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Catalytic Removal of Nitrogen Monoxide over Rare Earth Ion-Exchanged Zeolites in the Presence of Propene and Oxygen

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Ce- and Pr-exchanged zeolites were active for the catalytic removal of nitrogen monoxide (1000 ppm) in the presence of propene (166-1000 ppm) and oxygen (2%).

Catalytic removal of nitrogen oxides in the presence of oxygen, e.g., from the exhaust gas of diesel engines, has recently attracted much attention. Use of hydrocarbons has been suggested in patents$^{1)}$ and it was recently confirmed that Cu-zeolites$^{2,3)}$ and zeolites themselves$^{4)}$ effectively reduce nitrogen oxide in the presence of hydrocarbons and oxygen. In this work we examined the catalytic activities of several rare-earth ion-exchanged zeolites and found Ce-ZSM-5 that is known to be thermally stable was active.

Rare-earth ion-exchanged zeolites that are denoted by RE-ZSM-5 and RE-Y (RE=La, Ce, Pr, Sm, Tb) were prepared by the ion-exchange of parent Na-ZSM-5 (SiO_2/Al_2O_3=23.3) and Na-Y zeolite (4.8) in aqueous solutions of rare-earth acetates (Tb-Y from terbium chloride). Cu-ZSM-5 with excess loading of copper was prepared according to the literature.$^{5)}$ CeO_2/Al_2O_3 (CeO_2 5wt%) was prepared by impregnating γ-Al_2O_3 with the aqueous solution of cerium acetate. The exchange levels of rare-earth ions were 50-60% for RE-Y, 16% for RE-ZSM-5, and 150% for Cu-ZSM-5. The reactions were performed with a flow reactor by passing a mixed gas of 1000 ppm NO, 2.0% O_2 and 166 - 1000 ppm propene (in He) at a rate of 150 cm^3 min^{-1} (room temperature) over 0.5 g of catalyst. The effluent gases were analyzed by gas chromatography.

Table 1 summarizes the results. For most catalysts, the maximum conversion to N_2 was obtained when the conversion of propene oxidation was about 80-90%. Under the present reaction conditions (rather low space velocity), Ce-ZSM-5 was more efficient than Cu-ZSM-5. The maximum conversion to N_2 for Ce-ZSM-5 increased to about 60% at 1000 ppm of propene. No changes in the activity were found for Ce-ZSM-5 in a 30 h experiment. The reaction between NO and propene was much slower in the absence of oxygen. CeO_2/Al_2O_3 was not efficient. Al_2O_3 needed a very high temperature. The activity for propene oxidation of RE-Y was in the order of Ce > Pr> Tb > Sm > La, in general agreement with that reported for butane oxidationover rare-earth oxides.[6] It is remarkable that the efficiency of propene consumed, i.e., NO conversion/propene conversion, was quite different among rare-earth elements, as seen in the plots shown in Fig. 1 (this efficiency is important for the performance of this type of systems). The oxidation activity was different between Ce and Pr, but their efficiencies were very similar. On the other hand, although both Sm and Tb showed moderate oxidation activities, the conversion levels of NO were low and there were no maxima. The difference seen in Fig. 1 probably reflects the capability of the catalysts to adsorb or activate NO.

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Table 1. Catalytic Removal of Nitrogen Monoxide in the Presence of Propene and Oxygen

Catalyst	Maximum conv. of NO to N_2/%	Max. NO conv. at Temp/K	Max. NO conv. at Conv. of propene/%
Ce-ZSM-5	32.0	623	75
Ce-ZSM-5[a]	59.0	673	43
Ce-Y	18.4	673	82
La-Y	6.9	873	97
Pr-Y	18.3	723	80
Sm-Y	3.8	(723)[b]	(24)[b]
Tb-Y	1.6	(773)[b]	(59)[b]
Cu-ZSM-5	20.5	523	75
H-Y	3.5	773	42
γ-Al_2O_3	24.6	873	89
CeO_2/Al_2O_3	5.4	723	89

a) C_3H_6: 1000 ppm (166 ppm for the others).
b) Temperature dependency was low (Fig. 1).

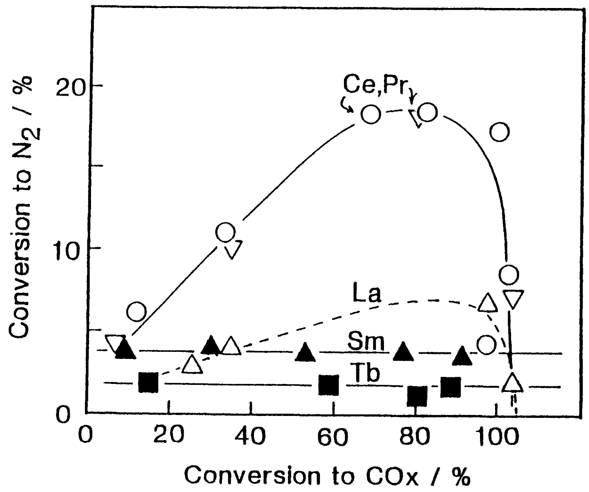

Fig. 1. Relationships between the conversions of NO and C_3H_6 for RE-Y. Propene: 166 ppm. Temp.: 473-923 K.

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