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Selective catalytic reduction of N_2O with methane in the presence of excess oxygen over Fe-BEA zeolite

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An Fe ion-exchanged BEA zeolite (Fe-BEA), which effectively performs selective catalytic reduction of N_2O with methane in the presence of excess oxygen, is much more active than Fe-MFI zeolite reported in the literature.

Nitrous oxide (N_2O) and methane (CH_4) are strong greenhouse-effect gases with a global warming potential (GWP) per molecule of *ca.* 300 and 30 times that of carbon dioxide (CO_2), respectively.[1] N_2O is also identified as a contributor to the destruction of ozone in the stratosphere.[2] From the point of view of the environment, therefore, it is of interest to study selective catalytic reduction (SCR) of N_2O by CH_4 which can lead to simultaneous abatement of N_2O and CH_4 in emission gases. Recently, the groups of Segawa[3,4] and Turek[5,6] reported that the SCR of N_2O by hydrocarbons such as C_3H_6 and C_3H_8 took place effectively over Fe-MFI catalysts even in the presence of coexistent gases such as excess O_2 and H_2O. However, little detailed work with respect to other catalysts and/or reductants in the SCR of N_2O has been performed. We have been studying the SCR of N_2O with hydrocarbons over different Fe ion-exchanged zeolite catalysts (*e.g.* Fe-MFI, Fe-MOR, Fe-NaY, *etc.*).[7] During the course of this study, an Fe ion-exchanged BEA (Fe-BEA) catalyst was found to be much more active for the SCR of N_2O than Fe-MFI zeolite reported in the literature. We report here that the Fe-BEA catalyst performs effectively for the SCR of N_2O with CH_4 even in the presence of an excess of oxygen.

Fe-BEA (SiO_2/Al_2O_3 = 27.3) catalyst was prepared by ion-exchange with a dilute solution of $Fe(SO_4)$ at 50 °C for 20 h under a nitrogen atmosphere, and calcined in air for 12 h at 500 °C.[3,4] For comparison, Fe-MFI (SiO_2/Al_2O_3 = 23.8) was also prepared by the same procedures as Fe-BEA. The zeolite supports (H-BEA, Na-MFI) were supplied by TOSOH Co. The loading weight of Fe on BEA and MFI supports was 0.77 wt% (25 % exchanged with Fe^{2+}) and 2.90 wt% (80% exchanged with Fe^{2+}), respectively. The reaction was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of N_2O (950 ppm), CH_4 (500 or 3000 ppm) and O_2 (10%) in an He flow at a total flow rate of 50 $cm^3\ min^{-1}$ over 50 mg of catalyst [total pressure: 1 atm; space velocity (SV): 60 000 h^{-1}]. The samples were pretreated at 500 °C with O_2 for 1 h in a flow reactor, followed by a He purge at the initial reaction temperature. Catalytic experiments on various reaction systems were performed as detailed in Table 1. The products were monitored by an on-line gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5A (N_2, CH_4, CO) and Porapak Q (N_2O, CO_2, H_2O) columns. The catalytic activity for the reduction of N_2O with CH_4 was evaluated by the percentage conversion of N_2O and CH_4 to N_2 and CO_x (CO_2 and/or CO), respectively.

Figs. 1 and 2 show N_2O and CH_4 conversions in the different reaction systems (over Fe-BEA and Fe-MFI catalysts), respectively. As shown in Fig. 1, the catalytic activities of N_2O decomposition on both Fe-BEA and Fe-MFI catalysts were significantly promoted by adding CH_4, while N_2O decomposition was inhibited in the presence of O_2. Compared with the N_2O (950 ppm)/O_2 (10 %)/CH_4 (500 ppm) system, the N_2O conversion curve shifted to lower temperature in the absence of O_2 (O_2: 10 → 0%: **No. 3** and **4** in Fig. 1), while the N_2O conversion was scarcely affected by the composition of CH_4 in this range (CH_4: 500 → 3000 ppm: **No. 4** and **5** in Fig. 1). For both Fe-BEA and Fe-MFI, increases of CH_4 conversions correlated well with that of N_2O conversions. N_2, H_2O and CO_2 were observed as the main products in the $N_2O/CH_4/O_2$ system for both catalysts. Moreover, it was found that there was a plateau in CH_4 conversion after N_2O conversion reached 100% (*ca.* 350–450 °C, Fig. 2). This is due to the fact that N_2O in the mixture gas was completely consumed by reaction with CH_4 at such temperatures. It should be noted that oxidation of CH_4 by O_2 over the Fe-BEA catalyst began above 450 °C (**No. 6** in Fig. 2). These results indicate that the reduction of N_2O and the oxidation of CH_4 in this reaction system ($N_2O/CH_4/O_2$) concomitantly take place at much lower temperature than each of original reaction temperatures in the N_2O decomposition (N_2O alone: **No. 1** in Fig. 1) and the CH_4 oxidation (CH_4/O_2

Table 1 List of the reaction systems on the catalytic experiments

		Feed composition in mixture gases		
Reaction No.	Catalyst	N_2O (ppm)	O_2 (%)	CH_4 (ppm)
1	Fe-BEA	950	0	0
2	Fe-BEA	950	10	0
3	Fe-BEA	950	0	500
4	Fe-BEA	950	10	500
5	Fe-BEA	950	10	3000
6	Fe-BEA	0	10	500
7	Fe-MFI	950	0	0
8	Fe-MFI	950	10	0
9	Fe-MFI	950	10	500

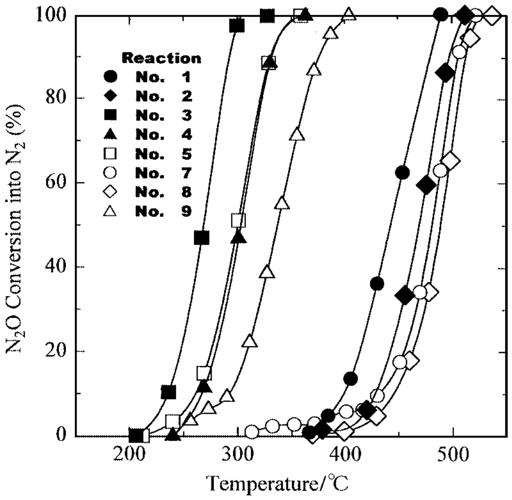

Fig. 1 N_2O conversion to N_2 over Fe-BEA and Fe-MFI. Reaction conditions (**No.**) are described in Table 1.

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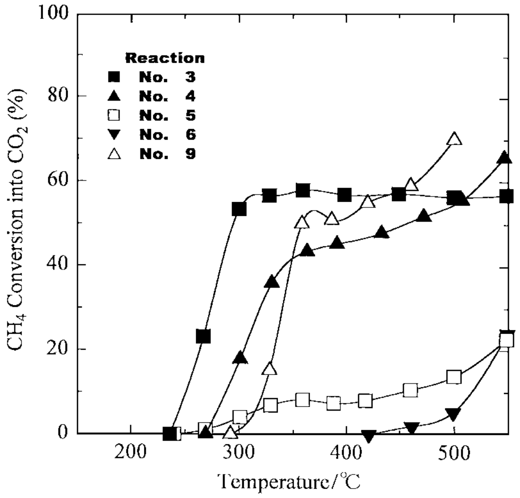

Fig. 2 CH_4 conversion to CO_2 over Fe-BEA and Fe-MFI. Reaction conditions (**No.**) are described in Table 1.

mixture: **No. 6** in Fig. 2). Therefore, O atoms from N_2O molecules are much more efficient in activating CH_4 than O atoms from O_2 molecules at low temperature (< 400 °C).

As also shown in Fig. 1, catalytic activities (per g cat) for the decomposition of N_2O and the selective catalytic reduction (SCR) of N_2O by CH_4 over the Fe-BEA catalyst are much higher than those over the Fe-MFI catalyst. Table 2 shows TOF values based on the catalytic activities in N_2O (**No. 1** and **7**) and $N_2O/O_2/CH_4$ (**No. 4** and **9**) systems over Fe-BEA and Fe-MFI. The TOF values were estimated by assuming that all of loaded Fe (exchanged with Fe^{2+}) act as active sites. These TOF values, of both the decomposition of N_2O and the SCR of N_2O by CH_4 over Fe-BEA are more than one order of magnitude higher than those over Fe-MFI. From the above results, it is strongly suggested that Fe-BEA zeolite is much more active than Fe-MFI zeolite. The difference in the catalytic activities between Fe-BEA and Fe-MFI suggests that the decomposition of N_2O and the SCR of N_2O by CH_4 may be influenced by the structure of zeolite and/or states of the Fe ions.[7] On the other hand, the TOF values of N_2 formation on the SCR of N_2O by CH_4 were significantly higher than those for the decomposition of N_2O over both zeolites. This result indicates that the reaction mechanism for the SCR of N_2O by CH_4 is substantially different from that for the decomposition of N_2O.

Table 2 Comparison of TOF values for N_2O decomposition and SCR of N_2O

	10^{-4} TOF^a/s^{-1}		
		SCR of N_2O by CH_4^{c}	
Catalyst	Decomposition of N_2O^{b} N_2 formation	N_2 formation	CO_2 formation
Fe-BEA	16.8	21.8	4.35
Fe-MFI	1.19	1.73	0.07

[a] Turnover frequency (TOF: s^{-1}): number of product molecules per number of Fe ions s^{-1}. [b] At 430 °C (reaction **No. 1** and **7**). [c] At 300 °C (reaction **No. 4** and **9**).

The present results have demonstrated that the SCR of N_2O by CH_4 in the presence of an excess of O_2 occurs effectively over the Fe-BEA catalyst. Interestingly, the reaction temperatures for the SCR of N_2O by CH_4 and the selective oxidation of CH_4 by N_2O over Fe-BEA are much lower than those for N_2O decomposition ($2N_2O \rightarrow 2N_2 + O_2$) or CH_4 combustion ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) even in the presence of excess O_2. We are currently undertaking further investigations in our laboratory with respect to the detailed mechanism, the effect of coexistent gases (SO_2, NO, H_2O, *etc.*) and the characterization of active sites (Fe ion states *etc.*).

Notes and references

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