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Structure sensitivity of ion-exchanged Fe-MFI in the catalytic reduction of nitrous oxide by methane under an excess oxygen atmosphere

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Abstract

We investigated the effect of the loading amount of Fe over ion-exchanged Fe-MFI catalysts (Fe-MFI) on the catalytic performance in N_2O reduction with CH_4 under an excess oxygen atmosphere. It is found that the turnover frequency (TOF) was very low on $Fe/Al < 0.1$; in contrast, the TOF increased drastically with increasing Fe/Al in the range of $Fe/Al \geqslant 0.15$. In temperature-programmed reduction (TPR) with hydrogen, the reduction started at a lower temperature over higher loading catalysts. In the profiles of temperature-programmed desorption (TPD) of oxygen, two peaks were observed. The lower temperature desorption peak (673–873 K), which was not observed on Fe-MFI ($Fe/Al < 0.15$), appeared on Fe-MFI ($Fe/Al \geqslant 0.15$). The amount of O_2 desorption in the lower temperature range is closely related to the TOF of N_2O reduction with CH_4 under an excess oxygen atmosphere. This suggests that the active site is Fe species which can give a lower temperature O_2-TPD peak, and it is thought that this is a binuclear Fe ion species judging from the loading amount dependence of the properties. Furthermore, according to the pulse $CH_4 + N_2O$ reaction over Fe-MFI ($Fe/Al = 0.10$ and 0.40), Fe^{2+} ions can promote a $CH_4 + N_2O$ reaction over both catalysts, and Fe^{3+} ions can also promote it over Fe-MFI ($Fe/Al = 0.40$), but not over Fe-MFI ($Fe/Al = 0.10$). This indicates that the reduction and oxidation processes were balanced at a much higher level on Fe-MFI ($Fe/Al = 0.40$) than on Fe-MFI ($Fe/Al = 0.10$). This can be due to binuclear Fe ion species present on Fe-MFI ($Fe/Al = 0.40$), and high catalytic activity can be caused by this property.

Keywords: Iron; MFI; Ion exchange; Nitrous oxide; Methane; Structure sensitivity; Redox

1. Introduction

Nitrous oxide (N_2O), which also contributes to catalytic stratospheric ozone destruction, is a strong greenhouse-effects gas with global warming potential (GWP) per molecule of about 300 times that of carbon dioxide (CO_2) [1,2]. Therefore, from an environmental point of view, the catalytic decomposition of N_2O ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$) [2–15] and the selective catalytic reduction (SCR) of N_2O with reductant such as various hydrocarbons [16–31] and ammonia [32–34] have been attracting much attention. Various kinds of metal oxides (including mixed oxides) [3,4], supported noble metals (Rh, Ru) [5–8], and transition metal-exchanged zeolites (Cu-MFI, Fe-MFI, etc.) [9–15] have been studied for N_2O decomposition. In the case of the SCR of N_2O over Fe-MFI catalysts, various reductants (except methane) such as propane [16,17], propene [18–22,24], ethane [25], and ammonia [32–34] have been utilized.

We have reported that Fe-BEA catalysts prepared by a wet ion-exchange method showed higher activity than Fe-MFI catalysts in the SCR of N_2O with light hydrocarbons [24–30]. Especially, we have been studying the SCR of N_2O by methane (CH_4) over Fe-zeolite. Generally speaking it is difficult to use CH_4 as the reducing agent since the reactivity of CH_4 is very low. We have found that CH_4 can play the role of reductant like other light alkanes [26–30], and that Fe-BEA catalysts are most active for the reduction of N_2O with CH_4 in Fe-zeolite catalysts (MFI, MOR, FAU) [28]. Furthermore, we have proposed that nascent oxygen formed from N_2O dissociation can drastically promote the activation of CH_4 in terms of the reaction mechanism [30,31].

Recently, studies on the structure and reactivity of Fe-zeolite catalysts, particularly Fe-MFI and Fe-BEA, have been carried out. Sachtler and co-workers have reported that Fe/MFI prepared by a sublimation method has a molar ra-

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tio of Fe to Al-centered tetrahedral of 1/1 and that the active species over MFI is an oxygen-bridged binuclear iron species [35,36]. Köningsberger and co-workers have determined the structure of the binuclear Fe complex with Fe–O–Fe bridges on Fe/ZSM5 catalysts, which were prepared by $FeCl_3$ by EXAFS [37]. Panov and co-workers have indicated that α-oxygen can participate in the direct catalytic oxidation of benzene to phenol by N_2O over Fe-MFI, and the oxygen species are related to the presence of a binuclear Fe complex [38–44].

In addition, it has been pointed out that another kind of structure of iron species appears with increasing amount of Fe loading [32,33,45]. Coq and co-workers have proposed that mononuclear iron-oxo cations, which exist mainly on low-exchange-level catalysts, are the most highly reactive sites for the reduction of N_2O by NH_3 over Fe-BEA catalysts, and binuclear iron-oxo species and iron oxides that are formed over high Fe loading catalysts are less active [32–34]. Moreover, when propene was used as reductant in the reduction of N_2O, even low-exchange Fe-ZSM-5 catalysts exhibited high activity [22]. From these comparisons, the active structure of iron species over zeolites is much dependent on the kind of reductant.

Therefore, it is worth elucidating the active site on Fe-MFI catalysts in the N_2O reduction with CH_4 under an excess oxygen atmosphere. In this study, we have investigated the dependence of the catalytic activity of N_2O reduction with CH_4 on the loading amount of Fe over MFI. We also carried out the catalyst characterization by means of H_2-TPR, O_2-TPD, and pulse reactions. From the comparison between the activity and characterization results, we discuss the structure of the active sites and the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

Fe-MFI catalysts were prepared by an ion-exchange method using an aqueous solution of $FeSO_4 \cdot 7H_2O$ (Wako Pure Chemical Industries Ltd., 98%) for 20 h at 323 K under a nitrogen atmosphere to avoid the precipitation of $Fe(OH)_3$. Na-MFI (TOSOH Co., $SiO_2/Al_2O_3 = 23.8$) was used as the catalyst support. The catalyst was separated from the solution by filtration after an ion-exchange procedure. It was washed thoroughly with distilled water and dried at 383 K overnight, followed by calcination in air at 773 K for 3 h. The loading amount of the Fe on MFI was determined by subtracting the Fe amount in the solution after the separation, analyzed by ICP analysis, from the total amount. The exchange efficiency of $FeSO_4$, percentage of the iron salt incorporated into the zeolite, was almost 100% in the case of $Fe/Al = 0.05$–0.24. On the other hand, it was almost 80% in the case of $Fe/Al = 0.40$. The catalyst is denoted as Fe(X)-MFI, where X stands for molar ratio of Fe/Al.

2.2. Activity test

Catalytic reduction of N_2O with CH_4 under an excess O_2 atmosphere was carried out in a fixed-bed flow reactor. Reactant gases were the mixture of N_2O (950 ppm), CH_4 (500 ppm), and O_2 (0–20%) balanced with He. All these research grade gases were purchased from Takachiho Trading Co. Ltd., and they were used without further purification. The catalyst weight was 50 mg, and total pressure was 0.1 MPa, and W/F (W (g) = catalyst weight, F ($\text{mol}\,\text{h}^{-1}$) = total flow rate) was 0.41 $\text{g}\,\text{h}\,\text{mol}^{-1}$. The catalysts were pretreated at 773 K with O_2 for 1 h in the reactor. As a reference, N_2O decomposition was also carried out. Reactant gase was N_2O (950 ppm) balanced with He. Other reaction conditions were the same as those in N_2O reduction as described above. The products were monitored by an on-line TCD gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5A column for N_2 and O_2, and Porapak Q column for N_2O, and an FID gas chromatograph (Shimadzu GC-14B) equipped with Gaskuropak 54 column and methanator for CO, CO_2, and CH_4. The sampling and analyzing of effluent gas were carried out for 1 h at each reaction temperature. This means that the results of the activity tests shown in the figures were obtained under steady-state conditions.

2.3. Catalyst characterization

Temperature-programmed reduction (TPR) with H_2 was performed in fixed-bed flow reactor. The sample was pretreated in 100% O_2 flow at 773 K for 1 h, and then it was cooled down to room temperature and exposed to helium flow in order to purge the line. The TPR profile of each sample was recorded from room temperature to 973 K under a flow of 5.0% H_2/Ar. The flow rate of 5.0% H_2/Ar was 30 ml/min, and the catalyst weight was 50 mg. The heating rate was 10 K/min and the temperature was maintained at 973 K for 10 min after it reached 973 K. The consumption of H_2 was monitored continuously with a TCD gas chromatograph equipped Molecular Sieve 5A in order to remove H_2O from the effluent gas.

Temperature-programmed desorption of O_2 (O_2-TPD) was carried out in a fixed-bed reactor equipped with a quadrupole mass spectrometer (Balzers QMS 200 F). The catalysts (30 mg) were pretreated with O_2 flow (100% O_2, 773 K, 1 h) or N_2O flow (10% N_2O/He, 773 K, 1 h). After the pretreatment, they were rapidly cooled down to room temperature. Helium gas (flow rate 55 ml/min) was introduced to the reactor, and the sample was heated with heating rate 10 K/min from room temperature to 1273 K. The sample temperature was kept at 1273 K for 30 min just after it reached 1273 K. Desorbed O_2 in He flow (flow rate, 55 ml/min) was analyzed with a quadrupole mass spectrometer.

Pulse reactions of $N_2O + CH_4$ were carried out in a fixed-bed reactor combined with TCD-GC. For Fe(0.40)-MFI and

Fe(0.10)-MFI, three kinds of pretreatment were carried out: H_2 (5% H_2/Ar, 30 ml/min) at 773 K for 1 h, O_2 (100% O_2, 30 ml/min) at 773 K for 1 h, and N_2O (10% N_2O/He, 30 ml/min) at 773 K for 1 h. The catalyst weight was 30 mg for Fe(0.40)-MFI and 120 mg for Fe(0.10)-MFI, where the amount of Fe on the catalyst was just the same (15 µmol). Pulse gas contained 0.82 µmol N_2O and 0.40 µmol CH_4. The gases (N_2O and CH_4) were analyzed by TCD-GC. The pulse was injected 25 times with 5-min intervals.

3. Results and discussion

Selective catalytic reduction of N_2O with CH_4 over ion-exchanged Fe-MFI catalysts was carried out in the $N_2O/CH_4/O_2$ system in the temperature range between 473 and 773 K. The gas consisted of 950 ppm N_2O, 500 ppm CH_4, and 10% O_2 diluted with He. Products of this reaction were N_2, CO, CO_2, and H_2O. NO_x was not detected in this reaction. Figs. 1a and b show the temperature dependence of N_2O and CH_4 conversion over Fe-MFI with various kinds of Fe loading, respectively. It is clear that the catalytic activity of N_2O reduction increased with increasing Fe amount. In the case of Fe(0.05)-MFI, the reaction started at about 600 K. On the other hand, the reaction can proceed even under 550 K over Fe(0.40)-MFI. As shown in Fig. 1b, CH_4 conversion increased with the reaction temperature and also with Fe loading. It is interesting that the behavior of N_2O and CH_4 is similar to each other over various Fe-MFI catalysts (Fig. 1c). Furthermore, it should be pointed that there was a plateau in CH_4 conversion at which N_2O conversion reached almost 100%, especially over Fe-MFI ($Fe/Al = 0.40$) (Fig. 1b). This indicates that the activation of CH_4 requires N_2O, and CH_4 can not be oxidized directly with O_2 even at 773 K. In addition, we also show CO_2 selectivity and (consumed N_2O)/($3CO + 4CO_2$) in Figs. 1d and e, respectively. CO_2 selectivity is estimated by $CO_2/(CO + CO_2)$. Regarding Fig. 1e, $3CO + 4CO_2$ represents the total amount of oxidizing agent assuming the equations:

$$CH_4 + 4[O] \rightarrow CO_2 + 2H_2O,$$

$$CH_4 + 3[O] \rightarrow CO + 2H_2O.$$

[O] is oxygen atom originated from N_2O and O_2. Therefore, the ratio of the consumption rate of N_2O to the formation rate of $3CO + 4CO_2$ corresponds to the contribution of N_2O in the total amount of the reacted oxidizing agents ($N_2O + O_2$). As shown in Fig. 1d, the selectivity of CO_2 increased with reaction temperature gradually. Fig. 1e shows the ratio of N_2O to total oxidizing agents (N_2O and O_2) in CH_4 oxidation to CO and CO_2. The ratio was located between 40 and 60%. This indicates that oxygen as well as N_2O is used as an oxidizing agent. Under the presence of excess oxygen, N_2O can be reduced with methane over Fe-MFI. Although the concentration of N_2O (950 ppm) is about 100 times as low as that of O_2 (10%), about half of the oxidizing agents was contributed by N_2O as shown in Fig. 1e. As described above, oxygen cannot react with CH_4 directly. Therefore, methane is at first activated with N_2O to give reaction intermediates (i.e., methoxy species, etc. [30]), which can react with both N_2O and O_2. The results of our FTIR studies [30,31] will be commented on later.

N_2O reduction with CH_4 in the absence of oxygen over Fe-MFI catalysts was also carried out. Figs. 2a and b show the temperature dependence of N_2O and CH_4 conversion over Fe-MFI with various kinds of Fe loading, respectively. As Fig. 2a is compared with Fig. 1a, N_2O conversion in the absence of oxygen was a little higher than that under the excess oxygen atmosphere (10%) over each Fe-MFI catalyst. Regarding CH_4 reactivity (Fig. 2b), the CH_4 conversion curve over each Fe-MFI catalyst showed a plateau at about 60%. This tendency is different from that under an excess oxygen atmosphere, where there was a plateau at about 80%. This is due to the contribution of oxygen in CH_4 oxidation. In terms of CO_2 selectivity, the presence of oxygen increased the CO_2 selectivity. Furthermore, the relation between CH_4 conversion and N_2O conversion shows that N_2O can react with CH_4 selectively in the presence and absence of oxygen (Fig. 1c and Fig. 2c).

Fig. 3 shows profiles of temperature-programmed reduction with H_2 over Fe-MFI catalysts after O_2 treatment at 773 K. The TPR profile of Fe_2O_3 is also shown in the figure. It is clear that the TPR profile of Fe-MFI was much different from that of Fe_2O_3. The peak at 670–680 K can be assigned to the reduction from Fe^{3+} ions to Fe^{2+} ions [32,34,35]. The peak at 850 K can be assigned to the reduction of Fe_2O_3 by comparing to TPR profile of Fe_2O_3 reference compound (Fig. 3f). This small peak appeared only on Fe(0.40)-MFI catalysts. This is due to the aggregation of Fe ions on the catalyst with high Fe loading. A molar ratio of consumed H_2 to Fe on Fe-MFI can be estimated to be 0.5 on all the Fe-MFI catalysts on the basis of the equation $Fe^{3+} + \frac{1}{2}H_2 \rightarrow Fe^{2+} + H^+$ (Table 1). These results indicate that most of Fe species on Fe-MFI catalysts exist as Fe^{3+} ions after O_2 pretreatment. In addition, it should be noted that the starting temperature of Fe reduction was lower on Fe-MFI with higher Fe loading. For example, the reduction started at ca. 600 K on Fe(0.05)-MFI, while it started at 450 K on Fe(0.40)-MFI. This indicates that Fe-MFI catalysts with higher Fe content contain more reducible Fe species. This suggests that the structure of Fe ion species is highly dependent on the Fe loading.

Profiles of temperature-programmed desorption of O_2 over the catalysts after O_2 treatment are shown in Fig. 4I. The desorption was observed in the range of 673 to 1273 K. On Fe(0.05)-MFI and Fe(0.10)-MFI, a single and broad peak is observed. In contrast, on Fe-MFI ($Fe/Al \geqslant 0.15$), a sharper peak appeared around 873 K. The results of O_2-TPD also strongly suggest that the structure of Fe ion species is highly dependent on the Fe loading. O_2-TPD profiles on the catalyst after N_2O treatment are also shown in Fig. 4II. It is found that the amount of O_2 desorption of the sample

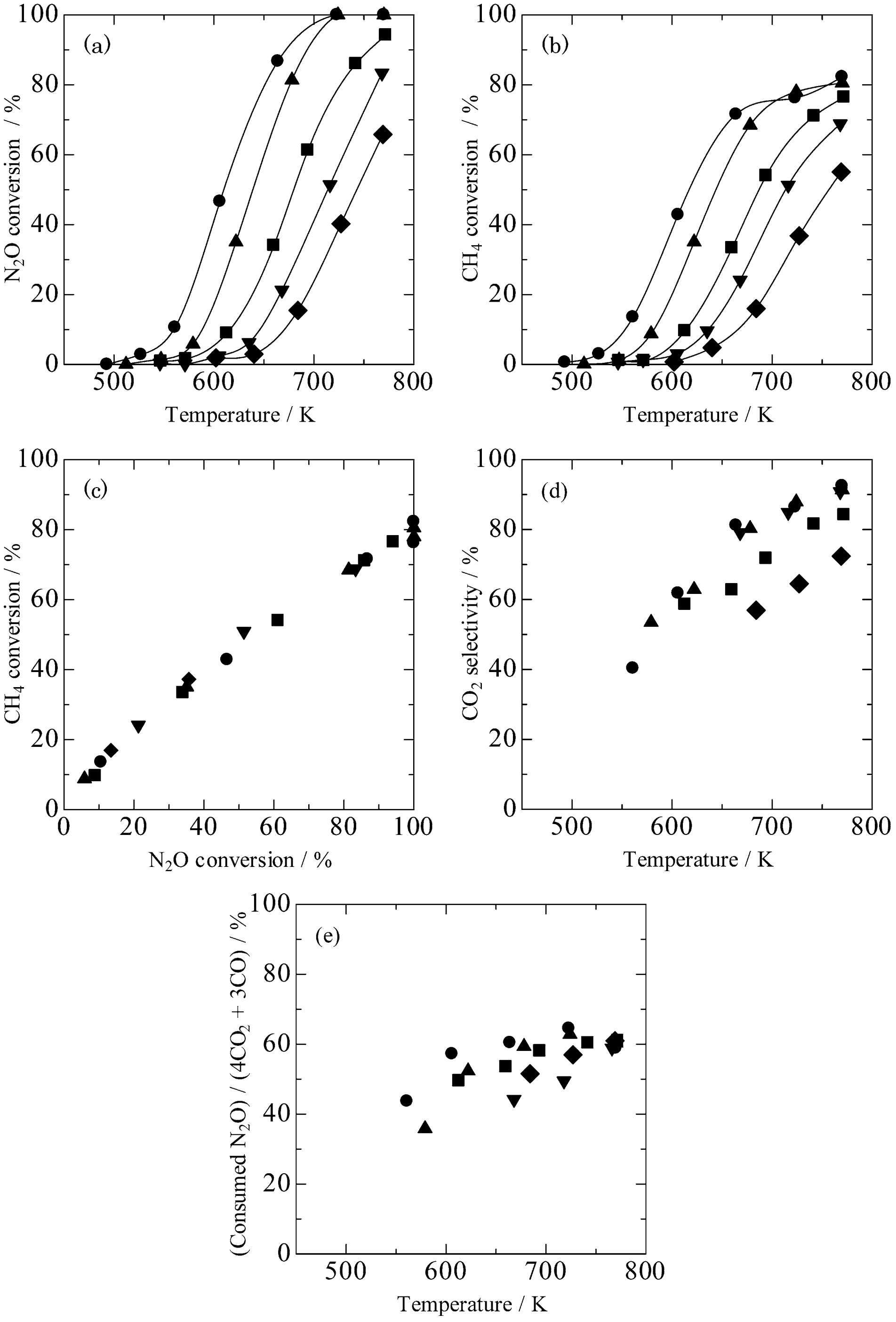

Fig. 1. Reaction temperature dependence of catalyst performance of Fe-MFI catalysts in N_2O reduction with CH_4 under an excess O_2 atmosphere. (a) N_2O conversion, (b) CH_4 conversion, (c) CH_4 conversion as function of N_2O conversion, (d) CO_2 selectivity ($CO_2/(CO + CO_2)$), (e) (consumed N_2O)/($4CO_2$ + 3CO). (●) Fe(0.40)-MFI, (▲) Fe(0.24)-MFI, (■) Fe(0.15)-MFI, (▼) Fe(0.10)-MFI, and (◆) Fe(0.05)-MFI. Reaction conditions: 950 ppm N_2O + 500 ppm CH_4 + 10% O_2 (He balance). (Consumed N_2O)/($4CO_2$ + 3CO) corresponds to the contribution of N_2O in total oxidizing agents.

after N_2O treatment is larger than that after O_2 treatment. Especially, this phenomenon is clearly observed on Fe(0.40)-MFI. The O_2-TPD profiles over Fe(0.40)-MFI after N_2O and O_2 treatments and their subtracted profile are shown in Fig. 4III. Although some fluctuation is contained in the subtracted spectrum, it indicates that N_2O-induced desorption is observed mainly at lower temperatures.

In order to estimate the desorption amount in each peak, the deconvolution of the desorption was carried out on the basis of the following assumptions: (i) O_2 desorption at the higher temperature peak starts at 793 K, at which the desorption on Fe-MFI (Fe/Al = 0.05 and 0.10) started. (ii) The peak top is located at 1043 K, where the peak top on Fe-MFI (Fe/Al = 0.05 and 0.10) was observed. (iii) Each peak has

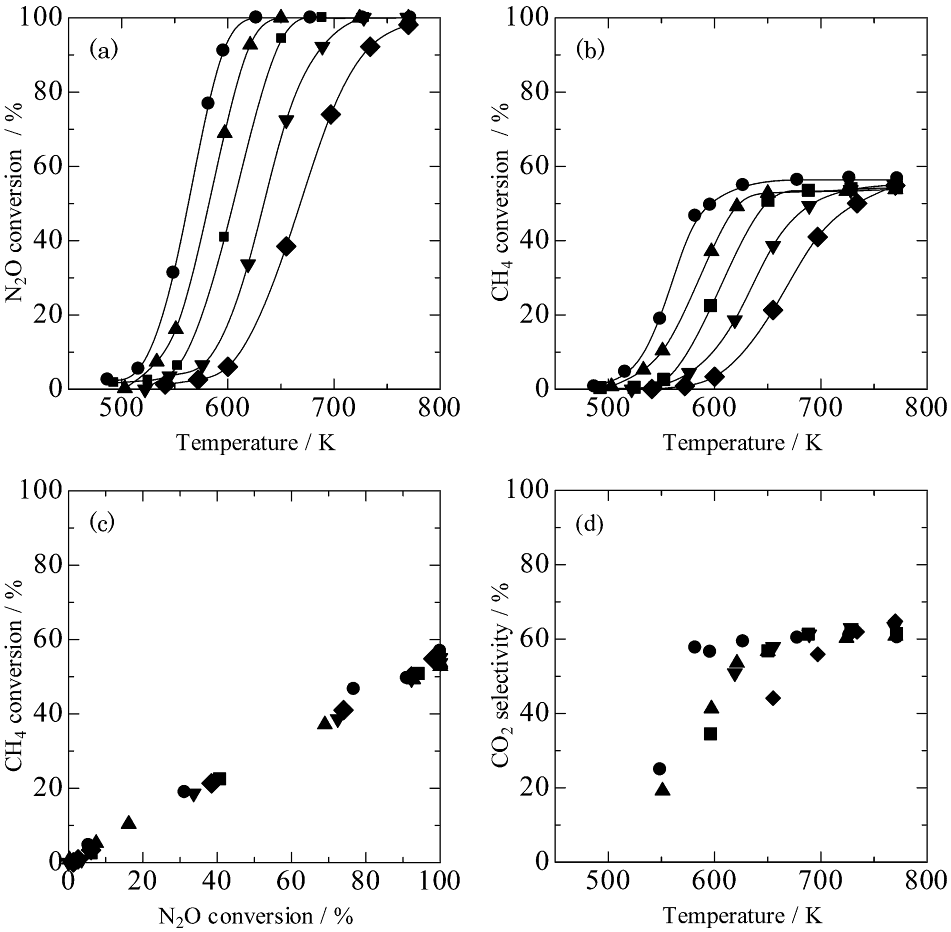

Fig. 2. Reaction temperature dependence of catalyst performance of Fe-MFI catalysts in N_2O reduction with CH_4 in the absence of O_2. (a) N_2O conversion, (b) CH_4 conversion, (c) CH_4 conversion as function of N_2O conversion, (d) CO_2 selectivity ($CO_2/(CO + CO_2)$). (●) Fe(0.40)-MFI, (▲) Fe(0.24)-MFI, (■) Fe(0.15)-MFI, (▼) Fe(0.10)-MFI, and (◆) Fe(0.05)-MFI. Reaction conditions: 950 ppm N_2O + 500 ppm CH_4 (He balance).

a symmetrical shape. The results of the deconvolution are shown in Fig. 5 and they are also listed in Table 1. The O_2-TPD profile of Fe(0.05)-MFI and Fe(0.10)-MFI after N_2O treatment was very similar to that of after O_2 treatment. This indicates that the amount of oxygen derived from N_2O dissociation ($N_2O \rightarrow N_2 + O(a)$) over O_2-treated Fe(0.05)-MFI and Fe(0.10)-MFI is very small. In addition, the catalytic activity of Fe-MFI in N_2O decomposition at 773 K is listed in Table 1. In terms of the activity of N_2O decomposition, both catalysts showed a much lower activity than Fe-MFI with a higher Fe content. This also supports that the activity of N_2O dissociation over Fe(0.05)- and Fe(0.10)-MFI was rather low. On the other hand, N_2O pretreatment significantly increased the amount of O_2 desorption on Fe(0.40)-MFI. Especially, it is found that the amount of O_2 desorption at lower temperature mainly increased by N_2O treatment. This indicates that N_2O can dissociate and oxygen atom is deposited on the catalyst surface on Fe-MFI with higher Fe loading and the oxygen atom (O(a)) is adsorbed on the Fe species which gives O_2 desorption at a lower temperature.

Related to this result, Panov and co-workers [38–44] have reported that Fe-MFI catalysts with low Fe loading that were treated at a high temperature are able to abstract an oxygen atom from an impinging N_2O molecule at 523 K; i.e., a special form of adsorbed oxygen (O(a)) is formed during N_2O treatment at 523 K. These authors observed that this special form of O(a) (so called α-oxygen) showed high reactivity with benzene (or CH_4) to form phenol (or CH_3OH) even at room temperature [38,39]. However, the extra O(a) species in our study, which gives O_2 desorption at the lower temperature, do not seem to be related to the α-oxygen species. The CH_4-pulsed experiments revealed that CH_4 cannot react with the O(a) species deposited by N_2O treatment at 773 K (or at 523 K) even at 600 K [30]. The coexistence of both N_2O and CH_4 in the gas phase was needed for the CH_4+ N_2O reaction [30]. Therefore, the nature of the extra O(a) species in our case appears to be quite different from that of the α-oxygen species.

In this work, the ion-exchanged Fe catalysts were prepared by calcination in air at 773 K. On the other hand, Panov et al. [38] prepared Fe-MFI catalysts by hydrothermal synthesis with the addition of iron as $FeCl_3$ to a starting gel. The Fe-MFI was transferred to the NH_4 form by exchange with an ammonia buffer and then calcined in air. Additional

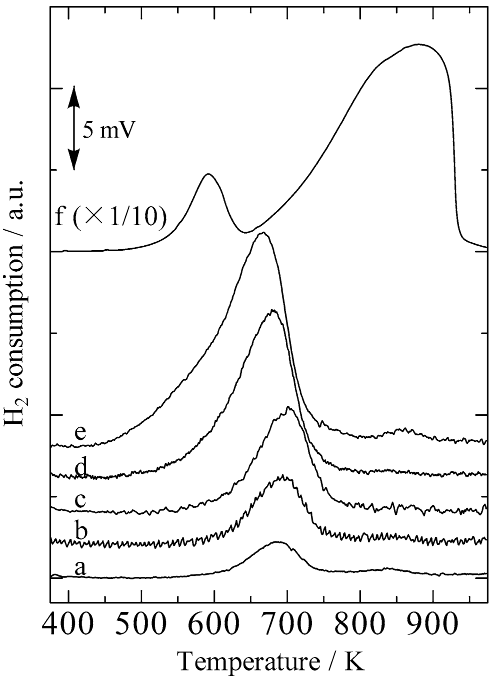

Fig. 3. Temperature-programmed reduction in hydrogen over Fe-MFI catalysts. (a) Fe(0.05)-MFI, (b) Fe(0.10)-MFI, (c) Fe(0.15)-MFI, (d) Fe(0.24)-MFI, (e) Fe(0.40)-MFI, and (f) Fe_2O_3 (10 mg).

calcination in vacuo at 1173 K was performed to increase the concentration of α-oxygen [39,41]. The calcination at the high temperature seems to be essential for the formation of the active α-sites. Delahay et al. [33] observed a sharp O_2-desorption peak at around 600 K after a Fe-BEA catalyst was pretreated in H_2 at 973 K followed by N_2O treatment at 973 K. In fact, we have observed a sharp O_2-desorption peak at 600 K after the Fe-MFI catalyst was treated in H_2 at 873 K or in vacuo at 1073 K followed by N_2O treatment at 523 K. The desorption temperature (600 K) was much lower than the lower peak (873 K) in Fig. 4, and the peak (not shown) was much more intense (and sharp), which might be related to a special form of O(a) such as α-oxygen species. Sachtler and co-workers [46] observed unusual TPR spike at 473 K after an Fe-MFI catalyst was treated in H_2 at 873 K followed by N_2O treatment at 523 K. This unusual TPR peak may also correspond to a special form of O(a). These results show that the states of O(a) species and/or structures of Fe ion species may depend strongly on the conditions of the pretreatment of Fe-zeolite catalysts as well as the Fe loading.

It seems that the behavior of TPD profiles on the Fe loading corresponds to that of H_2-TPR. The catalyst with a higher loading than that of $Fe/Al > 0.10$ has more reducible iron species in TPR profiles, which can desorb O_2 at lower temperatures in the TPD profiles. In addition we can compare the catalytic activity of N_2O reduction with CH_4 under the excess O_2 atmosphere and the characterization results. At first, it is possible to calculate the turnover frequency (TOF) of N_2O reduction activity: the N_2O conversion rate was divided by the total amount of Fe on the catalyst. The reaction rates of N_2O in the catalytic reaction in the presence of excess oxygen at 598 K on the basis of Fig. 1a and that in the absence of oxygen at 550 K on the basis of Fig. 2a are applied to the estimation of TOF, respectively. Since the conversion level over all the catalysts was lower than 40%, the reaction temperature 598 K in the presence of oxygen (10%) and the temperature 550 K in the absence of oxygen are applied to the estimation of TOF. Fig. 6 shows the dependence of TOF on the molar ratio of Fe to Al (Fe/Al) on Fe-MFI. In the range of $Fe/Al \leqslant 0.10$, the TOF was constant; however, it increased drastically with Fe loading ($Fe/Al \geqslant 0.15$). On the other hand, the relation between the desorption amount of oxygen atom derived from O_2 in the lower temperature peak per Fe content (O_{low}/Fe) and the Fe loading of Fe-MFI is also shown in Fig. 6. The O_{low}/Fe was very low level in the range of $Fe/Al \leqslant 0.10$; however, it increased at $Fe/Al \geqslant 0.15$. It is clear that the behavior of TOF is similar to that of O_{low}/Fe. This suggests that Fe species with low-temperature O_2 desorption gives much higher TOF of the N_2O reduction.

Table 1
Results of (a) O_2-TPD over Fe-MFI after O_2 and N_2O treatments, (b) N_2O decomposition, and (c) H_2-TPR

Catalyst	(a) O_2-TPD					(b) N_2O decomposition[a]	(c) H_2-TPR
	Treatment	Total, O_2 amount		Lower-temperature peak, O_2 amount		N_2O conversion (%)	H_2/Fe
		µmol	O/Fe	µmol	O/Fe		
Fe(0.40)-MFI	O_2	1.8	0.23	0.54	0.072	84	0.5
	N_2O	2.4	0.32	0.96	0.13		
Fe(0.24)-MFI	O_2	1.3	0.28	0.33	0.071	43	0.5
	N_2O	1.4	0.31	0.43	0.092		
Fe(0.15)-MFI	O_2	0.88	0.31	0.18	0.064	13	0.5
	N_2O	0.87	0.31	0.18	0.064		
Fe(0.10)-MFI	O_2	0.59	0.32	0.0	0.00	5	0.5
	N_2O	0.62	0.33	0.0	0.00		
Fe(0.05)-MFI	O_2	0.36	0.38	0.0	0.00	3	0.5
	N_2O	0.36	0.36	0.0	0.00		

Reaction conditions: N_2O (950 ppm) balanced with He, $W/F = 0.41$ g h/mol, catalysts were pretreated in O_2 at 773 K for 1 h.

[a] N_2O conversion was measured at 773 K.

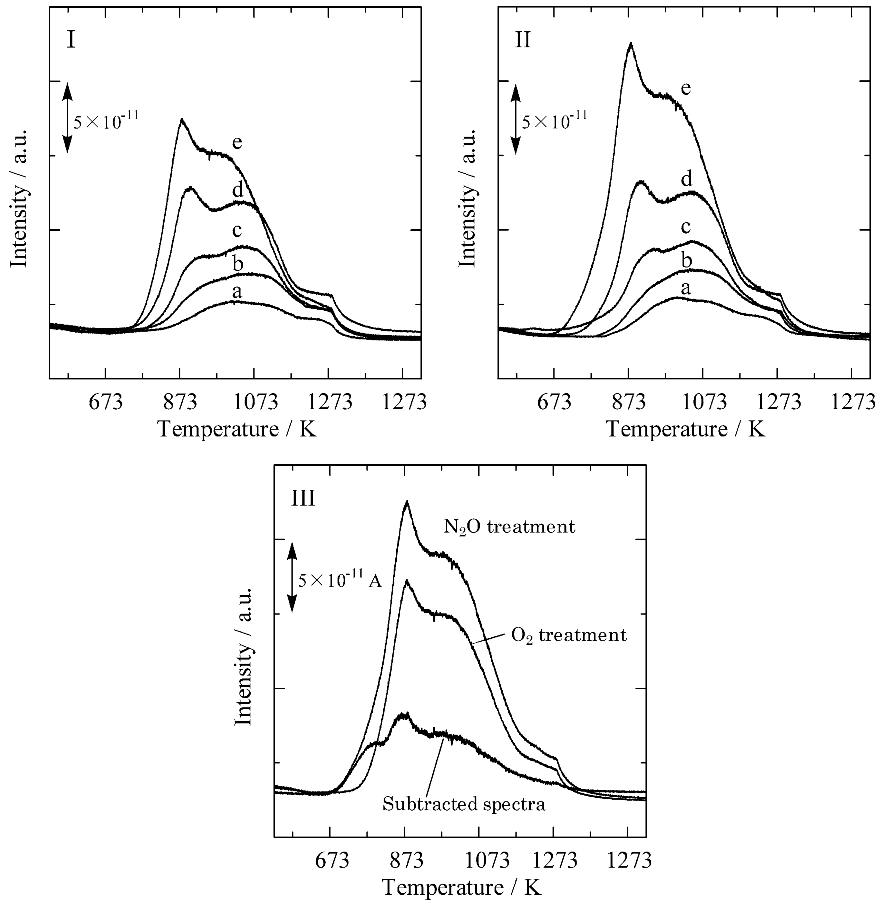

Fig. 4. Temperature-programmed desorption of oxygen (I) after O_2 treatment, (II) after N_2O treatment, and (III) subtracted spectra: (II-e) − (I-e). (a) Fe(0.05)-MFI, (b) Fe(0.10)-MFI, (c) Fe(0.15)-MFI, (d) Fe(0.24)-MFI, and (e) Fe(0.24)-MFI.

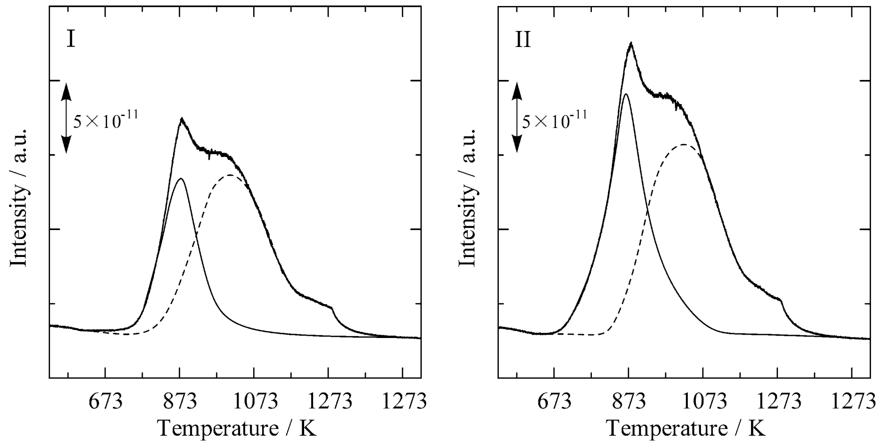

Fig. 5. The results of the deconvolution of O_2 desorption peak over Fe(0.40)-MFI after (I) O_2 treatment and (II) N_2O treatment. Solid line, lower temperature peak; broken line, higher temperature peak.

The activity of N_2O decomposition is also related to the lower temperature O_2 desorption. As listed in Table 1, the activity of N_2O decomposition at 773 K over Fe(0.05)- and Fe (0.10)-MFI was rather low, and much higher activity was observed on Fe-MFI ($Fe/Al \geqslant 0.15$). This behavior agrees with the previous report by Pirngruber [47]. Furthermore, Pérez-Ramírez et al. [48] have reported that the isolated iron sites are the most active species in N_2O reduction with C_3H_8 and CO. This relation is not consistent with our finding in N_2O reduction with CH_4. We think that this difference is caused by the reducing agents. As stated above, we have already reported that CH_4 cannot react with oxygen deposited from N_2O dissociation [30]. From the result that CH_4 can be activated to methoxy species when N_2O and CH_4 was in-

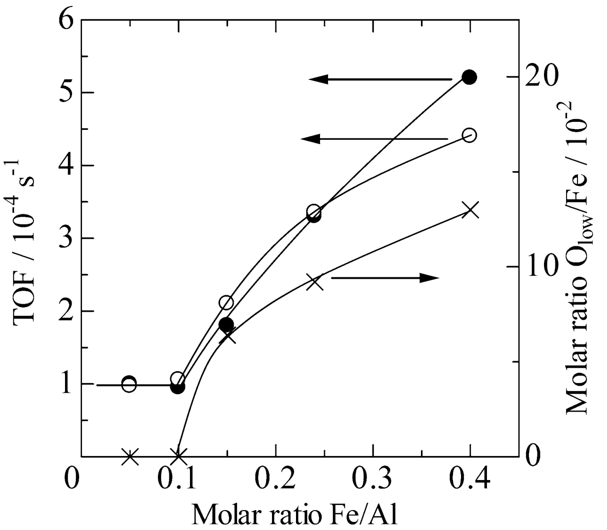

Fig. 6. Dependence of TOF (●, in the presence of 10% oxygen; ○, in the absence of oxygen) in N_2O reduction with methane and molar ratio O_{low}/Fe (×) obtained from TPD profile on the molar ratio Fe/Al in Fe-MFI catalyst. TOFs are estimated from the reaction rate of N_2O in the activity test at 598 K in the presence of 10% oxygen and total Fe amount on the basis of Fig. 1a, and that at 550 K in the absence of oxygen on the basis of Fig. 2a, respectively. Molar ratio O_{low}/Fe is determined by the desorption amount of oxygen atom derived from O_2 in the lower temperature peak after N_2O treatment and total Fe amount (see Fig. 4 and Table 1).

troduced to the catalyst at the same time, nascent oxygen originated from N_2O decomposition can play an important role in the activation of methane [30,31]. In contrast, we think that C_3H_8 and CO can react with adsorbed oxygen from N_2O, although we do not have enough data regarding N_2O reduction with C_3H_8 and CO. The difference in the mechanism of activation by reductants like C_3H_8, CO, and CH_4 can explain the difference in the active species.

Fig. 7 shows the effects of O_2 partial pressure on the catalytic activity and selectivity over Fe(0.40)-MFI. The activity of N_2O reduction decreased with increasing O_2 concentration as shown in Fig. 7a. In the case of $CH_4 + N_2O$ reaction without O_2, CH_4 conversion was constant at about 60% when N_2O conversion reached 100% (Fig. 7b), while the selectivity of CO_2 was lower than that under other conditions (Fig. 7d). When 2–20% oxygen was added to the reactant gas, a similar behavior regarding CO_2 selectivity and the contribution ratio of N_2O in all the oxidizing agents was observed, as shown in Figs. 7d and e. This indicates that O_2 addition to the reaction gases decreased the conversion level of N_2O and CH_4 a little, and the effect on the selectivity is not so significant. In contrast, the difference between $CH_4 + N_2O$ and $CH_4 + N_2O + O_2$ reactions was larger. As a result, O_2 addition decreased N_2O conversion and increased CH_4 conversion. This indicates that CH_4 is oxidized with both N_2O and O_2 in $CH_4 + N_2O + O_2$ reactions. However, CH_4 conversion reached a plateau when N_2O conversion reached 100% even though a large amount of O_2 is present. These results also indicate that CH_4 cannot react with O_2 directly. This strongly suggests again that N_2O is essential for the activation of CH_4. From these results, it is suggested that N_2O dissociates to N_2 and adsorbed oxygen atoms, at first, and then the adsorbed oxygen atoms activate CH_4 molecules.

According to our previous reports on Fe-BEA by means of FTIR studies, methoxy (CH_3O–) and formate (HCOO–) species on Fe ion sites have been observed [30,31], and kinetic parameters in the oxidation of methoxy and formate species with N_2O and O_2 were determined. It is concluded that the oxidation rate of methoxy species with N_2O is much higher than that with O_2; in contrast, the oxidation rate of formate species with N_2O was comparable to that with O_2 under the conditions of N_2O 1000 ppm and $O_2$10% at temperatures where $N_2O + CH_4 + O_2$ reactions can proceed. This indicates that methane can be totally oxidized with both N_2O and O_2. These results also suggest the formation of methoxy species over Fe-MFI, which can be oxidized with N_2O and O_2 in $CH_4 + N_2O + O_2$ reactions. Furthermore, this indicates that the dissociative adsorption of N_2O can influence the catalytic activity of $N_2O + CH_4 + O_2$. According to the results of O_2-TPD, the increase in the amount of desorbed O_2 by N_2O treatment was more significant over Fe-MFI with higher Fe loadings. This suggests that more sites for N_2O dissociation are present over the catalysts with higher Fe loadings. In addition, the result that N_2O conversion decreased with higher O_2 pressure (Fig. 7a) means the inhibition of N_2O dissociation by the presence of oxygen. In addition, it has been reported that O_2 molecules can be activated by surface oxygen species derived from N_2O under the coexistence of N_2O and O_2 [49]. Therefore, there may be the reaction path of methane activation by O_2; however, the contribution is thought to be very small. This is because methane conversion in $CH_4 + N_2O$ reactions was higher than other contributions in $CH_4 + N_2O + O_2$ reactions.

In order to investigate the effect of oxygen partial pressure in detail, we carried out the pulse reactions of $CH_4 + N_2O$ over Fe-MFI after pretreatments in H_2, O_2, or N_2O. According to the results of H_2-TPR, Fe species is present as Fe^{3+} over the catalyst after O_2 treatment at 773 K, and the Fe species is reduced to Fe^{2+} after H_2 treatment at 773 K. Furthermore, it can be assumed that Fe species is oxidized to $Fe^{(3+\delta)+}$ after N_2O treatment at 773 K, especially on Fe-MFI (Fe/Al = 0.40). These kinds of pretreatment can control the chemical state of Fe species over Fe-MFI. The pulse gas consisted of CH_4 (0.40 μmol) and N_2O (0.82 μmol) balanced with He, and the ratio of N_2O molecules to Fe atoms in the catalyst was 1/19. Fig. 8a shows the results of $CH_4 + N_2O$ pulse reaction over Fe(0.40)-MFI after the pretreatments. When $CH_4 + N_2O$ pulse is introduced to Fe(0.40)-MFI after H_2 treatment, both CH_4 and N_2O conversions were very high. A part of N_2O oxidized Fe(0.40)-MFI; however, most of N_2O reacted with CH_4. Conversions of N_2O and CH_4 decreased with increasing pulse number. This is because of the gradual oxidation of the reduced Fe(0.40)-MFI with increasing pulse number. It should be noted that CH_4 conversion is higher at the initial stage. This indicates

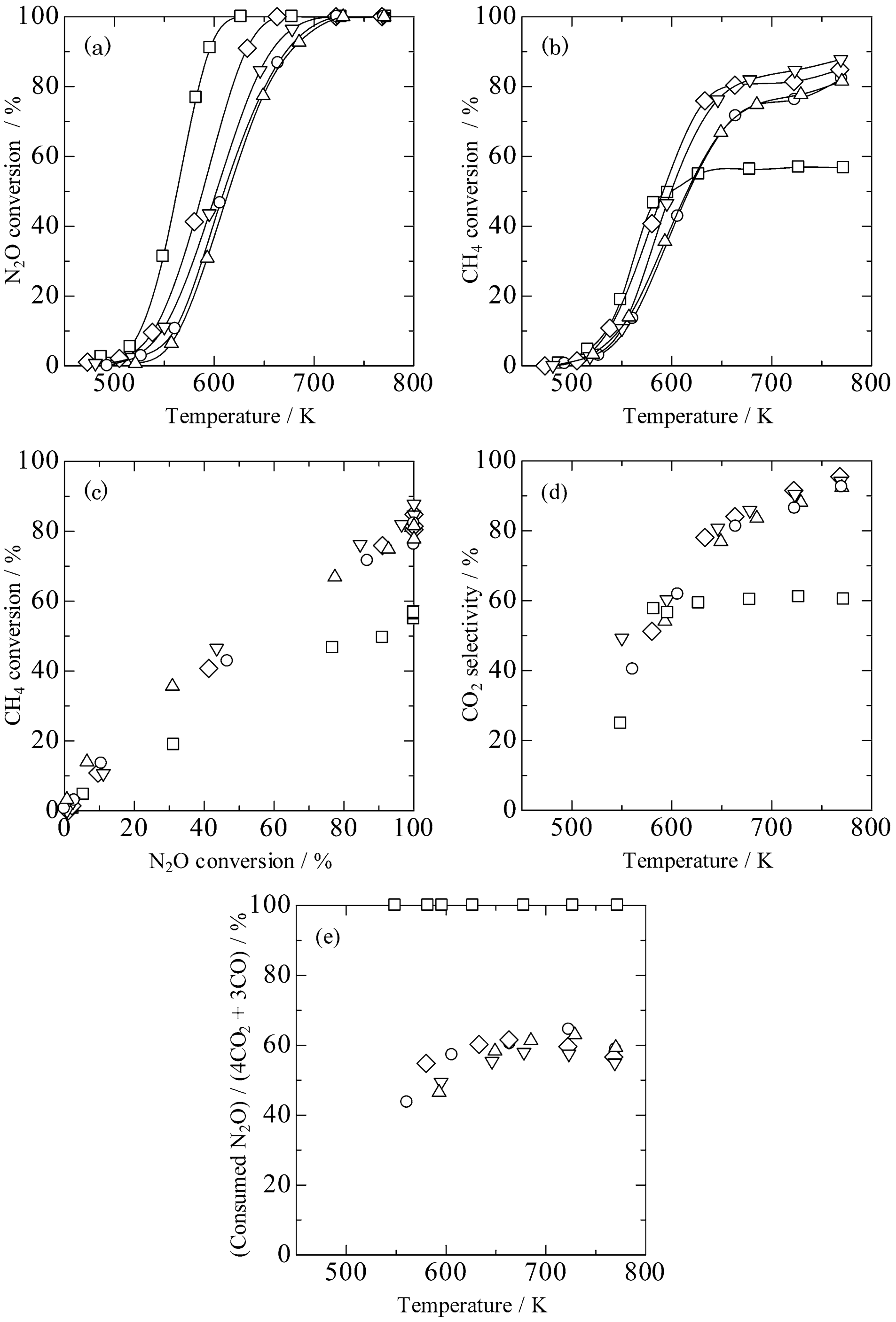

Fig. 7. Reaction temperature dependence of catalytic performance of Fe(0.40)-MFI catalyst in N_2O reduction with CH_4: the effect of partial pressure of O_2. (a) N_2O conversion, (b) CH_4 conversion, (c) CH_4 conversion as function of N_2O conversion, (d) CO_2 selectivity ($CO_2/(CO + CO_2)$), (e) (consumed $N_2O)/(4CO_2 + 3CO)$, (□) 0%, (◇) 2%, (▽) 5%, (○) 10%, and (△) 20%. Reaction conditions: 950 ppm N_2O + 500 ppm CH_4 + 0–20% O_2 (He balance). (Consumed $N_2O)/(4CO_2 + 3CO)$ corresponds to the contribution of N_2O in total oxidizing agents.

that the reaction does not proceed with the stoichiometry of catalytic $N_2O + CH_4$ reaction. In the catalytic $CH_4 + N_2O$ reaction, N_2O conversion was always higher than methane conversion as shown in Fig. 2. The results in the pulse experiments can be explained by methoxy and formate formation over the catalyst. In the pulse experiments, the introduced amount of N_2O and CH_4 was much smaller than the Fe amount. Therefore, oxygen species from N_2O dissociation is not enough for the oxidation of CH_4 to CO and CO_2. This phenomenon is observed by FTIR measurements [31]:

$$OH^-(a) + N_2O + CH_4 \rightarrow CH_3O^-(a) + N_2 + H_2O. \quad (1)$$

High methane conversion can be interpreted by reaction (1). As shown in Fig. 8a, the activity of $CH_4 + N_2O$

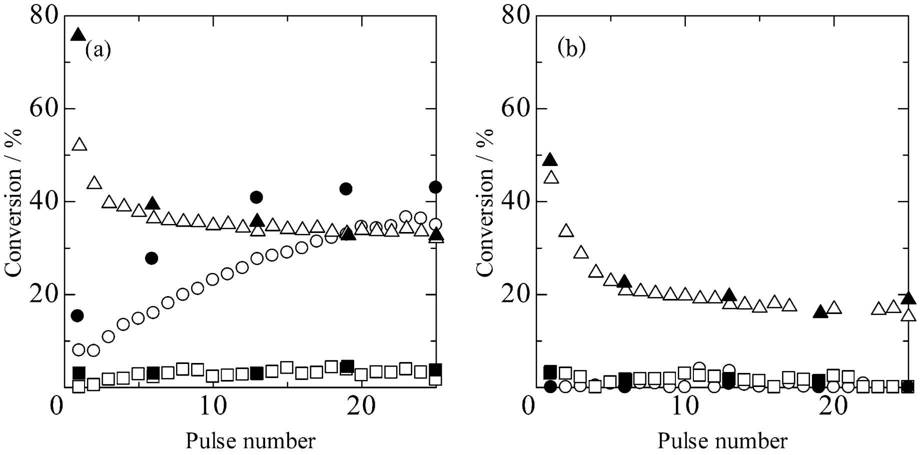

Fig. 8. Results of $CH_4 + N_2O$ pulse reaction over Fe-MFI catalysts after the pretreatments. (a) Fe(0.40)-MFI, (b) Fe(0.10)-MFI. Conversion: N_2O (open symbol), CH_4 (closed symbol). Pretreatment: H_2 treatment (▲, △), O_2 treatment (●, ○), and N_2O treatment (■, □). Pulse gas composition: 0.82 µmol N_2O and 0.40 µmol CH_4 (He balance). Reaction temperature: 523 K.

pulse over Fe(0.40)-MFI after O_2 treatment was much lower than that over the catalyst after H_2 treatment. This indicates that the activity over Fe^{2+} is higher than that over Fe^{3+}. In addition, it is very interesting that the activity of O_2-treated catalyst increased with increasing pulse number. From comparison between H_2 and O_2 treatments, the increase of the activity can be explained by the reduction of the catalyst after O_2 treatment during each pulse reaction. Furthermore, it should be noted that the pulse activity over the O_2-treated catalyst reached the constant level (N_2O conversion = 35%) and it was almost the same level of the constant activity over the H_2-treated catalyst. These results suggest that the oxidation and the reduction of the catalyst with $CH_4 + N_2O$ pulse are balanced at this conversion level. In addition, no pulse activity was observed on the N_2O-treated catalyst. Fig. 8b shows the result over Fe(0.10)-MFI. High activity was observed over H_2-treated Fe(0.10)-MFI; however, almost no activity was observed over O_2-treated and N_2O-treated catalysts.

In the results of Fe(0.40)-MFI and Fe(0.10)-MFI, a different behavior was observed over the O_2-treated catalysts. This difference is thought to be related to the results of O_2-TPD over O_2- and N_2O-treated catalysts. On Fe(0.40)-MFI, N_2O treatment enhanced the amount of O_2 desorption; in contrast, it did not increase that over Fe(0.10)-MFI. This indicates that Fe(0.10)-MFI after O_2 treatment does not have the ability to dissociate N_2O. The activity of the pulse reaction is closely related to the probability of N_2O dissociation. This is also supported by no activity on the N_2O-treated catalysts and high activity on the H_2-treated catalysts. On the basis of the above results, we discuss what determines the catalytic performance. On Fe(0.40)-MFI, the oxidation and the reduction with $CH_4 + N_2O$ pulse were balanced and its activity level was very high. This indicates that $CH_4 + N_2O$ reaction proceeds by redox mechanism of Fe^{2+} and Fe^{3+}. The important point is that Fe^{3+} can be reduced to Fe^{2+} during the reaction over Fe(0.40)-MFI. In contrast, since Fe^{3+} cannot be reduced to Fe^{2+} over Fe(0.10)-MFI, the oxidation and the reduction were not balanced on Fe(0.10)-MFI. Therefore, the steady-state activity under the presence of excess oxygen is expected to be the activity over O_2-treated catalyst. These are related to the catalytic activities of Fe(0.40)-MFI and Fe(0.10)-MFI (Figs. 1, 2, and 7). This can be caused by Fe species with higher reducibility in H_2-TPR and the ability to desorb oxygen at lower temperatures in O_2-TPD. In this study, the elucidation of the structure of this kind of Fe species is not enough. However, several studies about the structure of Fe species over Fe-MFI have been reported [35–38,40,50]. These reports suggest that this kind of Fe species is binuclear one. In contrast, it is interpreted that mononuclear Fe is present on Fe(0.10)-MFI. We think that the activity of N_2O reduction with CH_4 over binuclear Fe is much higher than that over mononuclear Fe. Considering the effect of oxygen partial pressure, the catalytic activity decreased with increasing oxygen partial pressure. As discussed above, in the case that this reaction proceeds via a redox mechanism between Fe^{2+} and Fe^{3+}, the ratio of Fe^{2+} to total Fe species can decrease under a higher pressure of oxygen. The activity of N_2O dissociation over Fe^{2+} is much higher than that over Fe^{3+} of Fe(0.40)-MFI. Therefore, the decrease of Fe^{2+} ratio causes the decrease of the activity.

4. Conclusions

1. The activity of N_2O reduction with CH_4 under an excess O_2 atmosphere over Fe-MFI catalysts increased with higher Fe loading on Fe-MFI catalysts.
2. The turnover frequency of the reaction drastically increased in the range of $Fe/Al \geqslant 0.15$.
3. From the characterization by means of H_2-TPR, more reducible Fe ion species were formed over Fe-MFI with higher Fe loading.
4. In the profiles of O_2-TPD, two kinds of desorption peak were observed. The catalysts with low Fe loading ($Fe/Al = 0.05$, 0.10) had only a high-temperature peak,

and in contrast, the catalysts with higher Fe loading ($Fe/Al = 0.15$, 0.24, and 0.40) also gave a lower temperature peak. This peak intensity increased with N_2O treatment.

5. The dependence of turnover frequencies on the Fe loading is similar to that of the amount of oxygen desorption in the lower temperature peak.
6. From the catalytic activity and characterization results, it is suggested that the active site is Fe species which is more reducible and gives a lower temperature O_2 desorption peak.
7. The pulse reaction of $CH_4 + N_2O$ over Fe(0.40)-MFI indicates that the reaction proceeds via a redox mechanism between Fe^{2+} and Fe^{3+}. On the other hand, the reaction did not proceed over Fe^{3+} in Fe(0.10)-MFI. It is found that the more reducible Fe^{3+} over Fe(0.40)-MFI plays an important role in high catalytic activity.
8. In a comparison between the previous reports and our result, the active species is thought to be binuclear Fe.

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