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Promotive Effects of the Addition of Alkaline Earth Metals to Ce-ZSM-5 Catalyst for the Reduction of Nitrogen Monoxide in the Presence of Propene and Oxygen

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The addition of alkaline earth metals to Ce-exchanged ZSM-5 enhanced remarkably the catalytic activity for the removal of nitrogen monoxide (1000 ppm) in the presence of propene (500 ppm) and oxygen (2%). The activity was great even at the space velocity of 10^5 h^{-1}.

Catalytic removal of nitrogen oxides in the presence of oxygen as in the exhaust gas of diesel or lean-burn engines has recently attracted much attention. Use of hydrocarbons has been suggested in patents[1] and was confirmed to be effective for such catalysts as Cu-zeolites,[2] Cu-silicate,[3] Fe-silicate,[4] zeolites themselves,[5] alumina,[6] etc. We previously reported that Ce-exchanged ZSM-5 was very active for this reaction at relatively low space velocity (SV).[7] In this work, we examined the influences of cation exchange level and coexisting metal ions for Ce-ZSM-5, and found that the addition of alkaline earth metals as well as the increase of the exchange level enhanced the activity remarkably. In particular, the addition of alkaline earth metals such as Sr and Ba resulted in much improved performance at high SV and high temperatures.

Ion-exchanged ZSM-5 catalysts were prepared as in the previous paper[7] by the ion exchange of parent Na-ZSM-5 (SiO_2/Al_2O_3 = 23.3) in aqueous solutions of acetates (In-ZSM-5 from indium chloride). Ce-ZSM-5 containing the coexisting ions were prepared by the ion exchange of Ce-ZSM-5 which had been prepared as stated above. The exchange level was determined by measuring the eluted Na ion with atomic absorption spectroscopy. The reactions were performed with a flow reactor by passing a mixed gas of 1000 ppm NO, 2% O_2 and 500 ppm propene (in He) at a rate of 150 cm^3 min^{-1} over 0.5 g of catalyst (SV = 10^4 h^{-1}), where the reaction temperature was decreased stepwise from the highest temperature for each experiment. The effluent gases were analyzed by gas chromatography. The catalytic activity

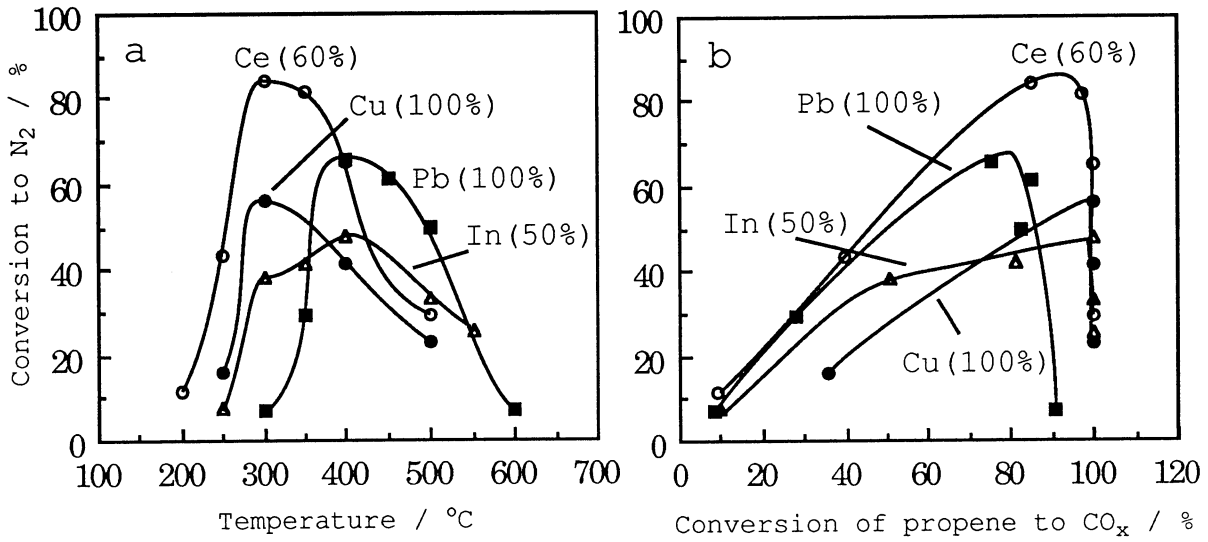

Fig. 1. Temperature dependence of the catalytic activities (a) and correlation between conversions to N_2 and CO_x (b) for NO reduction over various cation-exchanged (exchange level in parentheses) ZSM-5. NO; 1000 ppm, O_2; 2%, C_3H_6; 500 ppm, total flow-rate; 150 cm^3 min^{-1}, catalyst weight; 0.5 g.

was evaluated by the extent of conversion of NO into N_2.

Typical results for ion-exchanged ZSM-5 are shown in Fig. 1a. Under the present reaction conditions, Ce-ZSM-5 showed performance considerably better than Cu-ZSM-5 in a wider temperature range. High activities were also observed with In, Pb-exchanged ZSM-5 at higher temperatures. The selectivity is defined by the ratio of NO-propene reaction to O_2-propene reaction, as in Eq.1.

(% selectivity)

$$= (\%\ \text{conversion of NO to } N_2) \ / \ (\%\ \text{conversion of propene to } CO_x) \quad (1)$$

The correlations between the conversion to N_2 and that to CO_x are shown in Fig. 1b, where the selectivities are the slopes of the straight lines connecting each point and the origin. The conversion to CO_x increased with increasing reaction temperature, while the selectivity decreased, giving the maximum conversion to N_2 in the range of 300-400 °C. Figure 1b shows that the high activity of Ce-ZSM-5 is due to its high selectivity. It may be stated that the reaction between NO and propene occurred very selectively in this reaction system, if one considers that the number of oxygen atoms in NO is only 2.4% of whole oxygen atoms in the reaction gases.

Various ions were added to Ce-ZSM-5 as the second component to improve the performance. The activity for the NO removal decreased upon

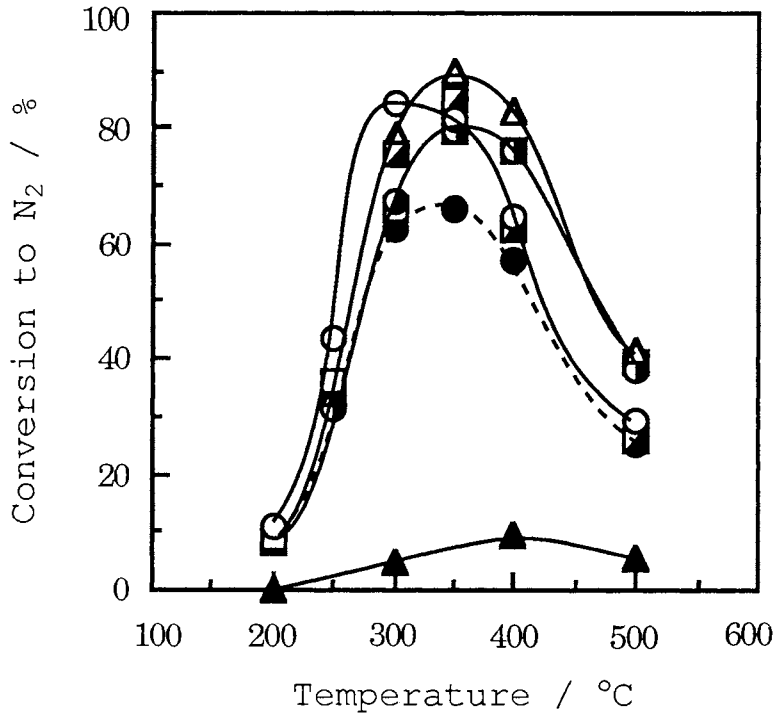

Fig. 2. Effects of the addition of alkaline earth metals to Ce-ZSM-5 for NO reduction

NO; 1000 ppm, O_2; 2%, C_3H_6; 500 ppm, total flow-rate; 150 cm^3 min^{-1}, catalyst weight; 0.5 g.
(●) Ce(21%) ; (□) Ce(21%)-Mg(18%) ; (◑) Ce(21%)-Ca(22%) ; (△) Ce(21%)-Sr(40%) ; (◪) Ce(21%)-Ba(43%) ; (○) Ce(60%) ; (▲) Sr(95%).

the addition of noble metal ions and copper ion which have high oxidation activities, because of the decrease in the selectivity. On the other hand, the addition of alkaline earth metals enhanced the activity particularly above 350 °C due to both the increase in the conversion of propene into CO_x and in the selectivity, as shown in Fig. 2. The activities of Sr- and H-ZSM-5 were very low under the present conditions. Results of Sr-ZSM-5 are given in Fig. 2. The promotive effects of alkaline earth metals were possibly brought about by the increase in the amounts of acid (or basic) sites or the change in the location of Ce ion in the zeolite. When the ion-exchange level of Ce in Ce-ZSM-5 was increased, the selectivity little changed but the conversion into CO_x increased with the increment of the exchange level, the effective temperature regions slightly being shifted to lower temperatures.

The dependences of the catalytic activities of Cu-, Ce-, and Ce-Sr-ZSM-5 on SV were measured and are shown in Fig. 3. Reaction temperature

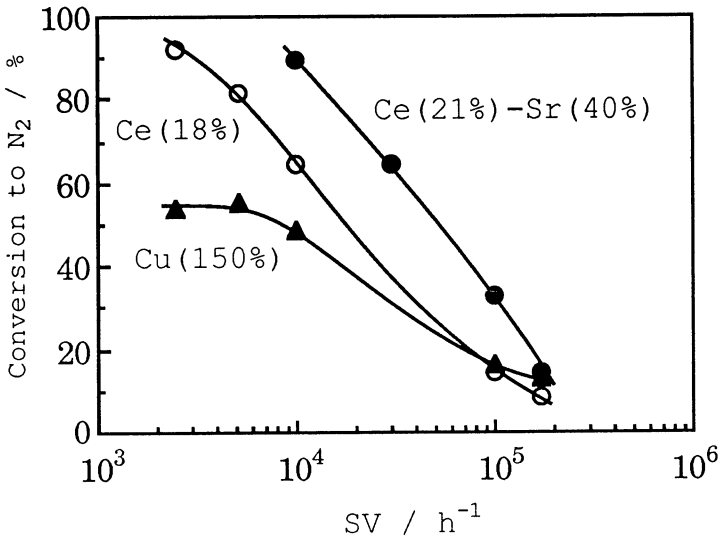

Fig. 3. Correlation between the catalytic activities and space velocity.
NO; 1000 ppm, O_2; 2%, C_3H_6; 500 ppm, total flow-rate; 150 cm^3 min^{-1},
catalyst weight; 0.03-2.0 g,
temperature: Cu; 300 °C, Ce; 350 °C, Ce-Sr; 350 °C.

was set for each catalyst at the temperature at which the highest activity was obtained; 350 °C for Ce and Ce-Sr, and 300 °C for Cu. The addition of alkaline earth metals showed a remarkable effect even at high SV conditions. Ce-Sr-ZSM-5 was more effective than Cu-ZSM-5 at SV = 1.8 x 10^5 h^{-1}, and was much more efficient for SV < 10^5 h^{-1}.

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