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Selective Reduction of Nitrogen Monoxide with Methane or Ethane on Gallium Ion-exchanged ZSM-5 in Oxygen-rich Atmosphere

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Selective reduction of nitric oxide with methane or ethane in the presence of excess oxygen was investigated using a gallium ion-exchanged ZSM-5 zeolite catalyst(Ga-ZSM-5). Ga-ZSM-5 was highly active and selective for NO reduction above 400 °C. The limiting molar ratios of reacted NO to consumed carbon in C_2H_6 and CH_4 at 500 °C were found to be 1.5 and 2, respectively.

The reduction of nitrogen oxides(NOx) to molecular nitrogen is an important task for environmental chemistry. A new type of catalytic reduction of NO with hydrocarbons has been reported using various cation-exchanged zeolites,1 - 4) metallosilicates,5, 6) Al_2O_3,7, 8) and SiO_2-Al_2O_3.9) It was shown in our previous work10) that gallium ion-exchanged zeolites were active, and were most selective for reduction of NO with C_3H_8 among these catalysts.

It has been reported by Iwamoto and co-workers11) that NO was reduced by C_2 or higher olefins and that H_2 and CO were ineffective for this reaction on Cu-ZSM-5. Hamada et al.12) have studied the catalytic activity of Al_2O_3 for reduction of NO with various hydrocarbons. They reported that NO was hardly reduced when CH_4 and benzene were used as reductants. Therefore, it has been considered that CH_4 and C_2H_6 are rather inactive for reduction of NO.

In this study, we have found that Ga-ZSM-5 shows high catalytic activity and extremely high selectivity for reduction of NO with CH_4 or C_2H_6. It was also found that the molar ratios of reacted NO to consumed carbon in CH_4 and C_2H_6 were 2 and 1.5, respectively.

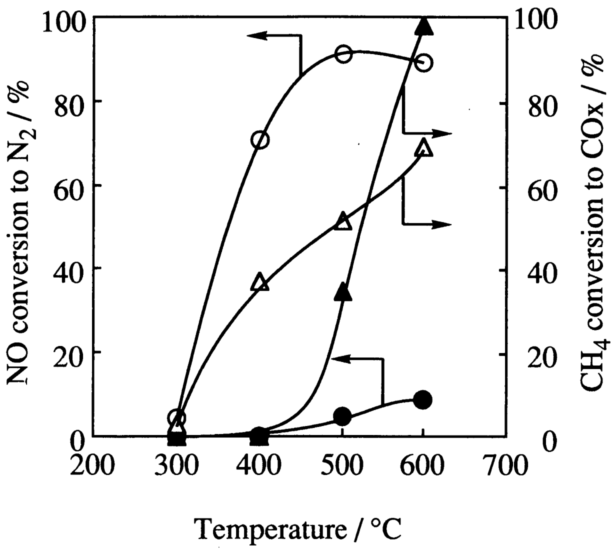

Fig.1. Variation in NO conversion and CH_4 conversion on Ga-ZSM-5(open symbol) and Al_2O_3(solid symbol) as a function of reaction temperature.
○ ●, NO conversion to N_2;
△ ▲, CH_4 conversion to COx.
NO, 1000 ppm; CH_4, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

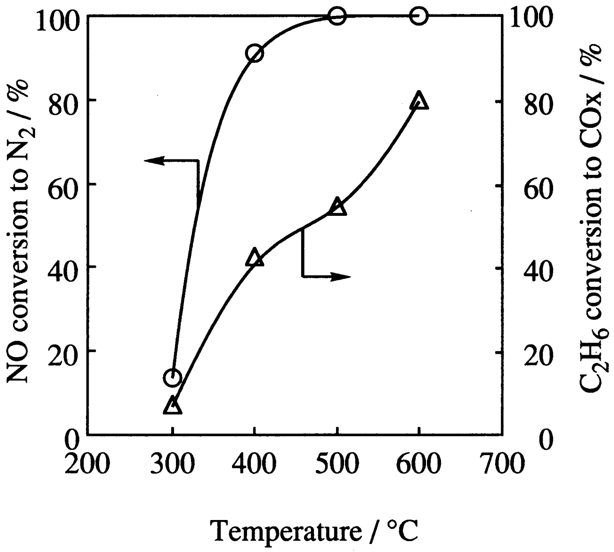

Fig.2. Variation in NO conversion and C_2H_6 conversion on Ga-ZSM-5 as a function of reaction temperature.
○, NO conversion to N_2;
△, C_2H_6 conversion to COx.
NO, 1000 ppm; C_2H_6, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.

Na form ZSM-5 having a molar SiO_2/Al_2O_3 ratio of 23.3 was supplied by Tosoh Corporation. Gallium ion-exchanged ZSM-5(Ga-ZSM-5(92)) was prepared by ion-exchange of ammonium form ZSM-5 using an aqueous solution of $Ga(NO_3)_3 \cdot 9H_2O$ at 95 °C for 24 h, followed by calcination at 500 °C. The solution was adjusted to give a concentration of gallium cations equal to one third of Al(100% ion-exchange level as Ga^{3+}). The value in parenthesis represents the level of gallium exchange. 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, 10% O_2, 150 - 1000 ppm CH_4 or C_2H_6 was fed on to 0.5 g catalyst at a rate of 100 cm^3(STP)$\cdot min^{-1}$. After reaching steady-state, effluent gases were analyzed by means of gas chromatography and chemiluminescence detection of NO and NO_2. The catalytic activity was evaluated by the level of NO conversion to N_2.

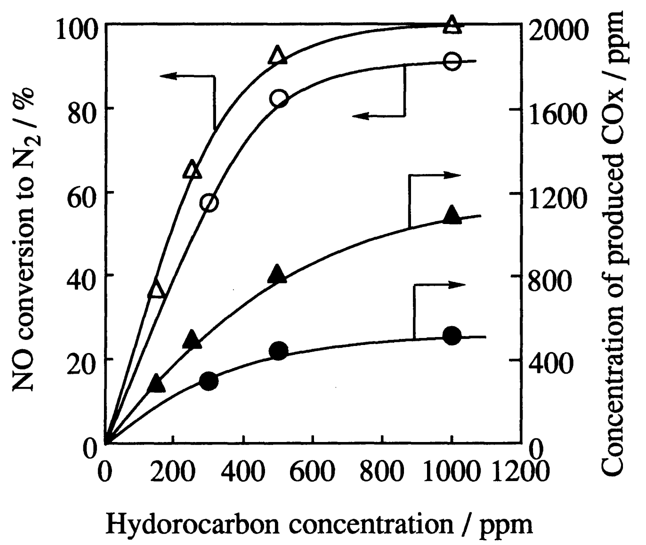

Fig.3. Variation in NO conversion(open symbol) and concentration of produced COx(solid symbol) of Ga-ZSM-5 as a function of hydorocarbon concentration.
Hydrocarbons: CH_4(○, ●); C_2H_6(△, ▲).
NO, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.
Reaction temperature, 500 °C.

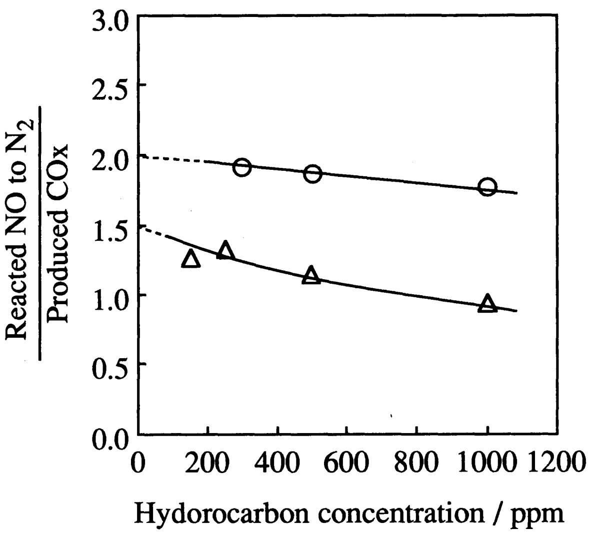

Fig.4. Ratio of reacted NO to produced COx on Ga-ZSM-5.
Hydrocarbons: ○, CH_4; △, C_2H_6.
NO, 1000 ppm; O_2, 10%; total flow rate, 100 $cm^3 \cdot min^{-1}$; catalyst weight, 0.5 g.
Reaction temperature, 500 °C.

Figure 1 shows the temperature dependence of the catalytic activity of Ga-ZSM-5 for NO reduction with CH_4 in comparison with Al_2O_3. NO was hardly reduced to N_2 at 300 °C on Ga-ZSM-5. The level of NO conversion, however, increased with increasing reaction temperature, and finally 90% NO was reduced above 500 °C. Hamada and co-workers reported12) that reduction of NO with CH_4 slightly proceeded on Al_2O_3 catalyst only when reaction temperature was higher than 500 °C. As shown in this figure, the catalytic activity of Al_2O_3 was extremely low compared with that of Ga-ZSM-5. On Al_2O_3 catalyst, CH_4 was mainly consumed by reaction with O_2, resulting in the low level of NO conversion. In contrast, NO was selectively reduced to N_2 on Ga-ZSM-5.

The results of reduction of NO with C_2H_6 on Ga-ZSM-5 were shown in Fig.2. The levels of NO conversion with C_2H_6 were comparable or a little higher than those with CH_4 on this catalyst.

Figure 3 shows the effect of hydrocarbon concentration on the catalytic activity of Ga-ZSM-5 at 500 °C. NO conversion increased with increasing concentration of CH_4 and C_2H_6.

It should be noted that Ga-ZSM-5 showed high catalytic activity for reduction of NO even in the presence of small amounts of CH_4 and C_2H_6. It was shown in our previous work[13) that gallium ion-exchanged zeolites showed high activity and selectivity for the reduction of NO with C_3H_8, and that the limiting molar ratio of reacted NO to produced COx was near unity.

Figure 4 shows the relationship between the molar ratio of reacted NO to produced COx and the concentration of reductants. The limiting molar ratio of reacted NO to consumed carbon in C_2H_6 and CH_4 was 1.5, and 2, respectively. These ratios were almost independent of the concentration of hydrocarbons. Reduction of NO with CH_4 and C_2H_6 proceeded predominantly on Ga-ZSM-5, and CH_4 and C_2H_6 were hardly consumed by the reaction with O_2.

We conclude from these results that reduction of NO proceeds on Ga-ZSM-5 even when CH_4 and C_2H_6 are used as reductants, and CH_4 was an effective reductant for selective reduction of NO.

References

1)S.Sato, Y. Yu-u, H.Yahiro, N.Mizuno, and M.Iwamato, *Appl.Catal.*, **70**, L1 (1991).
2)H. Hamada, Y. Kintaichi, M. Sasaki, and T. Itoh, *Appl. Catal.*, **64**, L1 (1990).
3)S.Sato, H. Hirabayashi, H.Yahiro, N.Mizuno, and M.Iwamato, *Catal. Lett.*, **12**, 193 (1992).
4)M. Misono, and K. Kondo, *Chem. Lett.*, **1991**, 1001.
5)E. Kikuchi, K. Yogo, S. Tanaka, and M. Abe, *Chem. Lett.*, **1991**, 1063.
6)T. Inui, S.Iwamoto, S. Kojo, and T. Yoshida, *Catal. Lett.*, **13**, 87 (1992).
7)Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki, and T. Ito, *Catal. Lett.*, **6**, 239,(1990).
8)Y. Torikai, H.Yahiro, N.Mizuno, and M.Iwamato, *Catal. Lett.*, **9**, 91 (1992).
9)H. Hosose, H.Yahiro, N.Mizuno, and M.Iwamato, *Chem. Lett.*, **1991**, 1859.
10)K.Yogo, S.Tanaka, M.Ihara, T.Hishiki, and E.Kikuchi, *Chem. Lett.*, **1992**, 1025.
11)M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo, and N. Mizuno, *Shokubai*, **32**, 430 (1990).
12)H. Hamada, Y. Kintaichi, M. Tabata, M. Sasaki, and T. Itoh, *Shokubai*, **33**, 59 (1991).
13)K.Yogo, M.Ihara, I. Terasaki, and E.Kikuchi, *Catal. Lett.*, submitted for publication.

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