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Selective reduction of nitric oxide by methane on H-form zeolite catalysts in oxygen-rich atmosphere

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Selective reduction of NO by CH_4 in the presence of excess oxygen was investigated using H-form zeolite catalysts. H-ZSM-5, H-ferrierite, and H-mordenite showed high catalytic activity and selectivity. On the contrary, H-USY and Al_2O_3 were not effective for this reaction. Both NO–CH_4 and O_2–CH_4 reaction hardly proceeded on H-ZSM-5. Higher NO_x conversion was obtained in the NO_2–O_2–CH_4 and NO_2–CH_4 systems than in the NO–O_2–CH_4 system under high GHSV condition. It seemed that NO_2 plays an important role for selective reduction of NO by CH_4 on H-form zeolites.

Keywords: Nitric oxide; selective reduction; methane; zeolite

1. Introduction

Recently, selective catalytic reduction of NO by hydrocarbons in oxygen-rich atmosphere has attracted considerable attention as a new type of reaction alternative for the traditional NH_3-SCR process. This reaction has been reported to proceed on various cation-exchanged zeolites [1–5], metallosilicates [6,7], Al_2O_3 [8,9] and SiO_2–Al_2O_3[10].

Iwamoto et al. [11] and Hamada et al. [12] have studied the reduction of NO by various hydrocarbons in the presence of oxygen on Cu-ZSM-5 and Al_2O_3 catalysts, respectively. They have classified reductants into two groups, selective (C_2H_4, C_3H_6, C_3H_8, C_4H_8), and non-selective (H_2, CO, CH_4, C_2H_6) reductants for NO reduction in the presence of O_2 [13]. The CH_4–O_2 reaction proceeded predominantly and the NO–CH_4 reaction hardly proceeded on Cu-ZSM-5 and Al_2O_3. It has been accepted that CH_4 is not effective for selective reduction.

However, hydrocarbon in the exhaust from a gas-cogeneration system is mainly CH_4. Therefore, it is expected to develop a catalyst which is active for selective reduction of NO by CH_4 in oxygen-rich atmosphere. Recently, Li and Armor [14]

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have reported that selective reduction by CH_4 proceeds on Co-ZSM-5. In our previous study, we have also found that Ga-ZSM-5 shows high catalytic activity and extremely high selectivity for reduction of NO by CH_4 or C_2H_6 [15]. We have recently found that various H-form zeolite catalysts are also active and fairly selective for this reaction. In this paper, we will report the catalytic properties of H-form zeolites and the role of O_2 for selective reduction of NO by CH_4.

2. Experimental

Zeolites used in this study were ZSM-5 (molar SiO_2/Al_2O_3 ratio, 23.3), mordenite (19.9), ferrierite (17.8), and USY (14.5), supplied by Tosoh Corporation. Alumina, as a reference catalyst, was obtained from Catalysts & Chemical Ind. Co.

Measurements of catalytic activity were conducted by use of a fixed-bed flow reactor. A mixture of 1000 ppm NO (or NO_2), 10% O_2, and 1000 ppm CH_4 was fed to 0.1–0.5 g catalyst at a rate of 100 cm^3(STP) min^{-1}. After reaching steady-state, effluent gases were analyzed by gas chromatography and chemiluminescence detection of NO_x. The catalytic activity was evaluated by the level of NO conversion to N_2.

3. Results and discussion

Fig. 1 shows the temperature dependence of catalytic activities of various H-form zeolites and Al_2O_3 for NO reduction by CH_4. Among these catalysts, H-ZSM-5 showed the highest activity at 500°C. H-USY was inactive under these

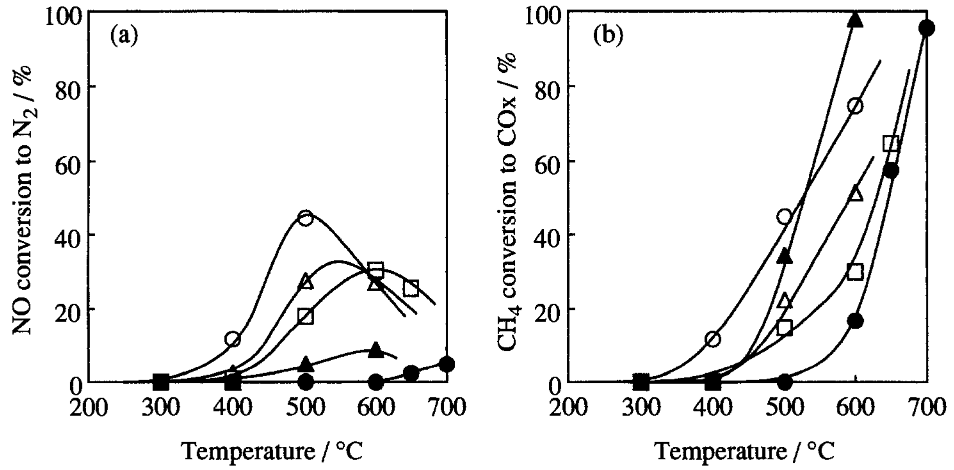

Fig. 1. Variation in NO conversion (a) and CH_4 conversion (b) on various zeolites as a function of reaction temperature. (○) H-ZSM-5; (△) H-mordenite; (□) H-ferrierite; (●) H-USY; (▲)Al_2O_3. NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

reaction conditions, and its activity was similar to that of Al_2O_3. The CH_4–O_2 reaction was predominant and NO reduction hardly proceeded on these catalysts.

The ratio of NO conversion to CH_4 conversion is a measure of selectivity. As shown in fig. 2, H-ferrierite was most selective and the order of the selectivity for this reaction on these zeolites was as follows:

H-ferrierite > H-mordenite > H-ZSM-5 >> H-2USY.

H-ferrierite exhibited the lowest activity for the CH_4–O_2 reaction, resulting in high selectivity for NO reduction. Although a high selectivity of Al_2O_3 catalyst for NO reduction by C_3H_8 has been reported [2], the selectivity for NO reduction by CH_4 was extremely low. On the contrary, NO was selectively reduced on H-ZSM-5, H-mordenite, and H-ferrierite.

It has been reported by Hamada and co-workers [2] that the acidity of catalysts is one of the important factors which control the catalytic activity for selective reduction of NO. Fig. 3 shows NH_3-TPD spectra of various zeolites used in this study. H-USY showed very small acidity with weak acid strength, suggesting that the low catalytic activity of H-USY is probably due to its poor acidity.

Fig. 4 shows the catalytic activities of H-ZSM-5 for conversions of NO to N_2 and CH_4 to CO_x in various reaction temperatures. The NO–CH_4 reaction hardly proceeded at all temperatures in the absence of O_2, showing that NO reduction was promoted by O_2. Furthermore, CH_4 oxidation did not proceed below 500°C in the absence of NO. Since NO reduction occurred under the conditions where the CH_4–O_2 reaction did not proceed, NO_2 should be concerned in selective reduction. All the zeolite catalysts used in this study were inactive for reduction of NO with CH_4 in the absence of O_2 and for oxidation of CH_4 in the absence of NO. It has also

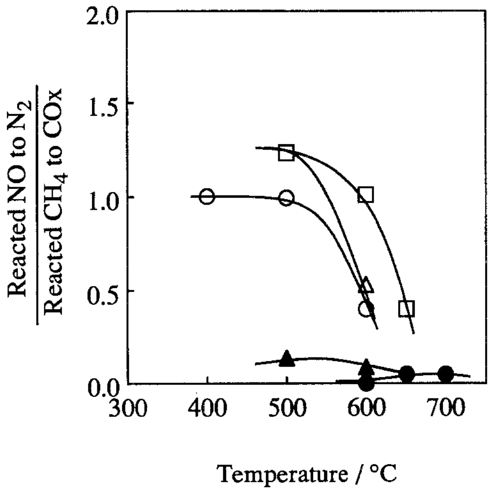

Fig. 2. Relationships between the ratio of reacted NO to consumed CH_4 and reaction temperature. (○) H-ZSM-5; (△) H-mordenite; (□) H-ferrierite; (●) H-USY; (▲) Al_2O_3. NO, 1000 ppm; CH_4, 1000 ppm; O_2 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.5 g.

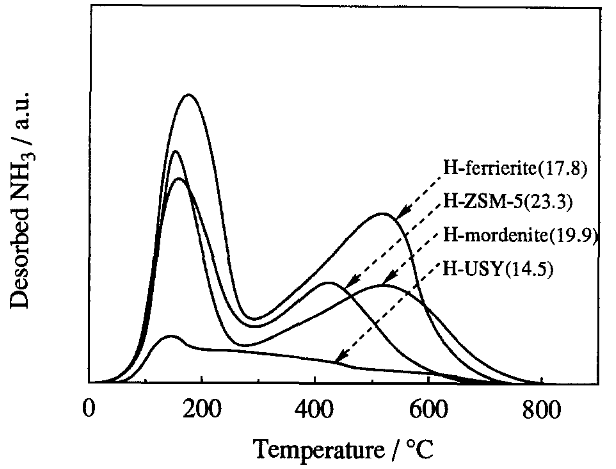

Fig. 3. NH_3-TPD spectra of various zeolites.

been reported by Hamada and co-workers [16] that selective reduction of NO with C_3H_8 on Al_2O_3 and H-form zeolites proceeds via NO_2–C_3H_8 reaction and that high selectivity was attributable to NO_2–C_3H_8 reaction and poor activity of these catalysts for C_3H_8 oxidation by O_2.

In fig. 5, we compare the level of NO_x conversion to N_2 as a function of reciprocal GHSV. Higher NO_x conversion was obvious in the NO_2–O_2–CH_4 and NO_2–CH_4 systems than in the NO–O_2–CH_4 system in high GHSV condition. In the latter system, NO conversion seems to show an induction period. These results

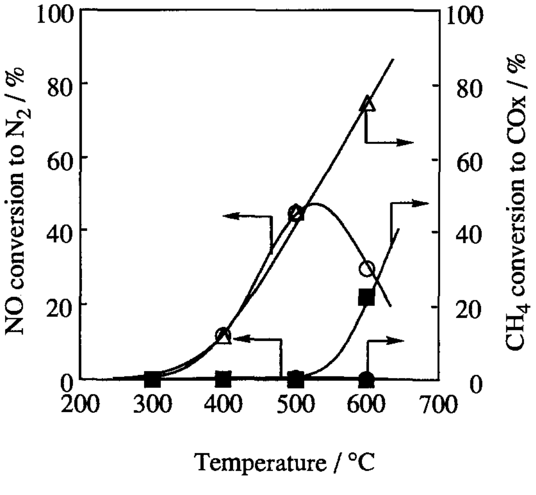

Fig. 4. Variation in NO conversion and CH_4 conversion on H-ZSM-5 as a function of reaction temperature. (○) NO conversion in NO–CH_4–O_2 reaction; (△) CH_4 conversion in NO–CH_4–O_2 reaction; (●) NO conversion in NO–CH_4 reaction; (▲) CH_4 conversion in NO–CH_4 reaction; (■) CH_4 conversion in CH_4–O_2 reaction.

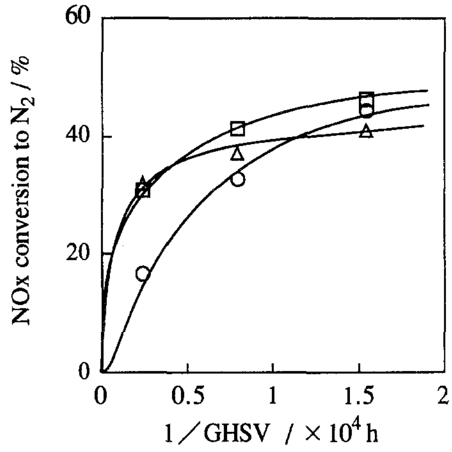

Fig. 5. Relationships between NO_x conversion and GHSV on H-ZSM-5. (○) NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; (△) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2 0%; (□) NO_2, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.1–0.5 g; reaction temperature, 500 °C.

lead us to deduce that the first step is NO oxidation to NO_2, which further reacts with CH_4 to give N_2, CO_x, and H_2O, similarly to the reduction of NO_x by C_3H_8 on H-form zeolites [16].

We conclude from these results that reduction of NO proceeds on various H-form zeolites even when CH_4 is used as reductant, and CH_4 can be an effective reductant for selective reduction of NO, and that NO_2 plays an important role in the selective reduction of NO by CH_4.

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