Catalysis Letters 17 (1993) 303–308

Gallium ion-exchanged zeolite as a selective catalyst for reduction of nitric oxide with hydrocarbons under oxygen-rich conditions

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Received 14 September 1992; accepted 1 December 1992

Selective reduction of nitric oxide with propane in the presence of excess oxygen was investigated using gallium ion-exchanged zeolite catalysts. Gallium ion-exchanged ferrierite (Ga-ferrierite) showed extremely high selectivity for this reaction under oxygen-rich conditions (10%). The molar ratio of reacted NO to consumed C_3H_8 was found to be near 3 on Ga-ferrierite.

Keywords: Nitric oxide; selective reduction; propane; gallium; zeolite

1. Introduction

Emission of nitrogen oxides (NOx) from combustion exhaust stream has attracted much attention. It had widely been accepted that selective catalytic reduction (SCR) in oxidizing atmosphere is only possible with ammonia, and hydrocarbons are ineffective for this reaction. Although ammonia SCR process is now practically applied to stationary sources, this process is unsuitable for small scale exhaust. Recently, Iwamoto et al. [1] reported that selective reduction of NO with hydrocarbons proceeds on copper ion-exchanged ZSM-5 (Cu-ZSM-5) in the presence of oxygen. Their study has induced many researches on the application of zeolite-based catalysts to the reduction of NO with hydrocarbons [2–4]. Although Cu-ZSM-5 is the most efficient catalyst for this reaction among the catalysts which have ever been reported, the selectivity for NO–hydrocarbon reaction is insufficient, due to the high ability of Cu-ZSM-5 to oxidize hydrocarbons in oxygen-rich atmosphere. Therefore, it has been expected for the practical performance to develop the catalyst having high

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selectivity for NO–hydrocarbon reaction even under oxygen-rich conditions like in ammonia SCR process. High catalytic selectivity of Al_2O_3 [5] and H-form zeolites [2] for NO–hydrocarbon reaction has been reported by Hamada et al., while their activities are not enough under high GHSV condition. In our previous experimental studies, it was found that gallium ion-exchanged zeolites show high activity and selectivity for the reduction of NO with C_3H_8 even in high oxygen concentration [6]. In this study, we have found that Ga-ferrierite shows extremely high selectivity and the molar ratio of reacted NO to consumed C_2H_8 is near 3. Such a catalyst showing higher selectivity than Ga-ferrierite has never been reported.

2. Experimental

Zeolites used in this study, ZSM-5 (molar SiO_2/Al_2O_3 ratio, 23.3), mordenite (19.3), ferrierite (17.8), and ultra stable Y (14.5) were supplied by Tosoh Corporation. Gallium ion-exchanged zeolites were prepared by ion-exchange of 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. The concentration of Ga cations in the solutions was adjusted to the level that the ratio of dissolved gallium ions to Al cations is one third (100% ion-exchange level as Ga^{3+}). Copper ion-exchanged ZSM-5, as a reference catalyst, was prepared according to the method reported by Iwamoto et al. [7]. The zeolites will be abbreviated, for instance, to Ga-ZSM-5 (100) etc. The values in parentheses represent the level of cation exchange.

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 C_3H_8 was fed to 0.5 g catalyst at a rate of 100 cm^3(STP) min^{-1} unless otherwise specified. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence detection of NO. The catalytic activity was evaluated by the level of NO conversion to N_2.

3. Results and discussion

Fig. 1 compares NO conversion on Cu-, H- and Ga-ZSM-5 as a function of reaction temperature. Ga-ZSM-5 showed higher catalytic activity than Cu-ZSM-5 in the temperature range of 300–600°C under these reaction conditions. C_3H_8 was almost completely consumed on Cu-ZSM-5 above 400°C because of the high ability of this catalyst for the oxidation of C_3H_8. The high oxidation ability would rather limit the reaction of NO to N_2 in the presence of excess oxygen.

The difference in the catalytic performance between gallium and proton type ZSM-5 are characteristic at higher reaction temperature than 500°C. Ga-ZSM-5

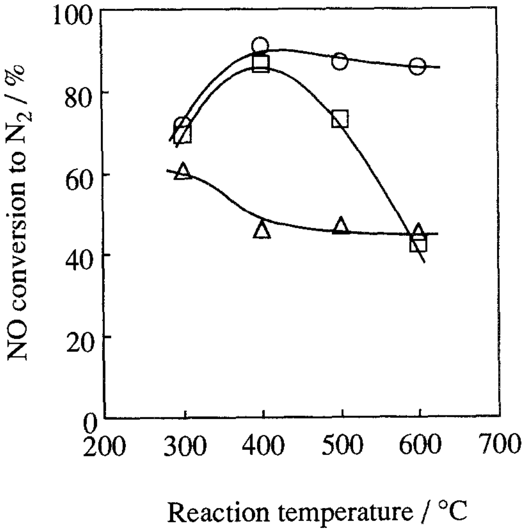

Fig. 1. Variation in the catalytic activities of various ion-exchanged ZSM-5 as a function of reaction temperature. Catalysts: (□) H-ZSM-5(100); (△) Cu-ZSM-5 (111); (○) Ga-ZSM-5 (79). NO, 1000 ppm; C_3H_8, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

was more active for this reaction than H-ZSM-5 above 500°C, although no remarkable difference was observed in the temperature range 300–400°C.

Fig. 2 shows the relationships between NO conversion and C_3H_8 conversion on these cation-exchanged ZSM-5 catalysts. The selectivity for NO-hydrocarbon

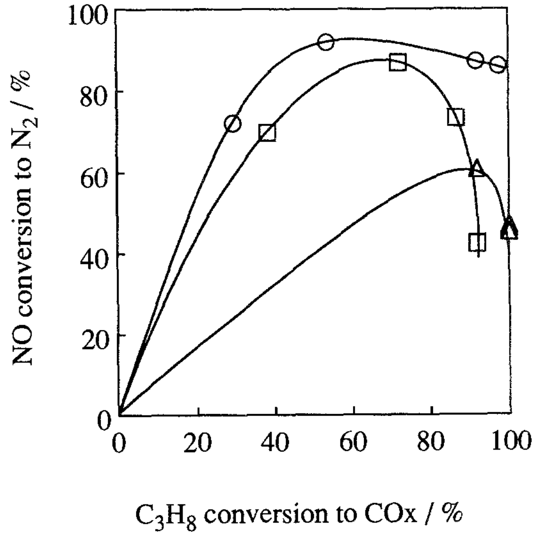

Fig. 2. Relationships between NO conversion and C_3H_8 conversion on various ion-exchanged ZSM-5. Catalysts: (□) H-ZSM-5 (100); (△) Cu-ZSM-5 (111); (○) Ga-ZSM-5 (79). NO, 1000 ppm; C_3H_8, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g; reaction temperature, 300–600°C.

Table 1
Catalytic activities of H-form and gallium ion-exchanged zeolites

Catalyst	NO conversion to N_2 (%) [C_3H_8 conversion to COx (%)]			
	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]
Ga-ferrierite (91)	65.5 [21.8]	69.1 [22.4]	98.5 [40.0]	100 [76.1]
Ga-mordenite (106)	37.5 [12.0]	87.4 [34.8]	92.4 [86.2]	83.3 [97.7]
Ga-USY (103)	4.7 [1.2]	9.4 [3.1]	13.0 [13.9]	17.4 [46.5]
H-ZSM-5	69.6 [38.5]	86.6 [72.2]	73.2 [86.5]	42.7 [92.1]
H-ferrierite	64.6 [22.6]	72.7 [24.2]	52.3 [24.4]	58.2 [47.8]
H-mordenite	28.9 [11.0]	74.0 [40.8]	72.7 [70.5]	40.6 [99.9]

Reaction conditions: NO, 1000 ppm, C_3H_8, 1000 ppm, O_2, 10%, total flow rate, 100 cm^3 min^{-1}, catalyst weight, 0.5 g.

reaction against hydrocarbon–O_2 reaction varied quite differently among these catalysts particularly at high temperature. The ratio of NO conversion to C_2H_8 conversion is a measure of selectivity, and the selective catalyst provides larger ratio. Ga-ZSM-5 was remarkably selective among these catalysts particularly at high temperatures.

Table 1 shows the effect of the kind of zeolite on the catalytic activity for NO reduction. The catalytic activity and selectivity for NO reduction varied with the kind of zeolite. Fig. 3 summarizes the results of these Ga- and H-zeolites. It must be noted that gallium ion-exchanged zeolites were more selective than

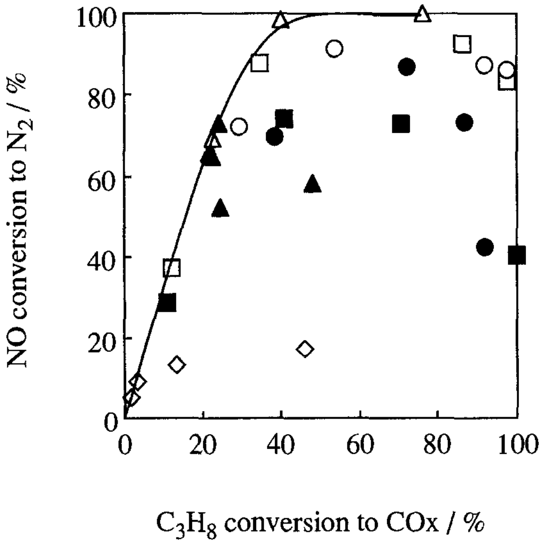

Fig. 3. Relationships between NO conversion and C_3H_8 conversion on Ga- and H-zeolites. Catalysts: (○) Ga-ZSM-5 (79); (●) H-ZSM-5; (△) Ga-ferrierite (91); (▲) H-ferrierite; (□) Ga-mordenite (103); (■) H-mordenite; (◇) Ga-USY (106). NO, 1000 ppm; C_3H_8, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g; reaction temperature, 300–600°C.

proton-type zeolites, irrespective of the kind of zeolite. Ga-ferrierite was most selective among these catalysts.

Fig. 4 shows the ratio in conversion of NO to that of C_3H_8 to COx on various catalysts at 500°C. The selectivity of Ga- and H-ZSM-5 lowered with increasing C_3H_8 concentration, due to increasing the contribution of combustion reaction. On the contrary, C_3H_8 reacted selectively with NO, and the reaction with O_2 hardly proceeded even under oxygen-rich conditions on Ga-ferrierite. The selectivity of Cu-ZSM-5 was extremely low under these reaction conditions. The limiting molar ratio of reacted NO to consumed C_3H_8 on Ga-ferrierite and Ga-ZSM-5 is near 3. This ratio corresponds to the following stoichiometry:

$$3NO + C_3H_8 + kO_2 = \tfrac{3}{2}N_2 + mCO + nCO_2 + 4H_2O, \quad k = \tfrac{1}{2}(m + 2n + 1). \tag{1}$$

According to this stoichiometry, 1000 ppm NO completely reduced to N_2 with 333 ppm C_3H_8 (33.3% C_3H_8 conversion under the present conditions). No catalyst showed higher selectivity than this ratio.

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 C_3H_8 than on Cu-ZSM-5 and on H-form zeolites. The molar ratio of reacted NO to consumed C_3H_8 is near 3 on gallium ion-exchanged zeolites. Ga-ferrierite is the most selective catalyst which has ever been reported. It is thus

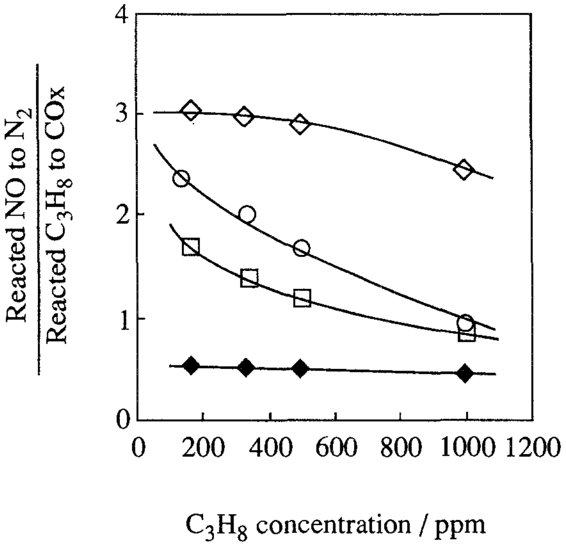

Fig. 4. Ratio in reacted NO to reacted C_3H_8 on various ion-exchanged zeolites. Catalysts: (o) Ga/H-ZSM-5 (79); (◇) Ga/H-ferrierite (91); (△) H-ZSM-5; (◆) Cu-ZSM-5 (111). NO, 1000 ppm; O_2, 10%; total flow rate 100 cm^3 min^{-1}; catalyst weight, 0.5 g; reaction temperature, 500°C.

concluded that gallium ion-exchanged zeolites are strong candidates for practical removal of NO, alternatively for ammonia SCR process.

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