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Catalytic Reduction of Nitrogen Monoxide by Propene in the Presence of Oxygen over Cerium Ion-Exchanged Zeolites. I.
General Characteristics of the Reaction and Effects of Alkaline Earth Metal Addition

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Catalytic reduction of dilute nitrogen monoxide by propene in the presence of excess oxygen was studied over various metal ion-exchanged zeolites. The presence of propene and oxygen was essential for the reaction. Ce–zeolites, particularly Ce–ZMS-5, showed a very high catalytic activity for the reduction of nitrogen monoxide. The high activity of Ce–ZSM-5 was attributed to its high selectivity (high efficiency of the use of propene for the reduction). The addition of alkaline earth metals to Ce–ZSM-5 enhanced the activity considerably and the Ce–ZSM-5 containing alkaline earth metals showed good performance even at a very high space velocity (GHSV=10^5 h^{-1}).

Nitrogen oxides, NO_x, are the major air pollutants that cause photochemical smog and acid rain. They are also injurious to the human body, especially to the nervous system and the respiratory organs. Artificial sources of nitrogen oxides are divided into stationary sources (e.g., power plants) and mobile sources (e.g., automobiles). Selective catalytic reduction (SCR) using ammonia as a reductant is currently applied to the former, using a V_2O_5 supported titania catalyst.[1] In case of the latter, nitrogen oxides from gasoline-engined automobiles are eliminated by means of so-called "three-way catalyst".[2] However existing catalysts cannot be applied to the emission of diesel and lean-burn gasoline engines, which are mobile and of small-scale and the exhaust gas of which contains excess oxygen.

Recently, Iwamoto et al.[3] and Held et al.,[4] in addition to early patents,[5] reported that catalytic reduction of nitrogen oxides occurs by using hydrocarbons as reductants in excess of oxygen over copper ion-exchanged zeolite. Afterwards many researchers reported various catalysts, for example, H-form zeolite,[6] alumina,[7] Fe-silicate,[8] Cu-silicate,[9] Ga-zeolite,[10] and Co-zeolite.[11]

We previously reported that Ce–zeolite was active for the reduction of nitrogen monoxide by propene in the presence of oxygen.[12] The activity was further enhanced by the addition of alkaline earths or an increase of Ce-doping.[13] In this work, we attempted to clarify the behavior of these reaction systems as functions of reaction temperature, partial pressures of oxygen and hydrocarbons, space velocity, etc., paying attention to the correlation between the production of N_2 and the combustion of hydrocarbons (selectivity). We also investigated in more detail the effects of the addition of various metal cations as a secondary component to the Ce–zeolite.

Experimental

Catalysts. The catalysts were prepared by the ion-exchange of Na–ZSM-5. The Na–ZSM-5 (SiO_2/Al_2O_3=23.3) was provided by Tosoh Corporation. To obtain the complete Na ion-exchanged ZSM-5 as a starting material for cation exchange, Na–ZSM-5 was stirred in sodium acetate solution (0.1 M, 1 M=1 mol dm^{-3}) for 24 h and then thoroughly washed by deionized water. Afterward the ion-exchange was done for 24 h by using aqueous solutions of various metal salts. The metal salts used were the acetate salts of metal compounds except for indium ($InCl_3$), platinum ($[Pt(NH_3)_4]Cl_2$), and palladium ($[Pd(NH_3)_4]Cl_2$). After the exchange the solid was filtered, washed with deionized water, and dried at 100 °C overnight. H–ZSM-5 was prepared by ion-exchange with ammonium nitrate solutions, followed by drying at 100 °C and calcination in air at 500 °C for 4 h. Since the ion-exchange of Ce ion to ZSM-5 was difficult and the highest ion-exchange level of Ce–ZSM-5 prepared as mentioned above was about 25%, the ion-exchange was done at 150 °C and 4 atm in an autoclave to obtain high ion-exchange levels for Ce–ZSM-5. Ce–ZSM-5 catalysts containing additional metal ion species were prepared by the ion exchange of Ce–ZSM-5 by the second metal ions.

The exchange level was estimated by measuring the concentration of Na ion eluted in the filtrate with atomic absorption spectroscopy. The amount of Ce eluted in the ion exchange of Ce–ZSM-5 with the second metal ion species was not measured. But it is considered that the additional metals are mostly exchanged for Na ion, because the amount of doped metals calculated from the amount of Na eluted was close to the total amount of metal salts contained in the aqueous solutions used for the second ion-exchange. Hereafter the sample was denoted by cation (exchange level)-Z (e.g., Ce(20)-Z). The exchange level of Ce-Z prepared in an autoclave was 60% and this was denoted by Ce(60)*-Z. Although it had the XRD pattern of ZSM-5, the peak intensities were about one third of those of Na-Z, and very weak broad peaks due to CeO_2 were observed, suggesting that a part of Ce exists in the form of CeO_2 supported on ZSM-5 in addition to Ce existing in ion-exchange sites. XRD patterns of the catalysts prepared by the ordinary ion exchange method were the same as that of Na-Z. The powder samples were pressed into tablets at 200 kgf cm^{-2} and then sieved to 36/60 powders, which were used for the catalytic reaction.

Reaction Procedure. The catalytic reduction of ni-

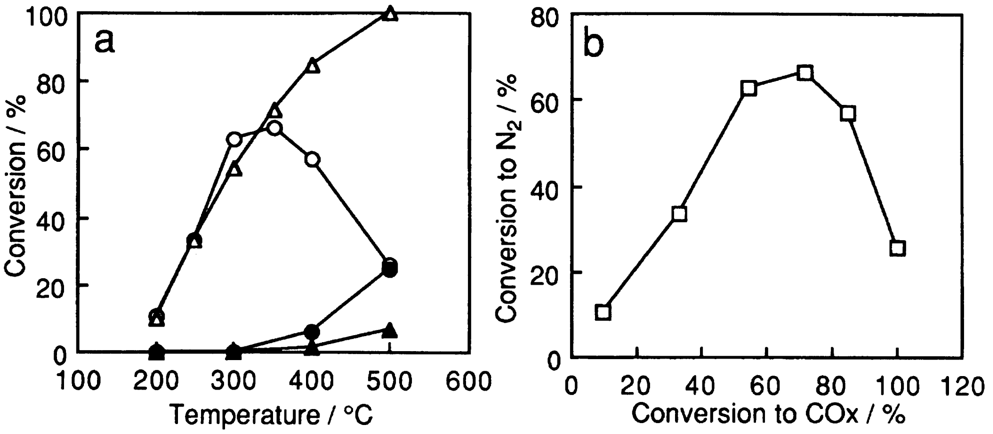

Fig. 1. (a) Comparison between $NO+C_3H_6$ and $NO+C_3H_6+O_2$ reactions over Ce(21)-Z and (b) correlation between the conversion of C_3H_6 to CO_x and the conversion of NO to N_2 for $NO+C_3H_6+O_2$ reaction. Conversions of NO to N_2 (●), (○) and of C_3H_6 to CO_x (▲), (△). ● and ▲ for $NO+C_3H_6$ reaction, ○ and △ for $NO+C_3H_6+O_2$ reaction, respectively. NO; 1000 ppm, C_3H_6; 500 ppm, O_2; 2%, total flow-rate; 150 $cm^3\,min^{-1}$, and catalyst weight; 0.5 g.

trogen monoxide was done with a fixed-bed flow reactor. The catalyst was treated at 500 °C for 2 h in He. Then a mixed gas of 1000 ppm NO, 2% O_2, and 500 ppm propene (in He) was fed to 0.5 g of catalyst at a rate of 150 $cm^3\,min^{-1}$ (space velocity$=10^4\,h^{-1}$); these are the standard conditions in this study. In most cases, the reaction temperature was lowered stepwise from 500 °C to 200 °C at 50 or 100-deg intervals. Steady states were confirmed at each temperature. When the temperature was raised stepwise from the low-temperature side, the carbon balances at lower temperatures were not good and the color of the catalyst turned to black, indicating that carbon was deposited on the catalyst. Although the steady-state activities at each temperature for the experiments in which the temperature was raised and those for the decreasing-temperature experiments were similar, the initials activity in the increasing-temperature experiments was much higher than steady-state activity and the carbon balance exceeded 100%. On the other hand, the activity changed little and reached steady-state rapidly in the decreasing-temperature experiments. Hence, in most experiments of this study the reaction temperature was decreased stepwise from the highest temperature after reaching steady-state.

Analysis. The effluent gas was analyzed by a gas chromatograph (TCD) with a molecular sieve 5A column for nitrogen and carbon monoxide and with a Porapak Q column for carbon dioxide, nitrous oxide, and propene. The catalytic activity for the reduction of nitrogen monoxide was evaluated by the conversion of NO to N_2.

Results and Discussion

In our previous study,[12] we reported that among lanthanide-doped Y zeolites, Ce–Y zeolite showed the highest catalytic activity for the reduction of nitrogen monoxide in propene and oxygen and that the order of activity was similar to that of the activity for propene oxidation. As for the carrier of Ce, the activity was in the order of Ce–ZSM−5>Ce–Y>CeO_2/Al_2O_3. Hence, ZSM-5 was chosen as the carrier in this study and various metal cations including lanthanides were added to ZSM-5.

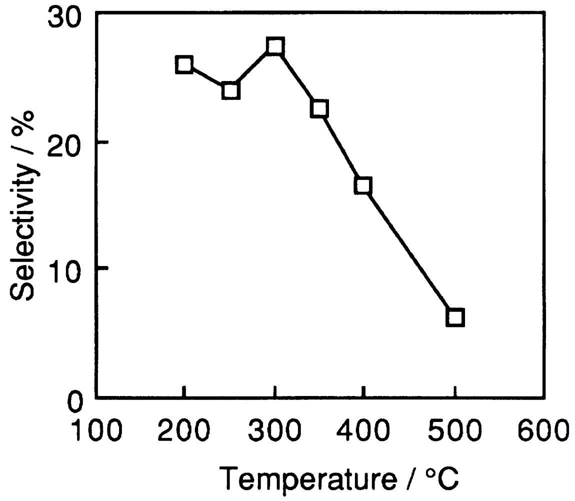

Fig. 2. Temperature dependence of the selectivity of $NO+C_3H_6+O_2$ reaction over Ce(21)-Z (the data correspond to those in Fig. 1).

In Fig. 1a, the results for $NO+C_3H_6$ and $NO+C_3H_6+O_2$ reactions over Ce-Z are compared. In the former system (absence of O_2), neither nitrogen monoxide nor propene reacted in the lower temperature range, and they gradually started to react above 400 °C. On the other hand, in the latter system (presence of O_2), nitrogen monoxide began to be transformed to nitrogen at as low as 200 °C. With increase in temperature, the conversion of NO to N_2 initially increased in parallel with the conversion of propene to CO_x, but with further increases in temperature the conversion to N_2 decreased, while the conversion to CO_x continued to increase. Under these conditions, neither N_2O and NO_2 were formed. These facts indicate that the presence of oxygen enhances significantly the reduction of nitrogen monoxide and that the reduction of nitrogen monoxide

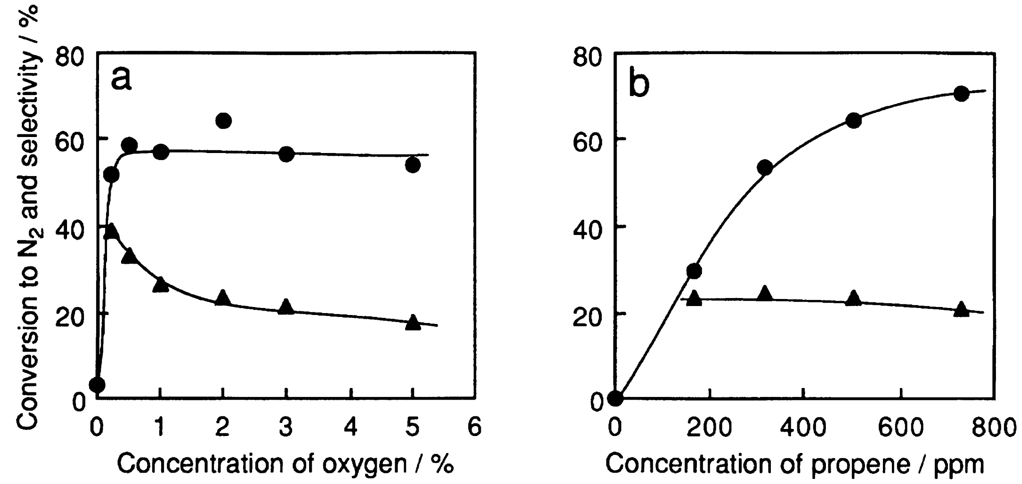

Fig. 3. Conversion of NO to N_2 (●) and selectivity (▲) as a function of (a) oxygen and (b) propene concentrations for Ce(18)-Z. (a) NO; 1000 ppm, C_3H_6; 500 ppm, O_2; 0 —5%, (b) NO; 1000 ppm, C_3H_6; 0—730 ppm, O_2; 2%. total flow-rate; 150 cm^3 min^{-1}, catalyst weight; 0.5 g, and reaction temperature; 350 °C.

Table 1. Maximum Conversions of Nitrogen Monoxide Observed for Various Ion-Exchanged ZSM-5

Catalyst	Maximum conv. to N_2/%	Conv. to CO_x/%[a)]	Sel./%[a)]	Temp/°C[a)]
Ce(21)-Z	66.2	71.8	22.5	350
Ce(60)*-Z	84.3	85.0	24.3	300
La(17)-Z	21.2	62.4	8.6	500
Pr(16)-Z	29.7	70.3	10.8	500
Nd(18)-Z	12.2	33.6	9.2	500
In(50)-Z	47.6	100	10.7	400
Pb(100)-Z	65.4	75.2	20.2	400
Cu(100)-Z	56.2	99.9	12.5	300
Sr(24)-Z	20.7	20.4	25.2	400
H(100)-Z	27.6	45.1	17.2	400
Na-Z	1.4	40.6	0.8	400

a) Conversion of C_3H_6 to CO_x, selectivity and the reaction temperature when the maximum conversion of NO to N_2 was obtained for each catalyst under the following conditions. NO; 1000 ppm, C_3H_6; 500 ppm, O_2; 2%, total flow-rate; 150 cm^3 min^{-1}, and catalyst weight; 0.5 g.

links closely with the combustion of propene, as in the case of Cu-ZSM-5 and H-ZSM-5.[3,6)]

In the $NO+C_3H_6+O_2$ system, it is inevitable that a part of propene is oxidized wastefully by oxygen as a side reaction (Reaction 2) in addition to being used for the reduction of nitrogen monoxide (Reaction 1). Figure 1b shows the correlation between the conversions of NO and C_3H_6 (data are from Fig. 1a). At low conversion levels, both conversions increase in parallel, but the conversion to N_2 declines as the conversion of C_3H_6 approaches 100%. A high conversion to N_2 would be obtained if the initial slope was steep and it continued to high conversion levels of C_3H_6.

$$NO,\ C_3H_6,\ O_2 \longrightarrow N_2,\ CO_x,\ H_2O \qquad (1)$$

$$C_3H_6,\ O_2 \longrightarrow CO_x,\ H_2O \qquad (2)$$

Here the concept of "selectivity" which is defined by Eq. 3 is introduced as the measure to express the preference of Reaction 1 to Reaction 2, that is, the efficiency of propene use.[12,13)] This applies when the product from NO is N_2 and those from C_3H_6 are CO, CO_2, and H_2O as in this case.

(% Selectivity)
= 100 × (number of oxygen atoms from NO consumed for oxidation of propene)/(number of total oxygen atoms consumed for oxidation of propene)
= 100 × (number of N_2 formed) × 2/
[(number of CO formed) + (number of CO_2 formed) × 2
+number of H_2O formed)] (3)

Figure 2 shows the temperature dependence of the selectivity of Ce-Z for the $NO+C_3H_6+O_2$ reaction (the data correspond to those in Fig. 1). The selectivity decreased with increasing temperatures above 300 °C, which indicates that Reaction 2 tends to prevail at higher temperatures. Although selectivities are only 25% at most in appearance, if one takes into account that the number of oxygen atoms in NO is only 2.4% of total oxygen atoms in the reaction gases, the selectivity of 25% means that Reaction 1 proceeds very selectively over Reaction 2.

The activity (=conversion of NO to N_2) is expressed by Eq. 4.

Activity(= % conversion of NO to N_2)
= (constant) × (% selectivity)
×(% conversion of C_3H_6 to CO_x) (4)

According to Eq. 4, the decrease in the activity at high temperature as shown in Fig. 1a is due to the decrease in the selectivity shown in Fig. 2, that is, the progress of

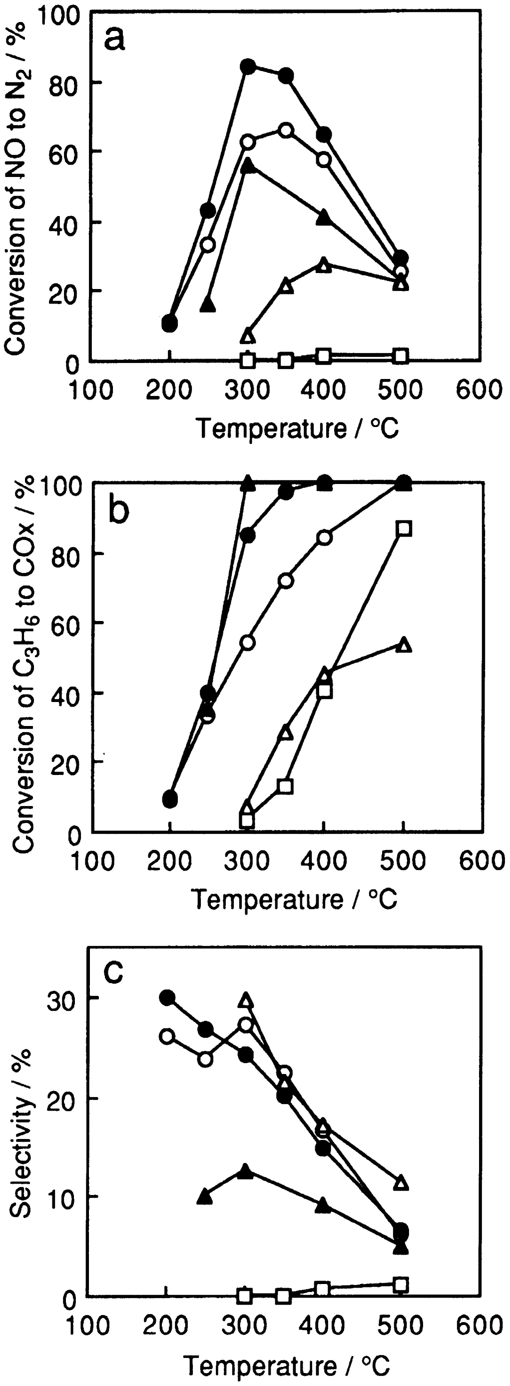

Fig. 4. Temperature dependence of (a) conversion to N_2, (b) conversion to CO_x, and (c) selectivity for $NO+C_3H_6+O_2$ reaction over various cation exchanged ZSM-5. NO; 1000 ppm, C_3H_6; 500 ppm, O_2; 2%, total flow-rate; 150 $cm^3\ min^{-1}$, and catalyst weight; 0.5 g. (○); Ce(21)-Z, (●); Ce(60)*-Z, (▲); Cu(100)-Z, (△); H-Z, and (□); Na-Z.

wasteful oxidation of propene with O_2 with increasing temperature (Reaction 2).

Figure 3 shows the conversion to N_2 as a function of oxygen and propene concentrations over Ce-Z at 350 °C. Nitrogen monoxide was hardly reduced in the absence of oxygen as described above (Fig. 1). The reduction began by the addition of a very small amount of oxygen (0.2%), and then the activity changed little up to 5% of O_2. On the other hand, the selectivity gradually decreased with increases in the oxygen concentration. Thus, the reason why there was little change of the activity with increasing oxygen concentration in spite of the decrease in the selectivity is the increased oxidation of propene (cf. Eq. 4). As for the dependence on the propene concentration, the activity increased from zero with increases in the propene concentration, while the selectivity changed little. This indicates that nitrogen monoxide does not directly decompose to nitrogen and oxygen ($2NO \rightarrow N_2+O_2$) under these conditions and that oxygen and hydrocarbons are indispensable for this reaction system and the role of oxygen is essential for the interpretation of the mechanism. We previously proposed a mechanism in which NO is oxidized to NO_2 first and then NO_2 reacts with propene.[14] In short, this mechanism was derived for example from the following facts. Over Na-Z, which had a low activity for NO oxidation, the $NO+C_3H_6+O_2$ reaction hardly took place, while the $NO_2+C_3H_6+O_2$ reaction proceeded significantly. On the other hand, Ce-Z, which had a high activity for NO oxidation, was highly active for both reactions, the rate of the latter being slightly greater. The reaction mechanism will be discussed in detail in a forthcoming paper.

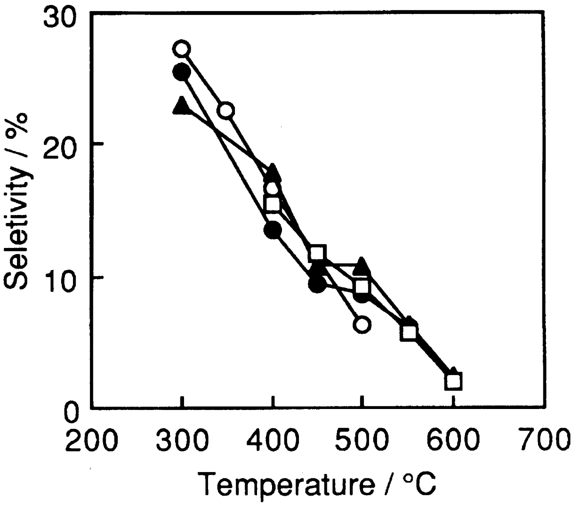

Fig. 5. Temperature dependence of the selectivity of $NO+C_3H_6+O_2$ reaction over lanthanide ion exchanged ZSM-5. Reaction conditions are the same as those for Fig. 4. (●); La(17)-Z, (○); Ce(21)-Z, (▲); Pr(16)-Z, and (□); Nd(18)-Z.

Typical results (conversions of NO to N_2 and of C_3H_6 to CO_x as well as the selectivity) for various ion-exchanged ZSM-5 catalysts are shown in Fig. 4. Ion exchange of Na-Z with these ions greatly enhanced the activity for NO reduction. All of these catalysts showed changes of activity and selectivity with reaction tem-

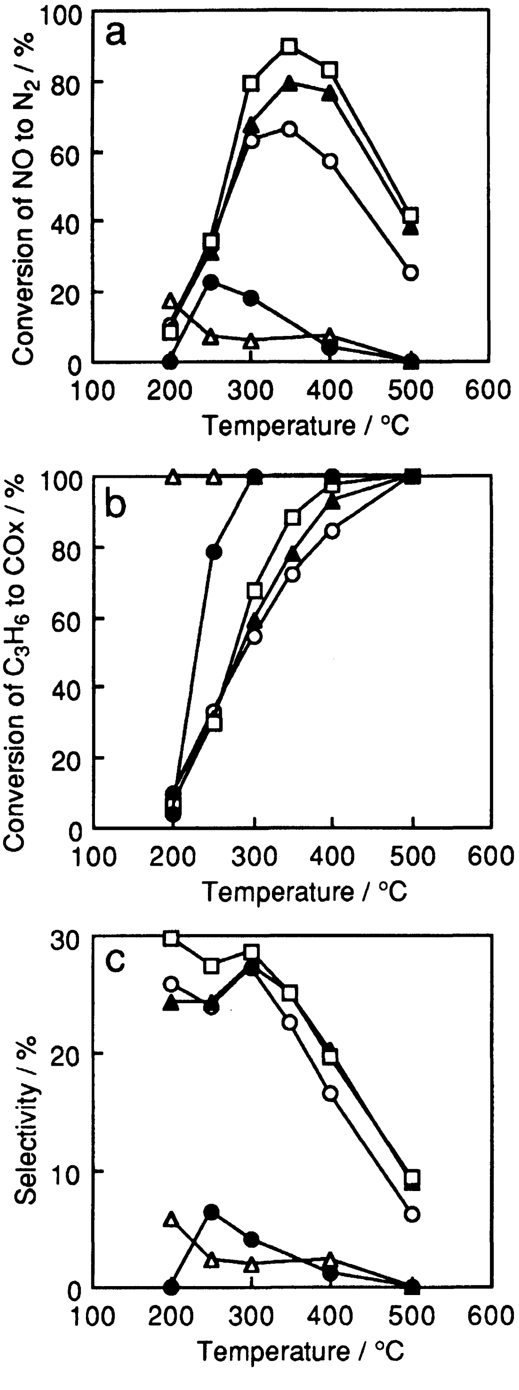

Fig. 6. Temperature dependence of (a) conversion of NO to N_2, (b) conversion of C_3H_6 to CO_x, and (c) selectivity of $NO+C_3H_6+O_2$ reaction over Ce-Z containing additional cations. NO; 1000 ppm, C_3H_6; 500 ppm, O_2; 2%, total flow-rate; 150 $cm^3 min^{-1}$, and catalyst weight; 0.5 g. (○); Ce(21)-Z, (▲); Ce(21)-Ca(22)-Z, (□); Ce(21)-Sr(40)-Z, (△); Ce(24)-Pt(15)-Z, and (●); Ce(24)-Pd(21)-Z.

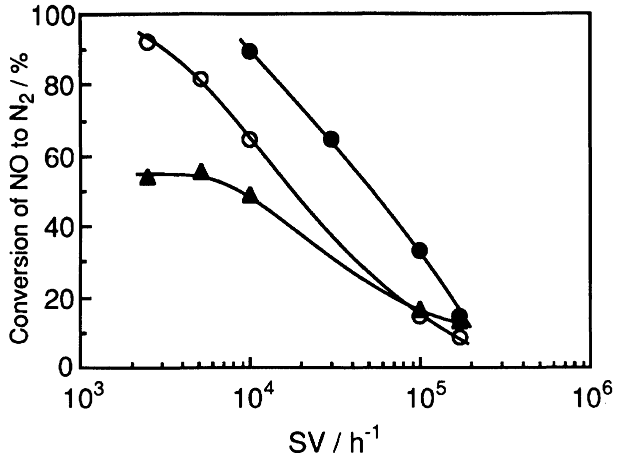

Fig. 7. Correlation between the catalytic activities and space velocity. NO; 1000 ppm, C_3H_6; 500 ppm, O_2; 2%, total flow-rate; 150 $cm^3 min^{-1}$, catalyst weight; 0.03—2.0 g, and reaction temperature: Cu; 300 °C, Ce; 350 °C, and Ce-Sr; 350 °C. (○); Ce(18)-Z, (●); Ce(21)-Sr(40)-Z, and (▲); Cu(100)-Z.

perature similar to those in Fig. 1; with increasing temperature the reduction of nitrogen monoxide started together with the oxidation of propene, and decreased due to the decrease in the selectivity with further increase of propene oxidation.

Highest activities for each catalyst obtained under the standard conditions, together with the reaction temperature at which the highest activity was obtained, are shown in Table 1. The conversion of C_3H_6 and the selectivity for the highest conversion of NO are also given in the table. Temperature regions where the catalysts showed high activities are different from one catalyst to another. For example, Ce- and Cu-Z showed maxima at lower temperatures and Pb-Z at a higher temperature. Under these reaction conditions, Ce-Z showed the highest performance, which was considerably better than Cu-Z and H-Z, which had been reported to have high activities for NO reduction by ethene and propane, respectively.[3,6]

Among Ce-, Cu-, and H-Z, as seen in Table 1 and Fig. 4, the selectivity was in the order of Ce=H>Cu, and the activity for the oxidation of propene; Cu>Ce>H. If one considers these orders and that the activity is expressed by the product of the selectivity and the extent of oxidation of propene as in Eq. 4, it may be understandable that Ce-Z becomes the most active. The high activity of Ce-Z is mainly due to its high selectivity, which is presumably brought about by the preferential reaction between NO_2 and propene.[14] Ce(60)*-Z showed a much higher activity than Ce(21)-Z due to the considerable increase in the activity for oxidation of propene in spite of slight decrease in the selectivity.

Interestingly, the selectivities of various lanthanide ion-exchanged ZSM-5 were similar to each other if they are compared at the same temperature as shown in Fig. 5, although the catalytic activity for the oxidation of propene was very different. Therefore the order of the catalytic activity for the oxidation of propene is directly reflected in the order of the activity for the reduction of nitrogen monoxide (Ce≫Pr>La>Nd) as seen in Eq. 4. Since the selectivity represents the preference of Reaction 1 to Reaction 2, the similar selectivites among lanthanide metals indicate that the ratios of the rates of the two reactions are similar, the ratio being apparently only the function of temperature, although the absolute values of the rates are quite different.

Temperature dependencies of (a) the activity, (b) the conversion of propene, and (c) the selectivity of Ce-Z containing the second metal ion species are shown in Fig. 6. The addition of noble metals such as Pt and Pd decreased the activity, especially at high temperatures due to the considerable decrease in the selectivity in spite of the increase in the activity for the oxidation of propene. This may be partly due to too high contents of noble metals. On the contrary, the addition of alkaline earth metals enhanced the activity significantly due to the increase in both the activity for the oxidation of propene and the selectivity. Sr-Z had a higher selectivity than Ce-Z (Ce-Z; 16.6%, Sr-Z; 25.2% at 400 °C), although the activity was much lower. It is possible that the higher selectivity observed for Sr-Z is reflected in the higher selectivity of Ce-Sr-Z. However, since the activity of Sr-Z is very low, another possible effect of Sr addition may be modification of the location of Ce ion in zeolite.

From the practical point of view, the activity at high space velocity is important. The dependencies of the catalytic activities of Cu-, Ce-, and Ce-Sr-Z on space velocity (SV) are shown in Fig. 7. Space velocity is defined here by (total flow-rate)/(catalyst volume). The reaction temperature was set for each catalyst to the temperature at which the highest activity was obtained under the standard conditions; that is, 350 °C for Ce-Z and Ce-Sr-Z, and 300 °C for Cu-Z. With increase in SV, the activity of all catalysts decreased together with the decrease in the oxidation of propene. It is noteworthy that, even at $SV>10^5\ h^{-1}$, Ce-Sr-Z was more effective than Cu-Z, which had been reported to be very active at high space velocity.[15)] When SV was decreased, the activity of Cu-Z reached a maximum at $SV=10^4\ h^{-1}$, as was previously reported.[15)] This is because the conversion of propene over Cu-Z already reached 100% at $SV=10^4\ h^{-1}$. On the other hand, in the case of Ce-Z and Ce-Sr-Z, propene did not expire at $SV=10^4\ h^{-1}$, so that the activities still increased with decreasing SV in this SV region. However, as the order of activity is very much dependent on the reaction system and conditions, discussion on small difference may not be very meaningful.

Conclusions

Ce-Z showed excellent performance for the reduction of nitrogen monoxide by propene in the presence of oxygen. Its high activity was primarily due to the high selectivity (high efficiency of hydrocarbon use). The high selectivity is presumably because of the preferential occurrence of the reaction between NO_2 and propene. The addition of alkaline earth metals to Ce-Z enhanced the activity significantly by increasing both the catalytic activity for the oxidation of propene and the selectivity. Ce-Sr-Z had a high activity even at high space velocity.

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