were performed using a fixed-bed flow reactor. A mixture of 1000 ppm NO_x, 1000 ppm hydrocarbon (CH_4 or C_3H_6) and 6% O_2 in helium was fed to 0.5 g of the catalyst at a rate of 100 ml/min. The effluent gas was analyzed with a gas chromatograph and a chemiluminescence NO_x analyzer after reaching a steady-state condition.

3. Results

The synthesized Zn–Al–Ga complex oxide was confirmed by X-ray analysis to be a solid solution having a spinel structure, as shown in figure 1. Al and Ga were also confirmed to be Al_2O_3 (γ) and Ga_2O_3 (β), respectively, having the spinel structure. Zn–Al and Zn–Ga were stoichiometric spinels as their own compositions, $ZnAl_2O_4$ and $ZnGa_2O_4$, respectively. The compositions of the prepared samples were considered to be nearly equal to the starting compositions, because the chemical analysis with ICP confirmed that the solutions after precipitation contained

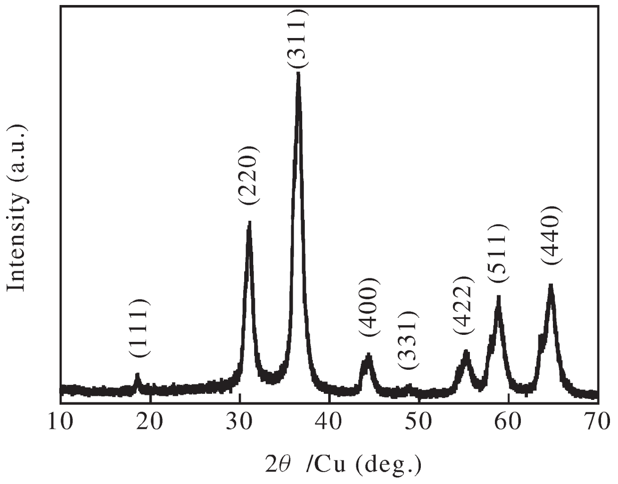

Figure 1. X-ray diffraction pattern of the Zn–Al–Ga complex oxides.

Table 1
Compositions and BET specific surface areas of prepared samples.

Catalyst	Phase	Composition (mol%)			Surface area
		ZnO	Al_2O_3	Ga_2O_3	(m^2/g)
Zn–Al–Ga	$ZnO–Al_2O_3–Ga_2O_3$ solid solution	30	35	35	56
Zn–Al	$ZnAl_2O_4$	50	50	0	20
Zn–Ga	$ZnGa_2O_4$	50	0	50	26
Al	Al_2O_3 (γ)	0	100	0	131
Ga	Ga_2O_3 (β)	0	0	100	16

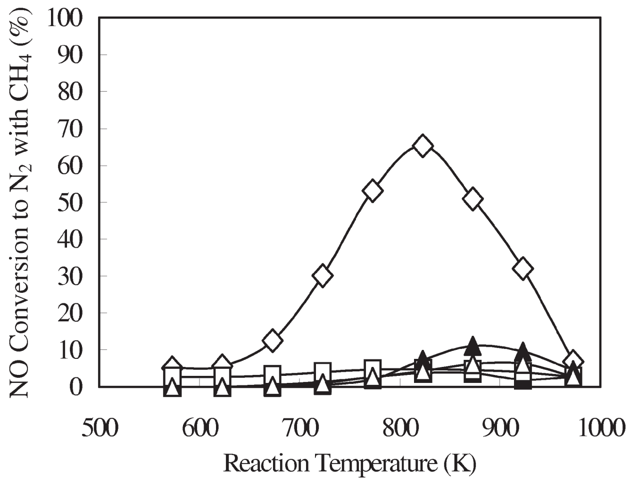

Figure 2. NO conversion in selective reduction with CH_4 on (◇) Zn–Al–Ga, (■) Zn–Al, (□) Zn–Ga, (▲) Al and (△) Ga oxide catalysts.

only trace amounts of metals. Their compositions and the specific surface areas are shown in table 1.

Figure 2 shows the temperature dependence of NO conversion to N_2 in the selective catalytic reduction with CH_4 over the prepared catalysts. Simple oxides (Al and Ga) and the complex oxides of the binary systems (Zn–Al and Zn–Ga) exhibited little activity. In contrast, the Zn–Al–Ga complex oxide successfully reduced NO with CH_4; NO was reduced above 700 K and the maximum NO conversion was about 65% at 823 K.

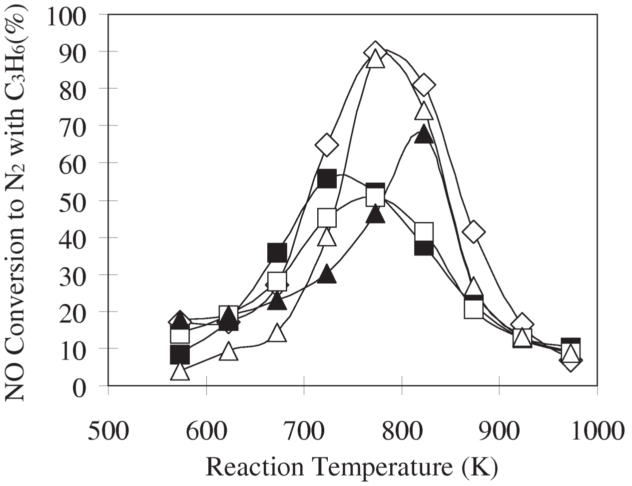

Figure 3. NO conversion in selective reduction with C_3H_6 on (◇) Zn–Al–Ga, (■) Zn–Al, (□) Zn–Ga, (▲) Al and (△) Ga oxide catalysts.

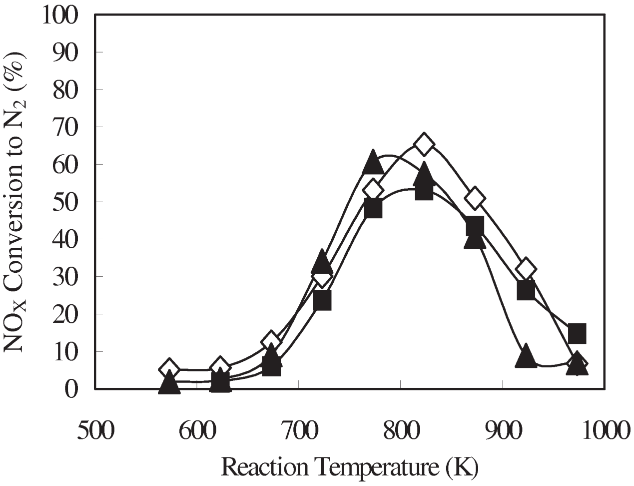

Figure 4. NO_x conversion with CH_4 on Zn–Al–Ga complex oxide catalyst in (◇) $NO–CH_4–O_2$, (■) $NO_2–CH_4–O_2$ and (▲) $NO_2–CH_4$ reactions.

Figure 3 shows the results of the reduction with C_3H_6, i.e., the temperature dependence of NO conversion to N_2 in the selective catalytic reduction with C_3H_6 over the prepared catalysts. Very high activities, i.e., nearly 90% in the conversion of NO at 773 K, were observed over Ga and Zn–Al–Ga. Referring to table 1, it was clear that the activities of these catalysts did not depend on only their specific surface areas; Ga with the smallest surface area exhibited higher activity, while Al with the largest surface area had relatively low activity. The decrease in the NO conversion above 800 K was due to the consumption of C_3H_6. Another possibility would be the change in the relative rate of NO reduction and hydrocarbon combustion with change in temperature. Although the NO conversions on Zn–Al and Zn–Ga were comparable to those on Zn–Al–Ga and Ga below 723 K, the decrease in the NO conversion was more significant at higher temperatures.

Figure 4 shows the NO_2 conversion to N_2 in the reduction of NO_2 with CH_4 over the Zn–Al–Ga complex oxide in the presence and the absence of oxygen as well as the

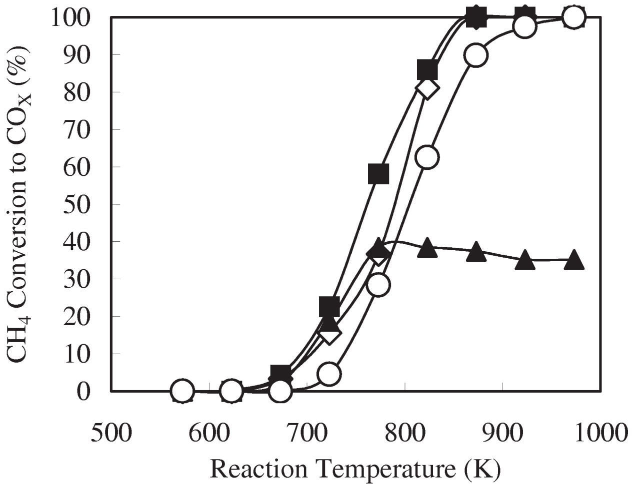

Figure 5. CH_4 conversion to CO_x on Zn–Al–Ga complex oxide catalyst in (◇) NO–CH_4–O_2, (■) NO_2–CH_4–O_2, (▲) NO_2–CH_4 and (○) CH_4–O_2 reactions.

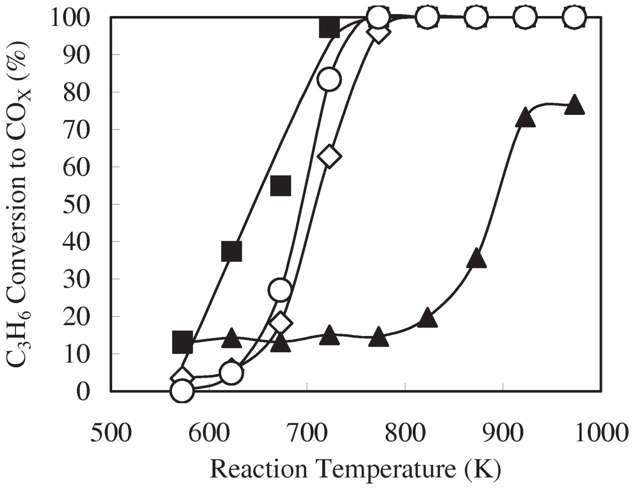

Figure 7. C_3H_6 conversion to CO_x on Zn–Al–Ga complex oxide catalyst in (◇) NO–C_3H_6–O_2, (■) NO_2–C_3H_6–O_2, (▲) NO_2–C_3H_6 and (○) C_3H_6–O_2 reactions.

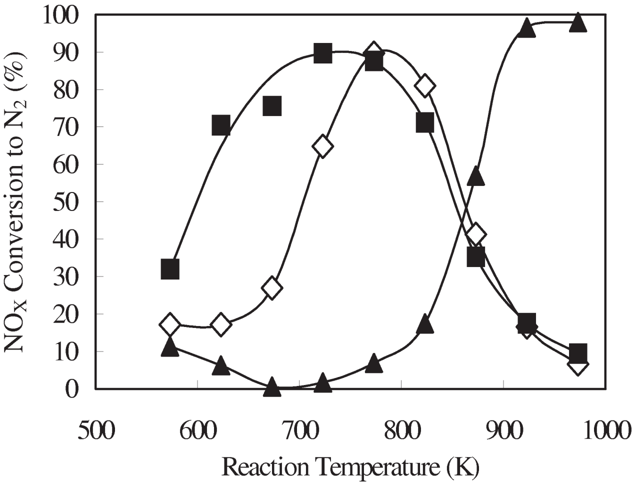

Figure 6. NO_x conversion with C_3H_6 on Zn–Al–Ga complex oxide catalyst in (◇) NO–C_3H_6–O_2, (■) NO_2–C_3H_6–O_2 and (▲) NO_2–C_3H_6 reactions.

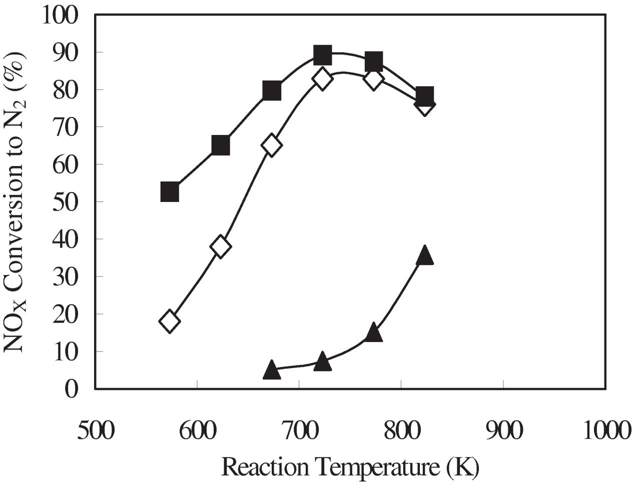

Figure 8. NO_x conversion with C_3H_6 on a mechanical mixture of Mn_2O_3 and Zn–Al–Ga complex oxide catalyst in (◇) NO–C_3H_6–O_2, (■) NO_2–C_3H_6–O_2 and (▲) NO_2–C_3H_6 reactions.

NO conversion in the NO–CH_4–O_2 reaction. The activity patterns were independent of the use of NO and NO_2: The NO_x conversion increased above 673 K, attained the maximum at 823 K, and then decreased because of the 100% consumption of CH_4, as shown in figure 5. In the NO_2–CH_4 reaction, although the NO_2 conversion changed in a similar way, the decrease in conversion at higher temperatures is considered to result from another reason. This is because the CH_4 conversion was below 50%, as shown in figure 5. A possible reason would be a decomposition of NO_2 into NO and O_2, which is thermodynamically favored at high temperatures. Actually, much NO was formed in the NO_2–CH_4 reaction at high temperatures. It should be noted that NO oxidation to NO_2 and NO_2 reduction to NO hardly occurred without hydrocarbons over this catalyst.

Figures 6 and 7 show the results in the reduction with C_3H_6. The NO_2 conversion in the NO_2–C_3H_6–O_2 reaction above 773 K was comparable to the NO conversion in the NO–C_3H_6–O_2 reaction. Below 673 K, however, the conversion in the reduction of NO_2 with C_3H_6 was much higher than that of NO, which is very different from the results of the reduction with CH_4 shown in figure 4. The absence of oxygen, on the other hand, resulted in quite low NO_2 conversion, i.e., less than 10% below 773 K. In these cases, coking, which was always a possible reason for low activities at low temperatures, was not observed.

In order to clarify the cause of the low NO conversion in comparison with that of NO_2 in figure 6, an oxidation catalyst was added to the Zn–Al–Ga complex oxide, and its effect on the reduction of NO_x was examined. Figure 8 shows the conversion of NO_x to N_2 over a mechanical mixture of Mn_2O_3 (1 wt%) and the Zn–Al–Ga complex oxide. Mn_2O_3 is known to be highly active for the oxidation of NO to NO_2 [8,9]. The addition of Mn_2O_3 enhanced the low-temperature activity in the NO–C_3H_6–O_2 reaction. As a result, the NO conversion in the NO–C_3H_6–O_2 reaction became close to that in the NO_2–C_3H_6–O_2 reaction. On the other hand, in the case of the NO_2–C_3H_6 reaction, the NO_2 conversion was not increased with the Mn_2O_3 addition.

4. Discussion

4.1. Catalytic activity and selectivity of Zn–Al–Ga complex oxide

The intermediate phase of the ZnO–Al_2O_3–Ga_2O_3 system, 30 mol% ZnO–35 mol% Al_2O_3–35 mol% Ga_2O_3 which had spinel structure, was more active for the NO_x selective reduction than the simple oxides, Al_2O_3 (γ) or Ga_2O_3 (β), and than the complex oxides of the binary system, $ZnAl_2O_4$ or $ZnGa_2O_4$. This high activity of the Zn–Al–Ga complex oxide was not only the effect of its specific surface area. In addition, it was active for the NO_x selective reduction with both an olefin and a paraffin. It should be also noted that only a few oxide catalysts have been reported to be active for the NO_x reduction with CH_4 [3,7,10]. Thus, the present catalyst has a possibility to be applied for various practical systems.

The present catalyst is the solid solution of ZnO–Al_2O_3–Ga_2O_3, which has a spinel structure. In the NO–C_3H_6–O_2 reaction, since the simple oxide of Ga exhibited as high catalytic activity as the Zn–Al–Ga complex oxide, the solid solution is not necessary responsible for the high activity and selectivity. In the NO–CH_4–O_2 reaction, on the other hand, the simple oxides of Ga and Al were much less active. A simple oxide of Zn exhibited only a slight catalytic activity. Thus, in this case, the formation of solid solution seems to be essential for the high activity. One possibility is the high dispersion of active metal, as suggested by Bethke et al. [6]. Another possibility is that the active metal such as Ga occupies a specific site in the spinel structure. This possibility is supported by the previous report that low-coordinate Ga ions are responsible for high activity of Ga_2O_3 catalysts [11]. Further study is in progress to elucidate the effect of local structure on the catalytic activity in the selective reduction of NO_x in the complex oxide catalyst.

4.2. Role of oxygen in the selective catalytic reduction of NO with CH_4 and C_3H_6

Although the Zn–Al–Ga complex oxide catalyst is effective for the selective catalytic reduction of NO_x with both CH_4 and C_3H_6, the catalytic behavior is significantly different from reductant to reductant, as can be seen from the comparison of figures 4 and 6.

In the case of CH_4 reductant, NO was reduced as much as NO_2 in all the temperature ranges, and the absence of oxygen did not affect the reduction of the NO_2. In the case of C_3H_6 reductant, NO_2 was reduced in the presence of oxygen much faster than NO at lower temperature, but the absence of oxygen remarkably decreased the NO_2 conversion. These results strongly suggest that the reaction mechanisms, especially the role of oxygen, are different from one another.

The CH_4–O_2 reaction without NO_x proceeded only above 723 K, as shown in figure 5, though the NO_2–CH_4 reaction proceeded even at 673 K. The addition of oxygen had little effect on the NO_2 conversion. These results indicate that CH_4 is oxidized more preferentially with NO_x than with oxygen. This is in line with the following reaction scheme reported by Yogo and Kikuchi [12]:

$$NO + (1/2)O_2 \rightarrow NO_2 \tag{1}$$

$$CH_4 + 2NO_2 \rightarrow CO_2 + 2H_2O + N_2 \tag{2}$$

The rate of the NO–CH_4–O_2 reaction was essentially equal to that of the NO_2–CH_4–O_2 reaction. This fact indicates that the NO oxidation (1) is faster than the reaction of CH_4 with NO_2 (2). The present reaction can be regarded as a competitive oxidation of hydrocarbons with NO and O_2. The reactant selectivity of NO in HC oxidation is defined as the ratio of oxygen atoms supplied from NO to all oxygen atoms reacted with CH_4 to CO and CO_2, which in the NO–CH_4–O_2 reaction can be represented by the ratio of $2N_2/(3CO + 4CO_2)$ [13]. Over the Zn–Al–Ga complex oxide catalyst, the selectivity at 723 K was 50%. This selectivity value is in good agreement with the above-mentioned scheme. Thus, in the NO–CH_4–O_2 reaction, the role of oxygen is considered to be the oxidation of NO but not the oxidation/activation of CH_4.

In the case of C_3H_6 reductant, oxygen also seems to be used to oxidize NO to NO_2, which is an active intermediate of selective reduction of NO, as reported previously [14,15]. This is because NO_2 was much reduced to N_2 with C_3H_6 in the presence of oxygen, compared with NO, and because the addition of Mn_2O_3, which is an active catalyst for the oxidation of NO to NO_2, increased the NO conversion to N_2 in a lower-temperature range.

In the absence of oxygen, however, NO_2 reduction with C_3H_6 to N_2 hardly proceeded below 800 K. This suggests that, besides the oxidation of NO to NO_2, oxygen plays an important role such as the partial oxidation of C_3H_6 to form an intermediate which reacts with NO_2 to form N_2. It has been reported that the first step of the NO–C_3H_6–O_2 reaction is the oxidation of C_3H_6 over the silica-supported cobalt catalyst [16]. This is in line with the results of NO_2–C_3H_6 reaction at high temperatures. As shown in figure 6, the NO_2 conversion into N_2 became larger only at high temperatures where most of NO_2 decomposed into NO and O_2. Therefore, oxygen is considered to be required for two processes; one is the oxidation of NO to form NO_2, and the other is the oxidation of C_3H_6 to form an active intermediate.

5. Conclusions

It was found that the Zn–Al–Ga complex oxide catalyst which had a spinel structure was highly active for the NO_x

selective reduction with both CH_4 and C_3H_6. In the case of the NO–CH_4–O_2 reaction, oxygen only oxidizes NO to NO_2 but does not activate CH_4. It seems that the direct reaction between NO_2 and CH_4 makes the NO_x reduction proceed. In contrast, using C_3H_6 as a reductant, oxygen is used in both the oxidation of NO to NO_2 and the oxidation of C_3H_6 to form an active intermediate. As a result of the reaction of these intermediates, NO is reduced to N_2.

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