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Catalytic Reduction of Nitrogen Oxides by Propene in the Presence of Oxygen over Cerium Ion-Exchanged Zeolites

II. Mechanistic Study of Roles of Oxygen and Doped Metals

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The mechanism of catalytic reduction of NO_x by propene in the presence of oxygen ($NO + C_3H_6 + O_2$ reaction) over Ce-ZSM-5 was studied, emphasizing on the roles of the coexisting oxygen and the doped metal ions. Na-, Sr-, and Cu-ZSM-5 were also studied for comparison. Catalysts having high activity for the oxidation of NO to NO_2 (Ce- and Cu-ZSM-5) were also very active for the $NO + C_3H_6 + O_2$ reaction. In contrast, Na- and Sr-ZSM-5, which have little activity for NO oxidation, were inactive for $NO + C_3H_6 + O_2$ reaction. Even the latter catalysts, however, became active in the case of the $NO_2 + C_3H_6 + O_2$ reaction. These results indicate that the initial step of the $NO + C_3H_6 + O_2$ reaction is the oxidation of NO to NO_2. NO_2 thus formed reacts with propene very rapidly to form N-containing organic compounds, as NO_2 rapidly disappeared even at a very low contact time for the $NO_2 + C_3H_6 + O_2$ reaction, and small quantities of C_2N_2 and HCN were formed, together with the imbalances of N, C, and O. It was further found for several ion-exchanged zeolites that the ratio between N_2 and N_2O produced by the reduction of NO was similar to those observed in the oxidations of nitromethane and trimethylamine for each catalyst, indicating that these two reactions proceed via similar reaction intermediate(s). On the basis of these results, the mechanism of the reduction of NO was deduced as follows. The overall reaction is divided into three steps: (1) NO is oxidized to NO_2 by oxygen, which is accelerated by Ce ion, (2) NO_2 reacts rapidly with propene to form organic nitro- or nitrite-compounds, and (3) these intermediates decompose to N_2 (probably in several parallel and consecutive steps) by the reaction with NO and/or O_2, where Ce ion also acts as a catalytic center.

$$NO + O_2 \underset{\text{step 1}}{\xrightarrow[\text{Ce}]{}} NO_2 \underset{\text{step 2}}{\xrightarrow{C_3H_6}} \begin{array}{c}\text{Organic compounds}\\ \text{containing N and O}\\ \text{(e.g., R-NO}_2\text{)}\end{array} \underset{\text{step 3}}{\xrightarrow[\text{Ce}]{NOx,\, O_2}} N_2, COx$$

INTRODUCTION

Iwamoto (1) and Held *et al.* (2), in addition to early patents (3), reported that the reduction of NOx by hydrocarbons proceeded in the presence of oxygen over Cu-zeolites. This reaction has attracted much attention in practical uses because the presence of oxygen accelerates the reaction. Since then several catalysts have been reported, including H-form zeolites (4), alumina (5), and Ga-zeolites (6). We reported that Ce-zeolites and Ce–Sr-zeolites showed very high catalytic activities for the reduction of NO by propene (7–9). However, the reaction is rather complicated and comprises several parallel reactions. Hence, deeper understanding of the mechanism is indispensable for the design of high-performance catalysts.

The essential feature of this reaction is that the reaction between NO and hydrocarbons is considerably accelerated by the presence of oxygen. This fact suggests two possibilities for the role of oxygen; oxygen reacts first either with NO or with hydrocarbons.

$$NO + 1/2O_2 \rightarrow \left.\begin{array}{r} NO_2 \\ \text{hydrocarbons}\end{array}\right\} \rightarrow\rightarrow N_2 \qquad [1]$$

$$\text{hydrocarbons} + O_2 \rightarrow \left.\begin{array}{r} \text{partially oxidized} \\ \text{intermediates} \\ NO \end{array}\right\} \rightarrow\rightarrow N_2 \qquad [2]$$

Hamada's group proposed (10) that the first step of this reaction was the oxidation of NO to NO_2 (Eq. [1]) over H-form zeolites and Al_2O_3, as suggested also by Kikuchi and co-workers (11). Hamada's group also indicated that over Cu-zeolites the partial oxidation of hydrocarbons was the first step, as also suggested by others (12, 13), Eq. [2]. Their proposal was based on the comparison of the conversions of C_3H_8 to COx for (a) $NO + C_3H_8 + O_2$, (b) $NO_2 + C_3H_8 + O_2$ and (c) $C_3H_8 + O_2$ reactions; (a) ≈ (b) > (c) for H-form zeolites and Al_2O_3, and (a) ≈ (c) for Cu-zeolites. However, Petunchi and Hall proposed that the oxidation of NO to NO_2 was the first step even for Cu-zeolites (14). Thus, the initial step of this reaction is still controversial. With regard to the steps following the first step, there have been very few reports except for those on Cu/Al_2O_3 (15), Cu-zeolites (12), and Al_2O_3 (16) that isocyanate species (-NCO) is probable intermediate and it decomposes to N_2.

In this study, we attempted to propose a mechanism for the reduction of NO by propene over Ce-zeolites which showed a high activity in our previous studies (7–9), focusing on the roles of oxygen and the doped Ce. First, we discuss the initial step by comparing the oxidation of NO to NO_2 and the reduction of NO (and NO_2) by propene over Na- and Ce-zeolites. In relation to the subsequent steps, temperature-programmed reaction was performed for adsorbed NO*x* in different atmospheres and the oxidation of nitromethane which is a model compound of the intermediates was compared with NO + C_3H_6 + O_2 reaction.

Ce-ZSM-5 has intermediate characteristics between Cu-ZSM-5 and H-ZSM-5. That is, Ce-ZSM-5 has a moderate activity for the oxidation of hydrocarbons (Cu-ZSM-5 > Ce-ZSM-5 > H-ZSM-5) (9) and, as described below, a high activity for the activation of NO. Hence, the essential part of the discussion below may be applicable to other related catalysts.

EXPERIMENTAL

Catalysts

Catalysts were prepared by the ion exchange of Na-ZSM-5 (SiO_2/Al_2O_3 = 23.3, provided by Tosoh Corporation: kind supply is greatly appreciated) and Na–Y (SiO_2/Al_2O_3 = 4.8, JRC-Z-Y4.8) in aqueous solutions of corresponding metal acetates (except for $[Pt(NH_3)_4]Cl_2$ and $[Pd(NH_3)_4]Cl_2$). The exchange level was estimated by measuring the concentration of Na eluted in the filtrate with atomic absorption spectroscopy. The details were described in the previous paper (9). Hereafter the catalysts are denoted by cation (ion exchange level)-Z (ZSM-5) and cation (ion exchange level)-Y (Y-zeolite), respectively (e.g., Ce(21)–Z, and Pt(10)–Y). The Ce-ZSM-5 catalyst prepared in this work showed higher activity for NO + C_3H_6 + O_2 reaction (Fig. 1b) than the Ce-ZSM-5 catalysts used in the previous work (9). This difference is probably attributed to the difference in the ion-exchange method. In this work, the ion-exchange of Ce was carried out twice at room temperature, while the ion-exchange was done once at 70–80°C in the previous work. Throughout this work the same Ce-ZSM-5, namely, Ce(19)–Z, was used.

Catalytic Reduction and Oxidation of NO

Five kinds of reactions were performed with a fixed-bed flow reactor; NO + O_2, NO + C_3H_6, NO + C_3H_6 + O_2, NO_2 + C_3H_6 and NO_2 + C_3H_6 + O_2 reactions. The catalysts were pretreated at 500°C for 2 h in He. Then a mixed gas (NO or NO_2, 1000 ppm; C_3H_6, 500 ppm; O_2, 2% (He balance)) was fed to 0.5 g of a catalyst at a rate of 150 $cm^3\ min^{-1}$ (space velocity = $10^4\ h^{-1}$). 10% conversion of NO*x* to N_2 under this conditions corresponds to the rate of N_2 formation of 6.24×10^{-7} mol min^{-1} g-cat^{-1}. The reaction temperature was lowered stepwise from the highest temperature after reaching steady-state at each temperature, by the reason described previously (9).

Temperature-Programmed Desorption/Reactions of Adsorbed NOx Species

TPD experiments were carried out in a fixed-bed flow reactor. Catalysts (0.5 g) were pretreated at 500°C for 2 h in He and cooled down to room temperature. Then a mixed gas of 3000 ppm NO and 2% O_2 (He balance) was fed at a rate of 150 $cm^3\ min^{-1}$ at room temperature. After the adsorption of NO was saturated (~2 h), the feed gas was changed to pure He to remove the gas phase and reversibly adsorbed NO*x*. After the NO*x* signal returned to the baseline level (~1 h), the temperature of the catalyst was raised at 5° min^{-1} to 500°C in various atmospheres: (1) He, (2) C_3H_6 (1000 ppm), (3) C_3H_6 (1000 ppm) + O_2 (2%), and (4) C_3H_6 (1000 ppm) + NO (3000 ppm). The effluent gases were analyzed as described in Analysis section.

Oxidation of Nitromethane

The oxidation of nitromethane was performed with a fixed-bed flow reactor. After the pretreatment at 500°C in He, a mixed gas of 1% CH_3NO_2 and 10% O_2 was fed to 0.5 g of a catalyst at a rate of 100 $cm^3\ min^{-1}$. Nitromethane was introduced to He by passing it through a saturator at 0°C.

Analysis

The effluent gases were analyzed by gas chromatographs (Shimadzu; GC-8A and Nippon Tyran; M-200, both are TCD) equipped with molecular sieve 5A columns for N_2 and CO and with Porapak Q columns for CO_2, N_2O, propene, C_2N_2, and HCN. The TCD sensitivities (peak area/concentration) of all components except for C_2N_2 and HCN were measured by using standard gases. The sensitivities of C_2N_2 and HCN were estimated in reference to N_2O by using the thermal conductivity data of C_2N_2, HCN and N_2O. NO*x* (NO and NO_2) were analyzed by a chemiluminescence NO*x* analyzer (Yanako; ELC-77A), which had two modes; the NO mode for the measurement of only NO and the NO*x* mode for NO + NO_2. The concentration of NO_2 was calculated by the difference between the values of the two modes.

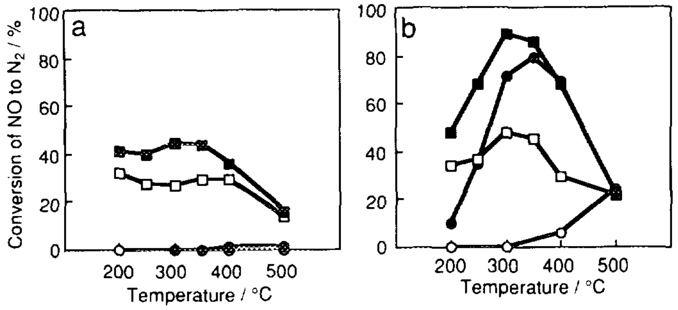


FIG. 1. Temperature dependence of conversion of NOx to N_2 for various reactions over (a) Na–Z and (b) Ce(19)–Z. ○, NO + C_3H_6; ●, NO + C_3H_6 + O_2; □, NO_2 + C_3H_6; and ■, NO_2 + C_3H_6 + O_2. NO or NO_2, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; total flow-rate, 150 cm^3 min^{-1}; catalyst weight, 0.5 g.

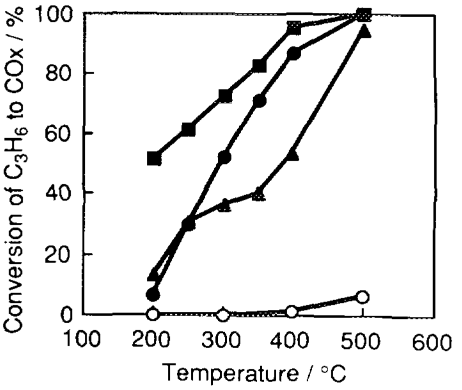


FIG. 2. Comparison of the conversions of propene to COx for NO + C_3H_6 (○), NO + C_3H_6 + O_2 (●), NO_2 + C_3H_6 + O_2 (■), and C_3H_6 + O_2 (▲) over Ce(19)–Z. NO or NO_2, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; total flow-rate, 150 cm^3 min^{-1}; catalyst weight, 0.5 g.

RESULTS

NO + C_3H_6 + O_2 and NO_2 + C_3H_6 + O_2 Reactions

Figure 1 shows the conversions of NOx to N_2 over Na-Z (Fig. 1a) and Ce-Z (Fig. 1b) for four reaction systems (NO + C_3H_6, NO + C_3H_6 + O_2, NO_2 + C_3H_6 and NO_2 + C_3H_6 + O_2 reactions). Hereafter conversion of NOx to N_2 is denoted by "reduction activity."

In the case of Ce-Z (Fig. 1b), NO and propene reacted very slowly in the absence of oxygen (NO + C_3H_6 reaction), but the presence of oxygen considerably promoted the reaction (NO + C_3H_6 + O_2 reaction). It is noteworthy that NO_2 reacted with propene even in the absence of oxygen (NO_2 + C_3H_6 reaction). The reduction activity for NO_2 + C_3H_6 + O_2 reaction was higher than that for NO + C_3H_6 + O_2 reaction in the low temperature region (NO_2 > NO), but they were identical in the high temperature region. On the other hand, in the case of Na-Z (Fig. 1a), although it showed little reduction activities for the NO reactions (NO + C_3H_6 and NO + C_3H_6 + O_2), it exhibited significant reduction activities for the NO_2 reactions (NO_2 + C_3H_6 and NO_2 + C_3H_6 + O_2). Thus, NO_2 reacted with propene regardless of the presence of oxygen on both Ce–Z and Na–Z, while NO reacted only in the presence of oxygen and Ce–Z.

The conversions of C_3H_6 to COx (CO + CO_2) for NO + C_3H_6, NO + C_3H_6 + O_2, NO_2 + C_3H_6 + O_2 and C_3H_6 + O_2 reactions over Ce-Z are shown in Fig. 2. The data in Fig. 2 for the first three reactions are from the same experiments shown in Fig. 1b. The ratios of CO_2 to CO observed for these reactions were about 2 to 4. The oxidation of propene started at about 200°C for both NO + C_3H_6 + O_2 and C_3H_6 + O_2 reactions, but the former became greater at 300–400°C where the conversion to N_2 showed a maximum for NO + C_3H_6 + O_2 reaction as shown in Fig. 1b. The oxidation of propene was faster for the NO_2 + C_3H_6 + O_2 reaction than those for the other two reactions. Thus, the presence of a small amount of NO or NO_2 (the concentration being 1/20 of oxygen) accelerated the oxidation of propene significantly.

Figure 3 shows the compositions of nitrogen-containing products from NO_2 + C_3H_6 + O_2 reaction over Na-Z and Ce-Z at 250 and 300°C. In the case of Na-Z, HCN was detected in addition to N_2, N_2O, and NO, and the nitrogen balance was not held, as reported previously (17). In contrast, no HCN was detected and nitrogen balance was held over Ce–Z at 300°C, although small amounts of HCN and the N imbalance were observed at 250°C. In all cases when the nitrogen balance was not held, the carbon and oxygen balances were also not good; the ratio (N : C : O) of the imbalances was approximately 1 : 1 : 1. The contents of nitrogen-containing products changed little at least for 6 h at 300°C over Na–Z, suggesting that the imbalances are mostly for the steady state. In order to determine the amount of N and C in the compounds adsorbed or deposited on the catalyst during the reaction, the com-

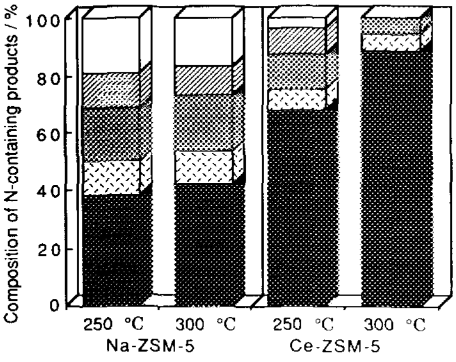


FIG. 3. Composition of nitrogen-containing products for NO_2 + C_3H_6 + O_2 reaction over Na– and Ce(19)–Z. ■, N_2; ▨, N_2O; ▩, NO; □, HCN; □, N imbalance {100-(N_2 + N_2O + NO + HCN)}.

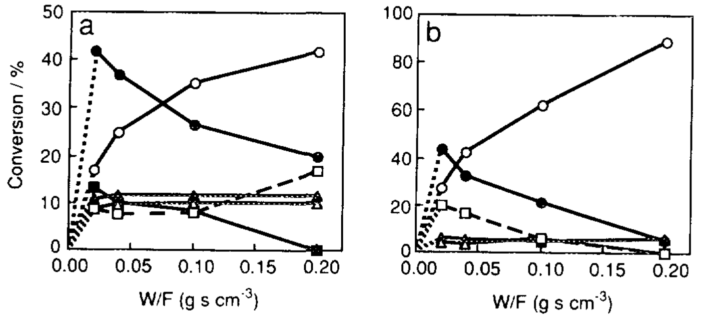


FIG. 4. Dependence of the % conversions to the N-containing products on contact time for NO_2 + C_3H_6 + O_2 reaction at 300°C over (a) Na–Z and (b) Ce(19)–Z. ○, N_2; ▲, N_2O; ●, NO; △, HCN; ■, C_2N_2; □, N imbalance.

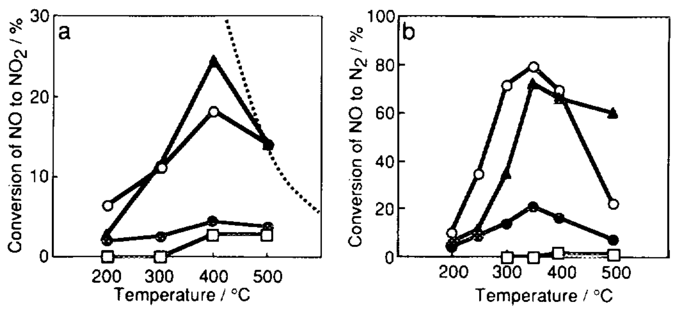


FIG. 5. Temperature dependence for (a) the oxidation of NO and (b) the reduction of NO over various ion-exchanged ZSM-5. (a) NO, 1000 ppm; O_2, 2%; (b) NO, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%. Total flow-rate, 150 cm^3 min^{-1}; catalyst weight, 0.5 g. □, Na–Z; ●, Sr(24)–Z; ○, Ce(19)–Z; ▲, Cu(19)–Z; ---, % conversion at equilibrium.

pounds were decomposed to N_2, N_2O, NO, CO, and CO_2 by heating the catalysts to 600°C in 2% oxygen. The amount of N collected accounted for only 5% of the whole N-imbalance. These facts indicate that the undetected compounds (N : C : O = 1 : 1 : 1) were formed mostly in the gas phase and a small part of them was deposited on the catalyst. Hereafter these compounds are denoted by the *undetected*.

Figure 4 shows the dependence of the conversions to the N-containing products on contact time (W/F) for NO_2 + C_3H_6 + O_2 reaction over Na–Z and Ce–Z at 300°C. Here the contact time is defined by W/F = (catalyst weight)/(total flow-rate). It was noted that NO_2 already disappeared even at W/F = 0.02 g s cm^{-3} (one tenth of the ordinary experimental condition) for both Ce–Z and Na–Z. There are two possible mechanisms with regard to this rapid disappearance of NO_2. One is that NO_2 reacts very fast with propene to form NO, and another is that it dissociates to NO ($NO_2 \rightarrow NO + 1/2O_2$). In order to examine these two possibilities, the dissociation of NO_2 was carried out over Na–Z and Ce–Z. The conversion of NO_2 to NO was only 2.9% over Na–Z and 3.7% over Ce–Z under the conditions of NO_2, 1000 ppm; O_2, 2%; temperature, 300°C; and W/F, 0.2 g s cm^{-3}, indicating the former possibility. Since NO_2 rapidly disappears, the reaction at higher contact time apparently becomes an NO + C_3H_6 + O_2 reaction. From this dependency on contact time, one might consider that NO is the reactive species rather than NO_2. However, as described below, it is likely that NO formed from NO_2 and propene is again oxidized to NO_2, which then reacts with propene.

Several compounds other than NO were formed rapidly, as well. C_2N_2 was detected in addition to HCN in the low W/F region with Na–Z. As W/F increased, C_2N_2 decreased, HCN little changed and the N imbalance slightly increased. On the other hand, over Ce–Z, no C_2N_2 was observed and the N imbalance diminished with an increase in W/F.

Oxidation of NO

The conversion of NO to NO_2 and the reduction activity for NO + C_3H_6 + O_2 reaction in the presence of catalysts are shown as a function of reaction temperature in Figs. 5a and b, respectively. The conversion of NO to NO_2 was only about 1% for an empty reactor at 30–500°C (NO, 1000 ppm; O_2, 2%; and total flow-rate, 150 cm^3 min^{-1}). Ce–Z and Cu–Z which had high reduction activities for NO + C_3H_6 + O_2 reaction showed high activities for the oxidation of NO, as well. On the other hand, Na–Z and Sr–Z showed low activities for both reactions. The conversions to NO_2 decreased above 400°C, as the reaction is limited by the thermodynamic equilibrium (a broken line). Even for Ce–Z and Cu–Z, the conversions of NO to NO_2 at the steady state (Fig. 5a) did not reach the equilibrium values below 400°C. In these experiments, a large quantity of NO was initially held by the catalyst and NO_2 was not observed just after the introduction of a mixed gas of NO + O_2, as shown in Fig. 6. Then NO_2

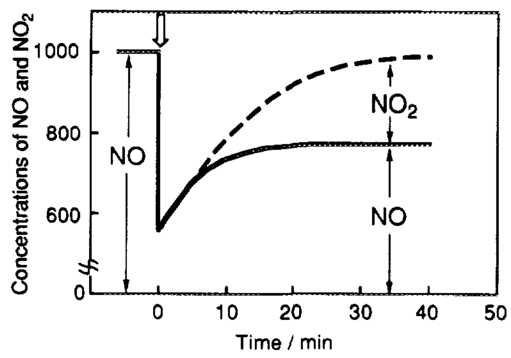


FIG. 6. Time course of the oxidation of NO over Ce(19)–Z at 300°C (change of the concentration at the exit at the initial stage). The open arrow indicates that a mixed gas of NO + O_2 was passed through the reactor at this point. NO, 1000 ppm; O_2, 2%; total flow-rate, 150 cm^3 min^{-1}; and catalyst weight, 0.5 g.

TABLE 1

Amount of Adsorbed NO*x* (NO + NO_2) Measured by TPD

Feed gas (adsorption temperature)	Amount of NO*x*/10^{-5} mol g^{-1}		
	Na-Z	Ce(19)-Z	Cu(19)-Z
NO + O_2 (200°C)	1.03	10.43	5.21
(300°C)	0.35	2.10	3.41
NO_2 + O_2 (300°C)	5.46	6.09	12.56

Note. Adsorption: a mixed gas of 1000 ppm NO and 2% O_2 is fed to 0.5 g of a catalyst at a rate of 150 cm^3 min^{-1}. Desorption: temperature is raised from room temp. to 600°C at 5° min^{-1} in He.

gradually appeared in the exit gas, the adsorption of NO being saturated. The uptake of NO was hardly observed when NO was introduced without O_2, indicating that NO adsorbed in oxidized states such as NO_2 and/or NO_3^-. As NO held by catalysts was entirely desorbed by TPD below 600°C, the amount was measured by TPD. Results are shown in Table 1. Ce-Z and Cu-Z which had higher activity for the oxidation of NO held much larger amounts of NO than Na-Z. Even Na-Z, however, held a substantial quantity of NO_2 in a NO_2 + O_2 stream.

Temperature-Programmed Desorption/Reactions of Adsorbed NOx

TPD profiles of NO*x* from Ce-Z are shown in Fig. 7. In a He stream (Fig. 7a), NO*x* species were desorbed mainly as NO_2 at 80, 110, and 360°C. NO_2 at 360°C was accompanied by the desorption of oxygen. The amount of NO*x* (NO + NO_2) desorbed in this temperature range was close to that adsorbed. Figure 7b shows TPD in the presence of C_3H_6. The NO_2 desorption peak at 360°C was gone, and N_2, N_2O, and NO were produced. N_2O was observed at 80°C, and NO and N_2 at 100 and 270°C, together with CO*x*. The total amount of nitrogen-containing products collected (NO_2, NO, N_2, and N_2O; 25-500°C) was 70% of the amount of adsorbed NO*x*. In the case of TPD in C_3H_6 + O_2, the amounts of N_2 and N_2O became greater than those observed for TPD in C_3H_6 only. The total amount of nitrogen-containing products observed in C_3H_6 + O_2 was 85% of the amount of adsorbed NO*x*.

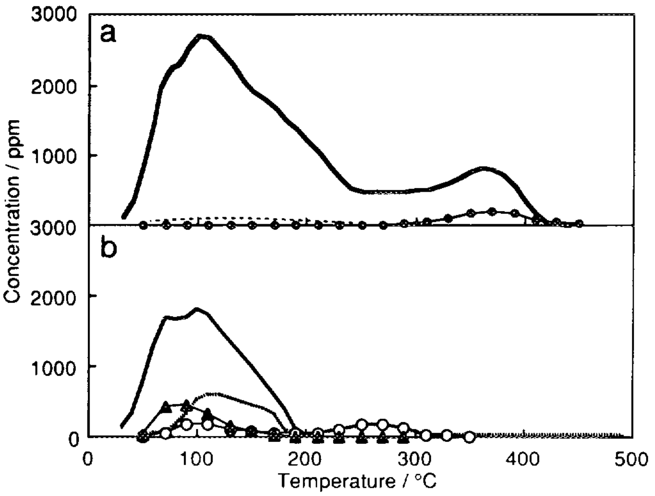


FIG. 7. Temperature-programmed reactions of adsorbed NO*x* species (a) in He and (b) in C_3H_6 (1000 ppm) over Ce(19)-Z. —, NO_2; ---, NO; —●—, O_2; —○—, N_2; —▲—, N_2O. Adsorption, NO (3000 ppm) + O_2 (2%); total flow-rate, 150 cm^3 min^{-1}; catalyst weight, 0.5 g; the rate of raising temperature, 5° min^{-1}.

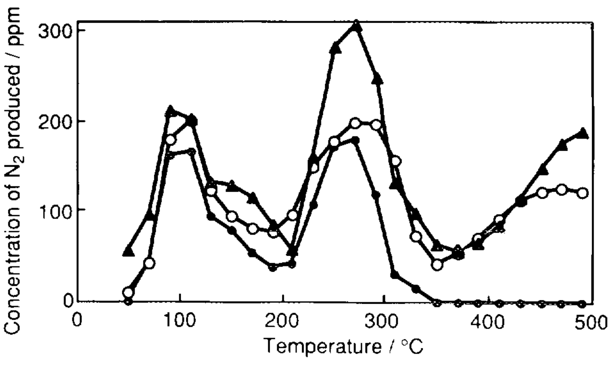


FIG. 8. Comparison of N_2 produced for temperature-programmed reaction in various atmospheres over Ce(19)-Z. ●, in C_3H_6 (1000 ppm); ○, in C_3H_6 (1000 ppm) + O_2 (2%); ▲, in C_3H_6 (1000 ppm) + NO (3000 ppm).

Figure 8 shows the comparison of N_2 formation for TPD in three different atmospheres; C_3H_6, C_3H_6 + O_2, and C_3H_6 + NO. The amount of N_2 formed was in the order of C_3H_6 + NO > C_3H_6 + O_2 > C_3H_6, indicating that the addition of NO or O_2 to C_3H_6 enhances the production of N_2 from the adsorbed NO*x*. In the case of C_3H_6 + NO, possibly N_2 was produced not only by the reaction between adsorbed NO*x* and propene, but also by the reaction between NO and propene which were fed in the gas stream. In order to examine this possibility, a mixture of C_3H_6 + NO was fed on a fresh catalyst. In this case N_2 was formed only at temperatures higher than 300°C. This fact indicates that N_2 produced below 300°C for TPD of adsorbed NO*x* in C_3H_6 + NO is derived from the reaction between adsorbed NO*x* and propene.

Oxidation of Nitromethane

The ratios between N_2 and N_2O produced for nitromethane oxidation over several metal ion-exchanged zeolites are shown in Fig. 9, together with the ratios observed for the reduction of NO and for the oxidation of trimethylamine (18) over the same catalysts. Although

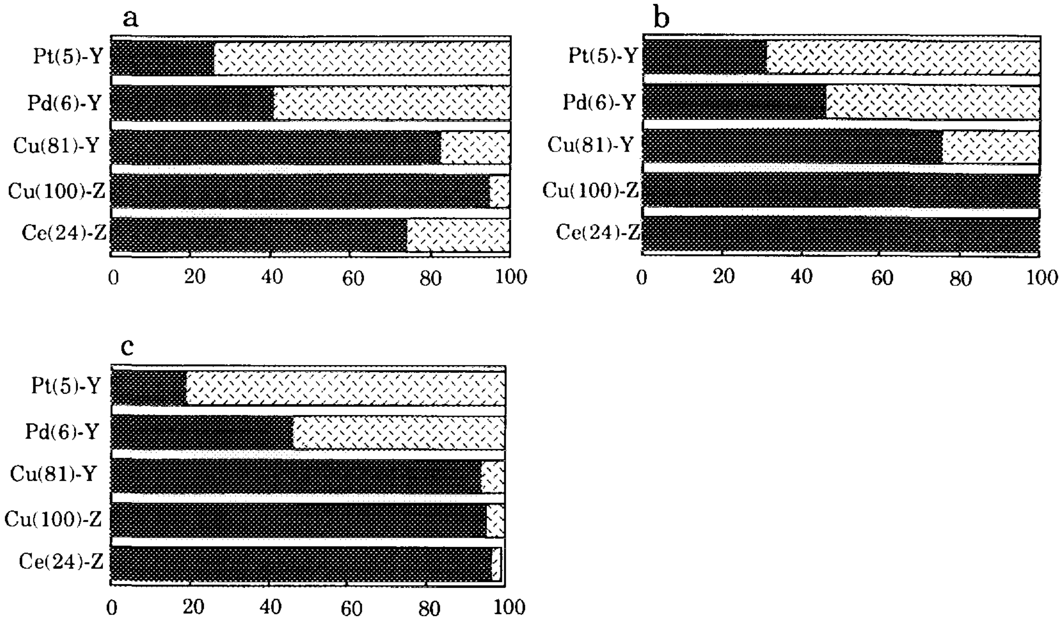


FIG. 9. Ratios between N_2 and N_2O (except NOx) in the products of (a) oxidation of nitromethane, (b) reduction of NO, and (c) oxidation of trimethylamine over various ion-exchanged zeolites. (a) CH_3NO_2, 1%; O_2, 10%; total flow-rate, 100 cm^3 min^{-1}; (b) NO, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; total flow-rate, 150 cm^3 min^{-1}; (c) $(CH_3)_3N$, 8000 ppm; O_2, 10%; total flow-rate, 50 cm^3 min^{-1}; all catalysts weight, 0.5 g; reaction temperature, 300°C (400°C only over Ce–Z and Cu–Z for (c)); ▩, N_2; ▨, N_2O.

NO was produced for the oxidation of nitromethane in addition to N_2 and N_2O, only the ratios between N_2 and N_2O are shown for comparison with the reduction of NO. It is remarkable that the ratios of the three reactions were similar for each catalyst. Difference is noted for the oxidation of nitromethane over Ce–Z, but N_2O in the products became very small at a slightly higher temperature (400°C), and the three ratios nearly agreed.

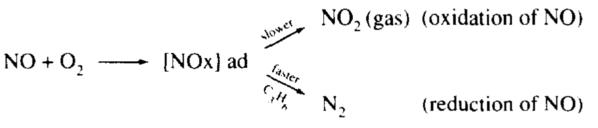
DISCUSSION

The mechanism of the reduction of NO by propene in the presence of oxygen over Ce–Z will be discussed, emphasizing on the roles of both oxygen and the doped Ce. The discussion below is mainly focused on the reaction in the low temperature region where the reaction between NO and propene hardly occurs in the absence of oxygen (below 350°C, Fig. 1b). As described in Introduction, oxygen plays an important role in the initial step of this reaction; oxygen reacts first with NO (Eq. [1]) or first with propene (Eq. [2]). Here, the discussion below is divided into two parts; the initial step and the subsequent steps.

The Initial Step

As shown in Fig. 5, correlation is noted between the rate of $NO + 1/2O_2 \rightarrow NO_2$ and that of $NO + C_3H_6 + O_2 \rightarrow N_2$. Both Ce–Z and Cu–Z which have high activities for the oxidation of NO are also active for $NO + C_3H_6 + O_2$ reaction. On the other hand, Na–Z and Sr–Z are less active for both reactions. Even over Na–Z, however, NO_2 readily reacts with propene to form N_2 ($NO_2 + C_3H_6 + O_2$ and $NO_2 + C_3H_6$ reactions) (Fig. 1a). As for Ce–Z, the significant reduction activities are observed both for $NO_2 + C_3H_6 + O_2$ and $NO + C_3H_6 + O_2$ reactions, although the former is higher than the latter in the low temperature region. These results indicate that the oxidation of NO is indispensable in the initial step for $NO + C_3H_6 + O_2$ reaction and that the doped metals play an important role in this step.

However, if the oxidation of NO is the initial step, there evolves a problem that the initial step is apparently slower than the overall reaction; the conversion of NO to NO_2 (Fig. 5a) is less than the conversion of NO to N_2 (Fig. 5b). This problem can be solved as follows. As shown in Fig. 6 and Table 1, a large amount of NO was held and the appearance of NO_2 was delayed in the case of the oxidation of NO. This fact suggests that the desorption of NO_2 is the slow step in the steady state of NO oxidation, while oxidized NOx species (NO_2 and/or NO_3^-) are formed rapidly on the surface (Eq. [3a]). On the other hand, in the case of $NO + C_3H_6 + O_2$ reaction, the oxidized NOx species on the surface can react with propene to form N_2 (Eq. [3b]) and this reaction can be faster.



$$NO + O_2 \longrightarrow [NOx]\ ad \begin{cases} \xrightarrow{\text{slower}} NO_2\,(\text{gas})\quad (\text{oxidation of NO}) & [3a] \\ \xrightarrow[C_3H_6]{\text{faster}} N_2\quad (\text{reduction of NO}) & [3b] \end{cases}$$

Here, another possible mechanism, that the partial oxidation of propene by oxygen takes place as the initial step, will be discussed. In fact, as shown in Figs. 1b and 2, NO started to be transformed to N_2, together with the propene oxidation in the case of the NO + C_3H_6 + O_2 reaction. However, there is a significant difference between the NO + C_3H_6 + O_2 and C_3H_6 + O_2 reactions above 300°C (Fig. 2). This fact, together with the close correlation between the $NO + 1/2O_2 \rightarrow NO_2$ reaction and the NO + C_3H_6 + O_2 reaction as discussed above, indicates that, in the case of NO + C_3H_6 + O_2 reaction, NO is first oxidized to NO_2, which reacts with propene more rapidly than oxygen. This consideration is supported by the fact that the addition of NO_2 to C_3H_6 + O_2 accelerates the propene oxidation more than the addition of NO (Fig. 2). These results were similar to the report from Hamada's group with regard to H-ZSM-5 and Al_2O_3 (10).

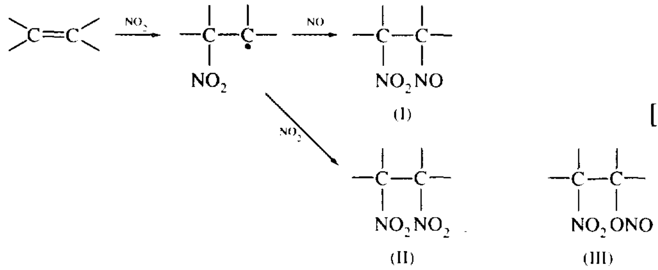
It may be appropriate to remark that the discussion here is focused on the main path of N_2 formation. Even though the oxidation of NO is the important initial step, the oxidation of propene by oxygen is dominant, the selectivity being at most 30%. The selectivity is defined by the ratio of the number of O atoms derived from NO to the number of O atoms of both CO*x* and H_2O produced (9).

Lastly, a comment may be made on the mechanism proposed by Inui *et al.* (19) and Burch *et al.* (20) that NO decomposes to N_2 and O_2 catalytically on the doped metal ions, which are readily oxidized but reactivated by the reduction by hydrocarbons. In the present study, the reaction between NO and propene is very slow in the absence of oxygen (Fig. 1b) and, moreover, the C_3H_6 + O_2 reaction is slower than the NO + C_3H_6 + O_2 reaction. These results indicate that this mechanism is less likely for Ce–Z under these reaction conditions.

The Subsequent Steps

After NO is oxidized to NO_2, three reactants are left; NO_2 (probably adsorbed NO*x* species), propene, and oxygen. NO_2 is able to react with propene to produce N_2 in the absence of oxygen (Fig. 1b), and this reaction is much faster than that between oxygen and propene (Fig. 2). This is the reason why the high selectivity of the utilization of propene was obtained for Ce–Z (9). Furthermore, as shown in Fig. 4, NO_2 disappears completely even at 1/10 of the ordinary W/F for NO_2 + C_3H_6 + O_2 reaction over both Na–Z and Ce–Z. Therefore, the step subsequent to the oxidation of NO must be the reaction between (probably adsorbed) NO_2 and propene (this step is termed the second step). The rate of the reaction between hydrocarbon and NO_2 may depend on the kind of hydrocarbons and catalysts. The reaction may not be rapid in the case of methane and catalytic centers such as Co (21), Ga (11), and Pd (22) seem to be necessary to activate hydrocarbons. In the third step, the compounds formed from NO_2 and propene are transformed to N_2.

Possible compounds formed from NO_2 and propene may be *R*-NO_2 and/or *R*-ONO, as reported in the literature for reactions of NO_2 with olefins (23–25). Examples are shown by Eq. [4]. First NO_2 is added to double bond of olefins to form organic nitro-compounds. Subsequently, nitronitroso- (I), dinitro- (II), and nitronitrite-compounds (III) are formed. We observed that the IR bands assignable to the organic nitro- and nitrite-compounds developed at room temperature to 200°C on the surfaces of Ce–Z (26), SiO_2, and Pt–SiO_2 (27) upon the exposure to a NO_2 + C_3H_6 + O_2 mixture, and the nitro-compounds were decomposed to N_2 by heating. This result indicates that the organic nitro-compounds may be the intermediates for the reduction of NO.

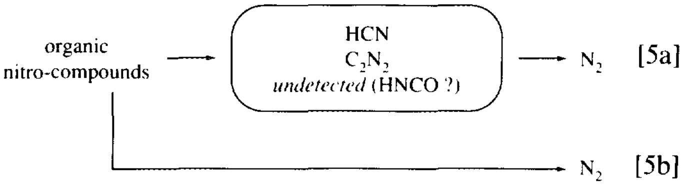


[4]

Results shown in Fig. 9 is additional circumstantial evidence to support the intermediacy of organic nitro-compounds. The ratio between N_2 and N_2O produced by the reduction of NO by propene is similar to that of the oxidation of nitromethane. Although the dependences of the N_2/N_2O ratio on contact time were not examined, the ratios probably reflect the initial product distribution, since the decomposition of N_2O to N_2 is very slow over these catalysts at 300°C, as reported by Li and Armor (28). Although it is unlikely that nitromethane is formed directly from NO_2 and propene, this result suggests that organic nitro-compounds formed from NO_2 and propene are the intermediates, which are transformed to N_2 and N_2O upon contact with O_2. Similar correlation has also been observed for the oxidation of trimethylamine for which N-oxides are the probable initial products (18).

Next, the third step where organic nitro-compounds are decomposed to N_2 will be discussed. As shown in Fig. 7b, adsorbed NO*x* species (e.g., NO_2 and NO_3^-) were converted to N_2, N_2O, and NO even in C_3H_6 only. However, the total amount of N-atom desorbed as contained in these products was smaller than that of adsorbed NO*x* species. If one considers that adsorbed NOx are all desorbed in TPD in He, the above fact indicates that a part of the adsorbed NOx species were transformed to the undetected compounds containing N and C, which are desorbed and/or deposited on the catalyst. As for TPD of NOx in C_3H_6 + O_2, the amount of N_2 detected was larger than that observed for the TPD in C_3H_6, and the desorbed N-atom was close to that of adsorbed NOx. The amount of N_2 produced is also larger in C_3H_6 + NO than in C_3H_6. These results indicate that oxygen and NO (and probably NO_2) promote the decomposition of the compounds containing N and C to form N_2 (the third step).

HCN, C_2N_2, and the *undetected* (compound(s) containing N : C : O in ca. 1 : 1 : 1 ratio) were observed for NO_2 + C_3H_6 + O_2 reaction (Figs. 3 and 4). Radtke *et al.* also reported that HCN was formed in the reduction of NO by propene and ethene over Cu-ZSM-5 (29). If one considers that an isocyanate species (–NCO) was observed on the catalyst by IR (26), HNCO can be a possible candidate of the *undetected*. These three compounds may be produced via the organic nitro-compounds formed initially from NO_2 and propene. As shown in Figs. 3 and 4, the amounts of these three compounds were smaller for Ce–Z than for Na–Z. The doped Ce probably accelerates the decomposition of the organic nitro-compounds to N_2 (Eq. [5b]) or the decomposition of HCN, C_2N_2, and the *undetected* into N_2 (Eq. [5a]).



Thus, the NO + C_3H_6 + O_2 reaction consists of several parallel and consecutive reactions and proceeds via several intermediates. The relative importance of these intermediates may change depending on the catalysts and reaction conditions. Detailed mechanism of nitrogen pairing is not clear yet. Both pairing from two nitro-molecules (e.g., Fig. 9a) and pairing between a nitro-molecule and NOx (e.g., Fig. 8) appear to exist.

As for Ce-ZSM-5, the roles of Ce ion are summarized as follows. The oxidation of NO (the first step) to NO_2 proceeds over the Ce ion. The second step (reaction between NO_2 and propene) does not need the Ce ion. The Ce ion plays an important role again in the third step (decomposition of organic nitro-compounds to N_2).

CONCLUSIONS

The reduction of NO by propene in the presence of oxygen over Ce–Z in the low temperature region is summarized as in Scheme 1.

$$\mathrm{NO} + \mathrm{O_2} \underset{\text{step 1}}{\xrightarrow[\mathrm{Ce}]{}} \mathrm{NO_2} \underset{\text{step 2}}{\xrightarrow{\mathrm{C_3H_6}}} \mathrm{R{-}NO_2} \underset{\text{step 3}}{\xrightarrow[\mathrm{Ce}]{\mathrm{NO}x,\ \mathrm{O_2}}} \mathrm{N_2}, \mathrm{CO}x$$

SCHEME 1

The overall reaction is divided into three steps. In the first step, NO is oxidized to NO_2. In the second step, NO_2 rapidly reacts with propene, forming organic nitro-compounds. The third step is the decomposition of them to N_2 in the presence of NOx or O_2 probably via several paths. It is supposed that the doped Ce and oxygen play important roles in both first and third steps.

As mentioned earlier, the mechanism discussed here is for the low temperature region of Ce–Z. However, a similar mechanism may be applied to catalysts having low activity for the oxidation of hydrocarbon such as H-ZSM-5 and Al_2O_3. As for the high temperature region or the other types of catalysts (e.g., Cu- and Pt-zeolites), mechanisms different from Scheme 1 may exist simultaneously.

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