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Selective Reduction of NO with Propane on Gallium Ion-exchanged Zeolites

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The reduction of NO with propane in the presence of excess oxygen was investigated using gallium ion-exchanged zeolite catalysts, among which ferrierite(Ga-ferrierite) and ZSM-5(Ga-ZSM-5) showed high activity in a wide range of reaction temperature.

The removal of nitrogen oxides(NOx) is a serious environmental problem. Iwamoto et al.[1] reported that copper ion-exchanged ZSM-5(Cu-ZSM-5) showed high catalytic activity for the reduction of NO with hydrocarbons in the presence of oxygen. This study has induced many researches on the application of zeolite-based catalysts to the reduction of NO with hydrocarbons.[2-4] Cu-ZSM-5 is the most efficient catalyst for this reaction among the catalysts which have been reported. However, it is very difficult to accomplish high selectivity for conversion of NO to N_2 on Cu-ZSM-5 if excess oxygen is present, like in diesel or gas turbine exhaust. It is due to the high ability of Cu-ZSM-5 to oxidize hydrocarbons in oxygen-rich atmosphere, resulting in the restriction of the selectivity for this conversion. Therefore, it has been expected for the practical performance to develop the catalyst having less selectivity for oxidation of hydrocarbons even under oxygen-rich conditions. In our experimental studies, it was found that gallium ion-exchanged zeolites showed high activity and selectivity for the reaction of NO with propane even in high oxygen concentration.

Parent zeolites, ZSM-5(molar SiO_2/Al_2O_3 ratio, 23.3), mordenite(19.3), ferrierite(17.8), and Y(14.5) were supplied by Tosoh Corporation. Gallium ion-exchanged

Table 1. Catalytic activities of various ion-exchanged ZSM-5

Catalysts [a]	Conv. of NO to N_2 / % [C_3H_8 to CO_X / %]			
	300 °C	400 °C	500 °C	600 °C
Ga-ZSM-5 (79)	71.9 [29.5]	91.1 [53.8]	87.2 [91.9]	85.9 [97.6]
Al-ZSM-5 (53)	62.8 [28.1]	85.0 [55.4]	74.8 [73.1]	43.4 [90.0]
Zn-ZSM-5 (97)	18.1 [7.1]	45.3 [18.6]	93.0 [88.0]	56.5 [96.0]
In-ZSM-5 (65)	76.0 [30.9]	85.8 [99.9]	53.8 [100]	57.7 [100]
Sn-ZSM-5 (104)	54.8 [23.8]	43.0 [47.0]	25.9 [69.7]	16.4 [97.1]
H-ZSM-5 (100)	69.6 [38.5]	86.6 [72.2]	73.2 [86.5]	
Cu-ZSM-5 (111)	60.5 [92.1]	46.1 [100]	46.9 [100]	45.2 [100]

a) Catalysts have been called cation-type of zeolite (degree of ion exchange / %).

zeolites were prepared by the ion-exchange of the ammonium form zeolites using aqueous solutions of $Ga(NO_3)_3 \cdot 9H_2O$ at 95 °C for 24 h, followed by calcination at 500 °C. Copper ion-exchanged ZSM-5, as a reference catalyst, was prepared according to the method reported by Iwamoto et al.[5] ZSM-5 catalysts exchanged with other cations were prepared using nitrate or chloride solutions.

The measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO, 10% O_2, 1000 ppm propane was fed on to 0.5 g catalyst at a rate of 100 $cm^3 \cdot (STP)\ min^{-1}$. After reaching steady-state, effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO.

Table 1 summarizes the activities of various ion-exchanged ZSM-5 catalysts. Ga-ZSM-5 showed high activity in a wide range of reaction temperature(300 - 600 °C). It should be noted that the conversion level of propane was lower on Ga-ZSM-5 than on Cu-ZSM-5, particularly in the low temperature region, although the conversion of NO on Ga-ZSM-5 was higher than on Cu-ZSM-5. Propane was almost completely consumed on Cu-ZSM-5 above 400 °C because of the high ability of this catalyst for the oxidation of propane. The high oxidation ability would rather limit the reaction of NO to N_2 in the presence of excess oxygen. The ability of Ga-ZSM-5 catalyst for the oxidation of propane was moderate, so that high

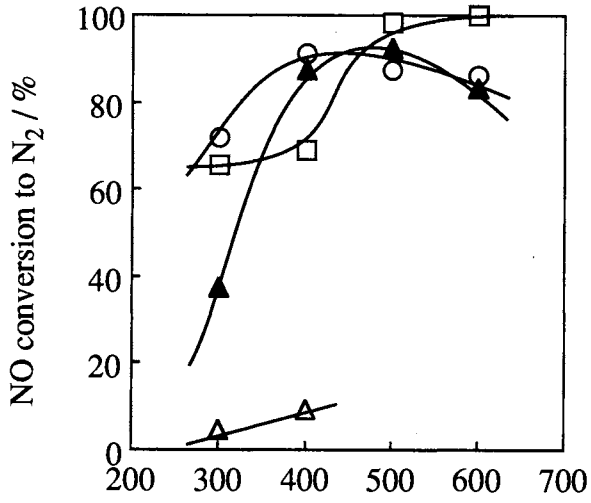

Fig.1. Variation in the catalytic activities of various gallium ion-exchanged zeolites as a function of reaction temperature.
Catalysts:
O, Ga-ZSM-5(79); ▲, Ga-mordenite(106);
□, Ga-ferrierite(91); △, Ga-USY(103).

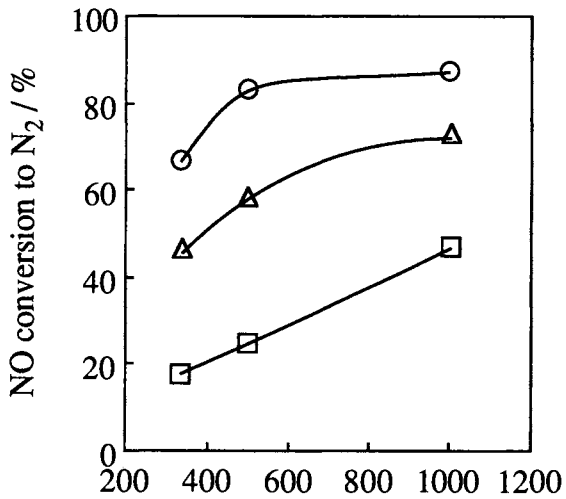

Fig.2. Selective reduction of NO as a function of C_3H_8 concentration over Ga-ZSM-5, H-ZSM-5, and Cu-ZSM-5.
Catalysts: O, Ga-ZSM-5(79);
△, H-ZSM-5(100); □, Cu-ZSM-5(111).
Reaction temperature, 500°C.

efficiency was attained for the reaction of propane with NO. Although Zn-ZSM-5 showed high activity at 500 °C, the activity was not high in the other temperature region.

The difference in the catalytic effects between gallium cation and proton on the catalytic activities of ZSM-5 are characteristic at higher reaction temperature than 500 °C. Ga-ZSM-5 was more active for the reduction of NO than H-ZSM-5 above 500 °C, although no remarkable difference was observed in the temperature range 300 - 400 °C.

Figure 1 compares the catalytic activities of various zeolites exchanged with gallium cations. The activity depended on the type of zeolites. Ga-ZSM-5 and Ga-ferrierite were highly active among these catalysts at all temperatures, and NO was completely reduced to N_2 above 500 °C on Ga-ferrierite under these reaction conditions. Although Ga-mordenite showed relatively high activity above 400 °C, the activity was poor below this temperature. Ga-Y showed low activity at these temperatures.

The difference in the catalytic performance of Ga-ZSM-5, H-ZSM-5, and Cu-ZSM-5 became more remarkable, when the concentration of propane in the reactant mixture was

smaller. Figure 2 shows the effect of propane concentration on the conversion of NO to N_2 at 500 °C. Propane was completely consumed on all these catalysts when the concentration of propane was smaller than 500 ppm. The conversion of NO on Cu-ZSM-5 remarkably decreased and less than 20% conversion was shown when the concentration of propane was lowered to 333 ppm. On the contrary, 67% conversion of NO was maintained on Ga-ZSM-5 under the same reaction conditions, although almost the same amount of propane was converted on both of these catalysts. The conversion of NO was lower on H-ZSM-5 than on Ga-ZSM-5 under all these conditions.

From these results, it is shown that Ga-ZSM-5 shows high activity and selectivity for the reduction of NO with propane, even in the presence of excess oxygen and in the wide range of temperatures(300 - 600 °C). No such catalysts showing high activity under these conditions have been reported. Although it has been reported that Cu-ZSM-5 shows high activity for this reaction at low temperatures and high SV, the working temperature range of Cu-ZSM-5 is somewhat limited due to its low selectivity for the reduction of NO with hydrocarbon compared with Ga-ZSM-5. High selectivity of Al_2O_3 catalyst for NO-hydrocarbon reaction has been reported,[6] while its activity is smaller than Ga-ZSM-5 catalyst.

Although further studies are required to understand the effect of gallium on the catalytic activity, it is concluded in this study that NO can more effectively be reduced into nitrogen on gallium ion-exchanged zeolites with smaller amounts of propane than on Cu-ZSM-5 and on proton type zeolites, and that gallium ion-exchanged zeolites have high possibility for the practical use under excess oxygen condition.

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