Catalytic reduction of N_2O by various hydrocarbons over Fe-ZSM-5: nature and reactivity of carbonaceous deposits

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Abstract

The catalytic reduction of dinitrogen monoxide (N_2O) by various hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8) in the absence and presence of O_2 has been studied over Fe-ZSM-5 catalysts. These hydrocarbon reductants are phenomenologically divided into three groups, namely CH_4, C_3H_6, and others (C_2H_4, C_2H_6, C_3H_8), referred to as the C_2H_4 group. Two types of carbonaceous deposits (Cα, Cβ) are formed on Fe-ZSM-5 during the reduction of N_2O by C_2 and C_3 hydrocarbons in the absence of O_2. In both cases of C_2H_4 and C_3H_6, the catalytic activity of Fe-ZSM-5 decreases with an increase in the amount of Cα, while it is not affected by the presence of Cβ. The Cα species is formed on Fe sites and the Cβ is mainly accumulated on the support. The formation of these carbonaceous deposits from the C_2H_4 group is suppressed by the presence of O_2 in the feed gas, and this promotes the catalytic reduction of N_2O. The amount and the chemical nature of Cα formed in the cases of the C_2H_4 group and C_3H_6 are similar, while those of Cβ are significantly different. The reactivity of Cβ with O_2 should be different and this may be responsible for the difference in the effects of O_2 addition on the reduction of N_2O between the C_2H_4 group and C_3H_6. In the case of CH_4, a high stable conversion of N_2O is obtained irrespective of the presence and absence of O_2 because the carbonaceous deposits are scarcely accumulated on the catalyst.
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Keywords: Fe-ZSM-5; N_2O reduction; Hydrocarbon; Carbonaceous deposit

1. Introduction

Dinitrogen monoxide (N_2O) is well known to be a greenhouse gas component and contribute to the catalytic destruction of ozone in the stratosphere [1]. Therefore, the removal of N_2O by suitable catalytic methods has been a very important subject in order to protect the global environment. Recently, several research groups have reported high catalytic performance of various metal ion-exchanged zeolites and other metal containing catalysts for decomposition [2–7] and reduction of N_2O with hydrocarbons [8–20], activated carbon [21–23], CO [24–27], and NH_3 [27,28]. In our previous work [13], the catalytic reduction of N_2O using CH_4

and C_3H_6 as reductants in the presence and absence of O_2 was studied with various metal ion-exchanged ZSM-5 catalysts. Pronounced activities were observed with Fe-ZSM-5, Pd-ZSM-5, and Pt-ZSM-5 catalysts, and no significant deactivation was detected with Fe-ZSM-5 in the presence of O_2, whereas the activities of Pt- and Pd-ZSM-5 decreased drastically by the presence of 5% O_2. Segawa et al. [10–12] studied the selective reduction of N_2O using C_3H_6 as a reductant and reported high reaction rates over Fe/MFI even in the presence of O_2 and H_2O. These authors assumed that the adsorption and protonation of C_3H_6 were important steps in the reduction of N_2O by C_3H_6 over Fe/MFI [11]. Kunimori and his co-workers [14–16] reported that ion-exchanged Fe-BEA and Fe/MFI show good performance in the selective catalytic reduction of N_2O by CH_4 and C_3H_6 in the presence of excess O_2. These authors [17,18] stated that the CH_xO_y(a) species such as methoxy and formate species formed at initial steps of

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the reduction of N_2O by CH_4, and may play an important role in the activation/oxidation of CH_4. Zhu et al. [20] indicated that the activity of Cu- or Co-loaded activated carbon in N_2O conversion was higher than that of Cu/ZSM-5 or Co/ZSM-5, respectively. They [22,23] also investigated the role of O_2 in NO– and N_2O–carbon reactions and reported that the presence of O_2 greatly enhanced the NO–carbon reaction while it suppressed the N_2O–carbon reaction. However, little fundamental study has been concluded pertaining to the reduction of N_2O by carbon species including reaction intermediates in the presence of O_2 over metal-loaded zeolites.

Several research groups have reported the nature and the role of oxygen species in the oxidation of hydrocarbons over metal-exchanged zeolites, Li and Armor [29] studied Pd-exchanged zeolites (ZSM-5, mordenite, and ferrierite) catalysts for CH_4 oxidation. They reported that Pd supported on these zeolites showed much higher activities than Pd/Al$_2$O$_3$ and suggested that extra-lattice oxygen atoms could be very active in the complete oxidation of CH_4 at low temperature. Panov et al. [30] proposed that a surface oxygen species, α-oxygen, generated in Fe-ZSM-5 under N_2O decomposition exhibited high reactivity in oxidation of methane, benzene and CO. They concluded that (1) α-oxygen was formed on Fe-ZSM-5 but not on the other iron catalysts and that (2) it was produced upon N_2O decomposition but not upon O_2 adsorption. Sachtler et al. [31] identified the oxygen deposited by N_2O decomposition on Fe/MFI by means of isotopic exchange technique. They suggested that $[Fe_2O_2]^{2+}$ type ions should be considered in addition to the mononuclear $[Fe=O]^{2+}$ ion as the oxo-species of dissociative N_2O adsorption on iron ions in partially pre-reduced and dehydrated Fe/MFI. However, little fundamental study has been made concerning the nature and the role of surface oxygen in the oxidation of hydrocarbons over Fe-zeolite catalysts.

Recently [32], we have reported that two types of carbonaceous deposits (Cα, Cβ) are formed on Fe-ZSM-5 catalysts during the N_2O reduction by C_2H_4 in the absence of O_2, and the catalytic activity decreases with an increase in the amount of Cα formed. The Cα species may be formed on the Fe sites. It was found that the catalytic reduction of N_2O by C_2H_4 is promoted by O_2, which prevents the accumulation of carbonaceous deposits on Fe sites. These carbonaceous deposits were scarcely accumulated by supplying only C_2H_4 over Fe-ZSM-5 or N_2O–C_2H_4 mixture over Na-ZSM-5 parent zeolite; therefore, these carbonaceous deposits are formed through the reaction between N_2O and C_2H_4 over Fe sites. In the present study, the reduction of N_2O by various hydrocarbons (CH_4, C_2H_6, C_3H_6, C_3H_8) in addition to C_2H_4 in the presence and absence of O_2 has been studied over Fe-ZSM-5. The reducing ability of the hydrocarbons has been discussed in terms of the accumulation of carbonaceous deposits on the catalyst. The nature and the structure of the carbonaceous deposits have been investigated by means of temperature-programmed oxidation (TPO) and X-ray photoelectron spectroscopy (XPS) analysis. The reactivity of the carbonaceous deposits and gaseous product (CO) with oxidant (O_2, N_2O) has been also investigated to elucidate the role of O_2 in the oxidation of carbonaceous deposits.

2. Experimental

2.1. Catalyst preparation

Fe-ZSM-5 catalysts were prepared by a conventional ion-exchange method using Na-ZSM-5 (SiO$_2$/Al$_2$O$_3$ = 23.8) supplied from Tosoh Co. Ltd. Na-ZSM-5 (4 g) was added to 100 cm^3 of FeSO$_4$·7H$_2$O aqueous solution of 2.45×10^{-2} M and the resulting mixture was then stirred at 343 K for 12 h. After filtration, the metal-supported zeolites were washed with distilled water, dried at 383 K for 24 h, and calcined in air at 773 K for 3 h. The content of Fe loaded was fixed at 3.4 wt.%, corresponding to 100% ion-exchangeable level.

2.2. N_2O reduction

The reaction was carried out in a conventional flow reactor at a W/F of 0.06 g s cm^{-3} and at 598 K. The reactor was made of 9 mm diameter Pyrex glass tubing in which a catalyst sample of 0.05 g was mounted on loosely packed quartz wool. Prior to the runs, the catalyst was treated in a stream of He at 773 K for 2 h and cooled to the reaction temperature.

The reactant gases used were N_2O and a hydrocarbon of CH_4, C_2H_4, C_2H_6, C_3H_6, or C_3H_8 diluted by He. The concentration used for CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and N_2O was 3000, 2000, 2000, 1300, 1300, and 2000 ppm, respectively. In our previous work [32], a 2000 ppm concentration of C_2H_4 was used. One mole of C_2H_4 is equivalent to six moles of O atoms if the following stoichiometry is assumed: $C + 2O \rightarrow CO_2$ and $H_2 + O \rightarrow H_2O$. The concentration of the other hydrocarbons was also adjusted to approximately have the same equivalent number of reducing C and H atoms. To examine the influence of O_2, it was introduced into the feed gas in different quantities up to 5%. The concentrations of N_2O, N_2, O_2, CO, CO_2, and hydrocarbons in the outflow gas were determined using gas chromatographs (Hitachi 663-50 and 063) with porapak Q and molecular sieve 5A columns. The concentration of NO_2 was monitored using a UV–vis spectrophotometer (Hitachi Model 100-10). Because of low concentrations of N_2O and hydrocarbons used, the total flow rate was practically constant throughout the catalyst bed.

2.3. Catalyst characterization

Temperature programmed oxidation experiments were carried out in the same reactor as used for the N_2O reduction. After the reaction, the reactor was cooled to room temperature, the stream of reactants was switched to He, and it was allowed to flow through for 60 min, and then programmed heating was started from room temperature to 773 K at a rate of 5 K min^{-1} in the stream of 5000 ppm O_2 in He. The

amounts of gases (CO, CO_2) evolved were determined from the peak areas of TPO curves.

X-ray photoelectron spectroscopy (XPS) analysis was performed in a ULVAC PHI ESCA 5600 instrument. Al Kα radiation (14.0 kV, 400 W) was used to excite photoelectrons, which were detected with an analyzer operated at 1253.6 eV constant pass energy. Correction of the energy shift due to steady state charging was accomplished by taking the C1s line from adsorbed carbons at 284.5 eV as an internal standard.

3. Results and discussion

3.1. N_2O reduction by various hydrocarbons

Fig. 1 shows the conversion of N_2O to N_2 as a function of reaction time in the reduction of N_2O (2000 ppm) by various hydrocarbons, CH_4 (3000 ppm), C_2H_4 (2000 ppm), C_2H_6 (2000 ppm), C_3H_6 (1300 ppm), or C_3H_8 (1300 ppm), in the absence and presence of O_2 (5000 ppm) over Fe-ZSM-5 at 598 K. These hydrocarbon reductants are phenomenologically divided into three groups, namely CH_4, C_3H_6, and others (C_2H_4, C_2H_6, C_3H_8), referred to as the C_2H_4 group. When CH_4 was employed for the reductant in the absence of O_2 (Fig. 1a), a stable conversion higher than 90% was observed during the reaction. On the other hand, when C_2H_4, C_2H_6, C_3H_6 and C_3H_8 were used, the conversions of N_2O decreased rapidly with time on stream at the initial stage of reaction and then changed gradually to steady-state values
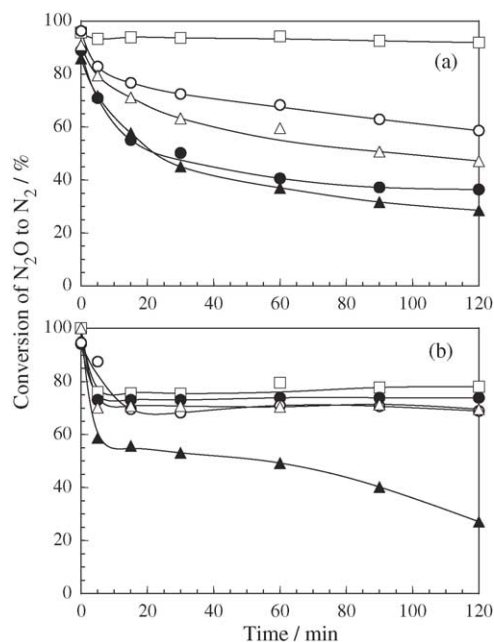
depending on the reductants used. As described in our previous report [32], the reduction of N_2O by C_2H_4 was strongly inhibited by formation of the carbonaceous deposits on the catalyst. The decrease in the conversion of N_2O observed with the other hydrocarbons could be also explained on the basis of the accumulation of carbonaceous deposits on the catalyst. When O_2 (5000 ppm) was added (Fig. 1b), the N_2O conversion rapidly decreased from about 95 to 75% and remained at around 75% in the N_2O reduction by C_2H_4, C_2H_6 and C_3H_8 in addition to CH_4. For C_3H_6, the N_2O conversion to N_2 also decreased rapidly at the initial stage of reaction but, in contrast, it then decreased gradually with time on stream. The influence of O_2 is significantly different between C_3H_6 and the other hydrocarbons.

3.2. Formation and influence of carbonaceous deposits on the activity of catalyst

TPO was used to characterize chemical species formed on the surface of catalyst after N_2O reduction. Fig. 2 shows TPO profiles after N_2O reduction over Fe-ZSM-5 by hydrocarbons, CH_4, C_2H_4, C_2H_6, C_3H_6, or C_3H_8, in the absence of O_2 at 598 K for 2 h. CO and CO_2 were observed to evolve along with a trace amount of H_2O. When CH_4 was used, CO and CO_2 were scarcely evolved. When C_2H_4, C_2H_6, C_3H_6, or C_3H_8 was used, the evolution peak of CO appeared at approximately 570 K and CO_2 peaks appeared at approximately 570 and around 670 K. The peaks centered at temperatures of 570 and 670 K are henceforth referred to as α- and β-peak, respectively. These TPO results show the formation and accumulation of carbonaceous deposits on the catalyst during the N_2O reduction by C_2 and C_3 hydrocarbons. In our previous work [32], we classified the carbonaceous deposits formed during N_2O reduction by C_2H_4 into two types by their reactivity with O_2 in TPO, and the carbonaceous deposits evolved

Fig. 1. The catalytic reduction of N_2O (2000 ppm) by hydrocarbons in the absence (a) and presence (b) of O_2 (5000 ppm) over Fe-ZSM-5 at 598 K. (□) CH_4 (3000 ppm); (●), C_2H_4 (2000 ppm); (○), C_2H_6 (2000 ppm); (▲), C_3H_6 (1300 ppm); (△), C_3H_8 (1300 ppm).

Fig. 2. TPO curves of carbonaceous deposits accumulated over Fe-ZSM-5 during N_2O (2000 ppm) reduction by hydrocarbons at 598 K for 2 h in the absence of O_2 ((○) CO; (▲) CO_2).
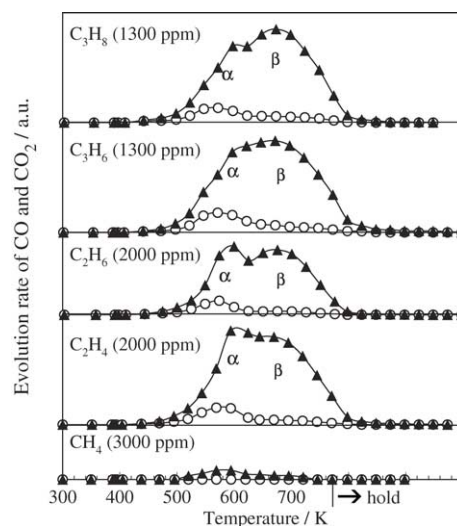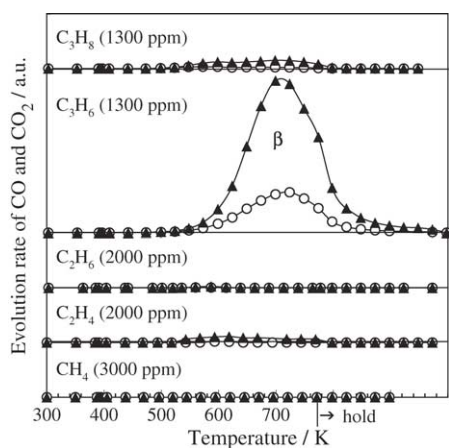
Fig. 3. TPO curves of carbonaceous deposits accumulated over Fe-ZSM-5 during N_2O (2000 ppm) reduction by hydrocarbons at 598 K for 2 h in the presence of O_2 (5000 ppm) (($\bigcirc$) CO; ($\blacktriangle$) CO_2).

as CO_2 and/or CO at α- and β-peak regions were named Cα and Cβ, respectively.

The influence of addition of O_2 into the feed gas was also investigated by TPO. Fig. 3 shows TPO curves of the carbonaceous deposits accumulated over Fe-ZSM-5 during the reduction of N_2O by hydrocarbons at 598 K for 2 h in the presence of O_2. In this study, as described in Section 2.2, the quantities of hydrocarbons used were approximately the same with respect to the quantities of such reducing species as C and H included; for example, 2000 ppm C_2H_4 and 1300 ppm C_3H_6 were used. The concentration of the other hydrocarbons was also adjusted to approximately have the same equivalent number of reducing atoms. If these inlet gaseous reactants react with each other completely, the stoichiometry of the reaction, for C_2H_4 for example, would be:

$$N_2O + C_2H_4 + 5/2O_2 \rightarrow N_2 + 2CO_2 + 2H_2O \qquad (1)$$
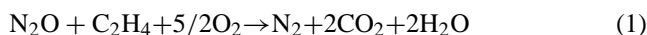
In this case, for example, 2000 ppm N_2O, 2000 ppm C_2H_4 and 5000 ppm O_2 give the stoichiometric composition and no accumulation of carbonaceous deposit may occur as expected by the Eq. (1). Under these conditions, when CH_4, C_2H_4, C_2H_6 and C_3H_8 were employed as the reductant, the evolution of CO and CO_2 was scarcely observed in the TPO runs. On the other hand, when C_3H_6 was used, β-peaks of evolution of CO and CO_2 were observed.

Table 1 summarizes the conversion of N_2O to N_2 obtained in the reduction of N_2O in the absence and presence of O_2 shown in Fig. 1 and the amounts of carbonaceous deposits (Cα, Cβ) determined by TPO shown in Figs. 2 and 3. As described previously [32], the accumulation of the carbonaceous deposits in the reduction of N_2O by C_2H_4 was suppressed and the catalytic reduction of N_2O was promoted by the presence of O_2. In the cases of C_2H_6 and C_3H_8, in a similar manner to C_2H_4, the accumulation of carbonaceous deposits scarcely occurred and the high stable values of N_2O conversion were obtained in the presence of O_2. When CH_4 was used, the high values of N_2O conversion were obtained

regardless of the presence of O_2, since the carbonaceous deposits were scarcely formed from CH_4. When C_3H_6 was used, a considerable amount of Cβ was accumulated exceptionally even in the presence of O_2.

Fig. 2 and Table 1 indicate that two types of carbonaceous deposits were formed on the catalyst irrespective of the kinds of hydrocarbons used expect for CH_4. The saturated amounts of Cα formed during the N_2O reduction in the absence of O_2 for 2 h were similar, 1.0–1.4 mmol g^{-1}, for C_2 and C_3, while those of Cβ were different. Previously, it was found that the composition of Cα is represented by approximately CH and that the amount of Cα formed on the Fe-ZSM-5 catalyst during N_2O reduction by C_2H_4 was saturated after 2 h (around 1.3 mmol g^{-1}). This saturated value, which corresponds to the C/Fe ratio of 2, did not depend on the reaction temperature and partial pressure of reactants [32]. Thus, it is presumed that the amount of Cα formed during N_2O reduction by C_2 and C_3 hydrocarbons in the absence of O_2 are similar irrespective of the kinds of hydrocarbons and the reaction conditions employed.

Fig. 4 shows the changes in the conversion of N_2O to N_2 and the amounts of Cα and Cβ accumulated during N_2O reduction by CH_4, C_2H_4, and C_3H_6 in the absence of O_2. In the case of CH_4, a stable N_2O conversion higher than 90% was observed as shown in Fig. 1a and Table 1, and little deposition of carbonaceous material was observed during the reaction. In both cases of C_2H_4, and C_3H_6, the conversion of
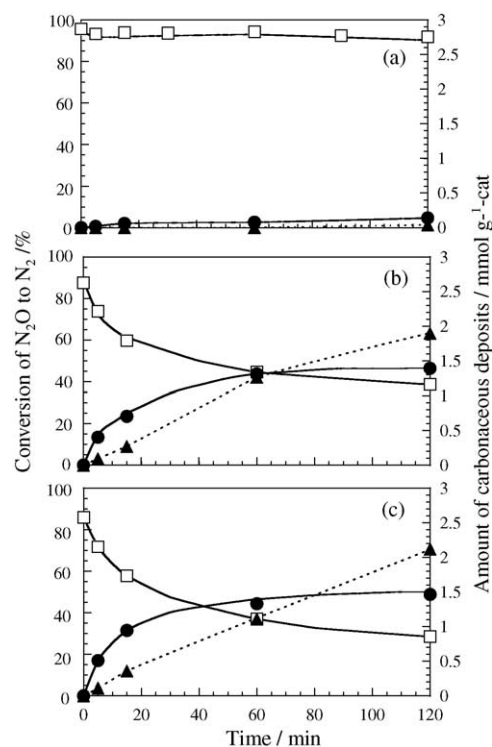
Fig. 4. Conversion of N_2O to N_2 and amounts of Cα and Cβ accumulated over Fe-ZSM-5 during the reduction N_2O (2000 ppm) by: (a) CH_4 (3000 ppm); (b) C_2H_4 (2000 ppm); and (c) C_3H_6 (1300 ppm) at 598 K (($\square$), conversion of N_2O to N_2; ($\bullet$), Cα; ($\blacktriangle$), Cβ).

Table 1
The amount of carbonaceous deposits accumulated over Fe-ZSM-5 during the reduction of N_2O by hydrocarbons at 598 K for 2 h

Reactant (ppm)			Conversion (%)	Amount of carbonaceous deposits (mmol g^{-1} cat.)	
Hydrocarbon	N_2O	O_2	N_2O to N_2	$C\alpha$	$C\beta$
CH_4 (3000)	2000	0	93.6	0.14	0.04
	2000	5000	78.1	Trace	Trace
	12000	0	60.0	0.013	0.005
	0	0	–	0	0
C_2H_4 (2000)	2000	0	38.7	1.39	1.85
	2000	5000	74.0	0.11	0.07
	12000	0	14.5	1.26	2.93
	0	0	–	0.07	0.09
C_2H_6 (2000)	2000	0	58.7	1.00	1.41
	2000	5000	68.9	0.01	0
	0	0	–	0.002	0.005
C_3H_6 (1300)	2000	0	28.6	1.46	2.12
	2000	5000	27.1	0	4.38
	12000	0	6.3	1.19	4.00
	0	0	–	0.63	0.18
C_3H_8 (1300)	2000	0	47.2	1.24	1.99
	2000	5000	69.6	0.12	0.20
	0	0	–	0.03	0.01

Fe (3.4 wt.%)-ZSM-5: 0.05 g.

N_2O decreases with time on stream, and this change corresponds well with an increase in the amount of $C\alpha$. However, the amounts of $C\beta$ increase linearly with time on stream for both C_2H_4 and C_3H_6. Thus, it is probable that the reduction of N_2O is inhibited by the presence of $C\alpha$; the deactivation of Fe-ZSM-5 catalyst in the absence of O_2 is caused by the accumulation of $C\alpha$ on its surface.

3.3. Characterization of carbonaceous deposits

The nature of $C\alpha$ and $C\beta$ deposits was characterized by means of XPS. Fig. 5 shows XPS spectra of C1s for Fe-ZSM-5 used for the reduction of N_2O with C_3H_6 in the absence of O_2 at 598 K. Fig. 5 (1) shows the XPS spectra of the Fe-ZSM-5 catalyst before reaction as a background. The dotted and broken curves shown in Fig. 5 (2) and (3) represent deconvoluted spectra of the solid curves. Fig. 5 (2) shows the C1s spectrum after the reduction of N_2O for 15 min, in which the carbonaceous deposits formed on the catalyst were mostly $C\alpha$ along with a small quantity of $C\beta$. A peak at 283.6 eV displayed by a broken line may indicate the formation of an isolated carbon [33], and $C\alpha$ can be regarded as carbonaceous species with the isolated carbon. Another small peak at 286.0 eV may be assigned to alcoholic groups [33] and could be due to the accumulation of $C\beta$. Fig. 5 (3) shows the C1s spectrum after the reduction of N_2O for a longer time of 120 min. The peak at 286.0 eV obtained for 120 min is larger than that for 15 min. A shoulder peak appearing at 282.0 eV may be assigned to carbide [33]. $C\beta$ species are formed on the catalyst for longer reaction time and, therefore, $C\beta$ can be regarded as the carbonaceous species with carbide and alcoholic groups.

Previously [32], it was suggested that $C\alpha$ and $C\beta$ formed over the Fe-ZSM-5 catalyst during the N_2O reduction by C_2H_4 were the carbonaceous species with isolated carbon and those with carboxylic groups, respectively, from XPS measurements. Furthermore, as described in Section 3.2, the amounts of $C\alpha$ formed in the cases of C_2H_4 and C_3H_6 were similar. Then, the chemical nature of $C\alpha$ obtained from C_3H_6 and C_2H_4 may be similar. On the other hand, in the case of $C\beta$ from C_2H_4, little amount of carbide was observed by XPS and, thus, there may be a significant difference in the chemical

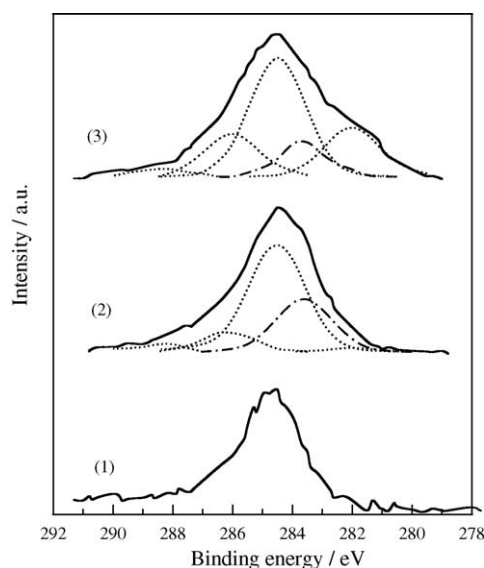

Fig. 5. XPS spectra of C1s for Fe-ZSM-5 catalyst before and after the reduction of N_2O (2000 ppm) by C_3H_6 (1300 ppm) in the absence of O_2 at 598 K. (1) Before reaction; (2) after 15 min; (3) after 120 min.

Table 2
Surface composition of Fe-ZSM-5 catalyst used for the reduction of N_2O (2000 ppm) by C_3H_6 (1300 ppm) in the absence of O_2 at 598 K as measured by XPS

Reaction time (min)	Type of C deposit	Content (at.%)		
		C	Fe	Si
Before reaction	–	9.4	1.2	24.4
15	Cα	12.1	0.84	24.8
120	Cα, Cβ	18.2	0.68	22.5

nature of Cβ between C_2H_4 and C_3H_6. The reactivity of Cβ with O_2 should be different and this may be responsible for the difference in the effects of O_2 addition on the reduction of N_2O between C_3H_6 and C_2H_4 (Fig. 1).

The elemental compositions of surface of the catalyst were also examined by means of XPS. The relative amounts of surface carbon, iron and silicon after the reduction of N_2O by C_3H_6 are listed in Table 2. It is seen that the C content increased with an increase in the reaction time and, in contrast, the Fe content decreased. The Cα species, which was mainly formed at the initial stage of N_2O reduction, may be accumulated on the Fe site, since the Fe content decreased by the formation of Cα while the Si content remained almost unaltered. On the other hand, Cβ species may be accumulated on the support, ZSM-5 zeolite, since the Si content decreased by the appearance of Cβ for a longer time of 120 min. Concerning the site for the formation of Cα and Cβ, these results with C_3H_6 agree with our previous results with C_2H_4 [32].

3.4. Influence of the partial pressure of O_2 on N_2O reduction

As described in Section 3.2, the deactivation of the Fe-ZSM-5 catalyst in the absence of O_2 was caused by the accumulation of Cα on its surface and the catalytic reduction of N_2O was promoted by the presence of O_2. The influence of the partial pressure of O_2 on N_2O reduction was further investigated. In Fig. 6, the amount of carbonaceous deposit and the partial pressure of N_2, CO_x (CO and CO_2) formed in the reduction of N_2O with CH_4, C_2H_4, and C_3H_6 at 598 K for 2 h are plotted against the concentration of O_2 added. When CH_4 was employed as the reductant, a little amount of carbonaceous deposit was formed in the absence of O_2 but not in the presence of O_2. The partial pressure of CO_x formed did not change markedly with the concentration of O_2. When C_2H_4 was employed, the amount of the carbonaceous deposit decreased rapidly with an increase in the concentration of O_2 between 0 and 0.5% and then it disappeared at O_2 concentrations above 1%. N_2O conversion obtained at O_2 concentrations below 0.1% was about 36%, while the value increased with an increase in the O_2 concentration up to 0.5%, at which a maximum value of 87.4% was obtained. The conversion of N_2O did not change with the concentration of O_2 above 1%. When C_3H_6 was employed, the amount of the carbonaceous deposit decreased with an increase in the concentration of O_2,
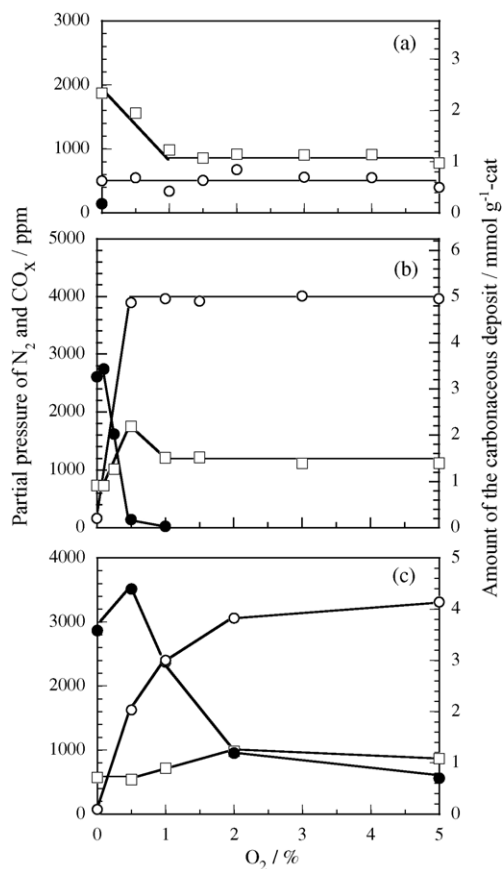

Fig. 6. The effects of partial pressure of O_2 on the conversion of N_2O to N_2 and the amount of the carbonaceous deposits formed on Fe-ZSM-5 during the reduction of N_2O (2000 ppm) by: (a) CH_4 (3000 ppm); (b) C_2H_4 (2000 ppm); and (c) C_3H_6 (1300 ppm) at 598 K for 2 h. (($\square$), partial pressure of N_2; ($\bigcirc$), partial pressure of CO_x; ($\bullet$), the amount of the carbonaceous deposit).

but a considerable quantity of the carbonaceous deposit still remained even at 5% O_2. The conversion of N_2O increased with an increase in the concentration of O_2 between 0.5 and 2%, and a maximum value of 49.2% was obtained at 2% O_2. The partial pressure of CO_x increased with an increase in the concentration of O_2 up to 2%, and the value did not change notably with the concentration of O_2 above 2%.

3.5. Reactivity of CO with O_2 and N_2O over Fe-ZSM-5

In the reduction of N_2O by various hydrocarbons, CO and CO_2 were produced. The conversion of CO and CO_2 was measured at various W/F (weight of catalyst/total flow rate of reactant gas) values to examine whether the formation of CO and CO_2 is either in parallel or in a consecutive manner. It was found that CO_2 might be mainly formed through CO consecutively. Then, the reactivity of CO with N_2O and O_2 was further investigated over Fe-ZSM-5 at 598 K to elucidate the role of CO in the reduction of N_2O in the presence of O_2. In Fig. 7, the reactivity of CO with N_2O in the absence and presence of O_2 is compared with that of CO with O_2. When N_2O was reacted with CO in the absence of O_2, N_2O
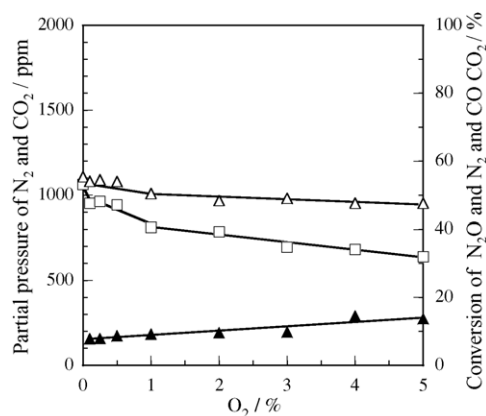
Fig. 7. The influence of partial pressure of O_2 on the conversion of N_2O to N_2 and CO to CO_2 in the reaction between N_2O (2000 ppm) and CO (2000 ppm) or O_2 and CO (2000 ppm) at 598 K for 2 h. (($\square$), conversion of N_2O to N_2; ($\triangle$), conversion of CO to CO_2 in the reaction between N_2O and CO; ($\blacktriangle$), conversion of CO to CO_2 in the reaction between O_2 and CO).

conversion was about 53%, while the value decreased about 10% by addition of 0.1% O_2 and further decreased gradually with an increase in the concentration of O_2 up to 5%. The total conversion of CO to CO_2 obtained in the reaction between CO and N_2O in the presence of O_2, however, did not change so much, since the decrease in the CO oxidation contributed by N_2O was compensated by addition of O_2. On the other hand, the conversion of CO to CO_2 in the reaction between CO and O_2 without N_2O was considerably low and slightly increased with an increase in the partial pressure of O_2. On the basis of these findings, it is presumed that N_2O is reduced easily by CO even in the presence of O_2 over Fe-ZSM-5.

3.6. Reactivity of O_2 and N_2O for various hydrocarbons

As previously noted in Table 1 and Figs. 1 and 2, most of the carbonaceous deposits were consumed by the reaction with stoichiometric composition of O_2. In order to compare the reactivity of N_2O with that of O_2 on the oxidative consumption of carbonaceous deposits, the stoichiometric composition of N_2O (12,000 ppm) was introduced in the place of the mixture of N_2O (2000 ppm) and O_2 (5000 ppm) for the reaction with CH_4, C_2H_4, and C_3H_6, and the results are also shown in Table 1. When C_2H_4 and C_3H_6 were used, a similar amount of carbonaceous deposits accumulated in spite of high partial pressures of N_2O (2000 and 12,000 ppm). This suggests that the carbonaceous deposits are unlikely to react with N_2O even at 12,000 ppm. In both cases, however, it was observed that Cα decreased slightly and Cβ increased apparently in the reaction with higher partial pressure N_2O. Particularly, in the case of C_3H_6, a large quantity of Cβ accumulated in the reaction with 12,000 ppm N_2O. Then, only hydrocarbon was provided over Fe-ZSM-5 to investigate the role of oxidant in the formation of carbonaceous deposits on the catalyst surface. Table 1 also summarizes the amount of carbonaceous deposits formed by providing of CH_4, C_2H_4, C_2H_6, C_3H_6, or C_3H_8 without oxidants. The formation of

Table 3
The amount of carbonaceous deposits accumulated over Fe-ZSM-5 during the reaction between O_2 and hydrocarbons at 598 K for 2 h

Reactant (ppm)		Amount of carbonaceous deposits (mmol g^{-1} cat.)	
Hydrocarbon	O_2	Cα	Cβ
CH_4 (3000)	1000	0	0
	6000	0	0
C_2H_4 (2000)	1000	0	0.99
	6000	0.07	0.12
C_3H_6 (1300)	1000	0	6.29
	6000	0	6.38

Fe (3.4 wt.%)-ZSM-5: 0.05 g.

carbonaceous deposits (Cα, Cβ) scarcely occurred without oxidants by providing hydrocarbons except C_3H_6. It is presumed that oxidants are necessary to accumulate the carbonaceous deposits on the catalyst. Most of carbonaceous deposits formed without gaseous oxidants might be produced by the reaction between hydrocarbon and the surface oxygen of catalyst. Only in the case of C_3H_6, one-half of saturated value of Cα may be formed by adsorption without oxidants.

The role of O_2 in the formation and the oxidation of carbonaceous deposits (Cα, Cβ) were further investigated by reactions between hydrocarbons and O_2 without N_2O, and the results are shown in Table 3. In these experiments, 1000 or 6000 ppm of O_2 was introduced in place of 2000 or 12,000 ppm N_2O. When CH_4 was used, no carbonaceous deposit formed on Fe-ZSM-5. On the other hand, when C_3H_6 was employed, the formation of a considerable extent of Cβ was observed, while little amount of Cα was formed. It is presumed that the presence of N_2O is necessary for the formation of the Cα type carbonaceous deposit over Fe-ZSM-5 or the Cα type carbonaceous deposit is reactive with O_2. Actually Kameoka et al. [16,17] stated that the presence of N_2O is necessary for the initial activation of hydrocarbons.

Table 4 summarizes the amount of reactants (hydrocarbon, N_2O, and O_2) consumed and those of products (CO, CO_2, C_2H_4, and C_3H_6) formed in the reduction of N_2O by CH_4, C_2H_4, C_2H_6, C_3H_6, or C_3H_8, over Fe-ZSM-5 at 598 K. These values were obtained at the steady state in the same experiments as shown in Tables 1 and 3 and summarized to elucidate the influence of the partial pressure of N_2O and O_2 on the basis of the carbon balance values between gaseous reactants and products. The last column of Table 4 shows the contribution of N_2O in the total amount of the reacted agents ($N_2O + O_2$). Yoshida et al. [19] reported the value of (consumed N_2O)/($3CO + 4CO_2$) to represent the ratio of the consumption rate of N_2O to the formation rate of ($3CO + 4CO_2$) for the reduction of N_2O by CH_4. In this case, ($3CO + 4CO_2$) represents the total amount of oxidizing agents assuming the equations: $CH_4 + 4[O] \rightarrow CO_2 + 2H_2O$, $CH_4 + 3[O] \rightarrow CO + 2H_2O$. [O] is oxygen atom originating from N_2O and O_2. Similarly the contribution of N_2O in the total amount of the oxidizing agents reacted ($N_2O + O_2$) are represented by the values of (consumed

Table 4
The reduction of N_2O by hydrocarbons over Fe-ZSM-5 at 598 K for 2 h

Reactant (ppm)			Amount of reactants consumed (ppm)		Amount of products formed (ppm)					Contribution of N_2O[a]
Hydrocarbon	N_2O	O_2	Hydrocarbon	N_2O	O_2	CO	CO_2	C_2H_4	C_3H_6	
CH_4 (3000)	2000	–	501	1872	–	348	153	0	0	1.13
	2000	5000	549	1562	605	219	330	0	0	0.79
	12000	–	1944	7200	–	588	1329	0	0	1.02
	–	1000	0	–	0	0	0	0	0	–
	–	6000	0	–	0	0	0	0	0	–
C_2H_4 (2000)	2000	–	394	774		56	104		0	1.83
	2000	5000	1942	1480	4040	2232	1660	–	0	0.17
	12000	–	638	1740	–	128	308	–	0	1.47
	–	1000	384	–	804	348	236	–	0	–
	–	6000	946	–	2034	1176	572	–	0	–
C_2H_6 (2000)	2000	–	510	1174	–	72	100	164	0	222
	2000	5000	1290	1378	3175	1280	1240	30	0	0.18
C_3H_6 (1300)	2000	–	484	572	–	27	47	33	–	2.93
	2000	5000	1114	542	2510	749	878	Trace	–	0.13
	12000	–	229	756	–	39	82	0	–	2.33
	–	1000	635	–	1000	105	174	17	–	–
	–	6000	1210	–	3050	958	901	14	–	–
C_3H_8 (1300)	2000	–	378	944	–	43	66	12	120	2.95
	2000	5000	1192	1392	3350	1576	1287	0	0	0.17

Fe (3.4 wt.%)-ZSM-5: 0.05 g.

[a] Normalized contribution of N_2O in the reaction between N_2O and hydrocarbon in the presence of O_2 [19]; CH_4: (consumed N_2O)/(3CO + 4CO$_2$); C_2H_4: (consumed NO)/(2CO + 3CO$_2$); C_2H_6: (consumed N_2O)/(5/2CO + 7/2CO$_2$); C_3H_6: (consumed NO)/(2CO + 3CO$_2$); C_3H_8: (consumed N_2O)/(7/3CO + 10/3CO$_2$).

N_2O)/(2CO + 3CO$_2$), (consumed N_2O)/(5/2CO + 7/2CO$_2$), and (consumed N_2O)/(7/3CO + 10/3CO$_2$) for the reduction of N_2O by C_2H_4 and C_3H_6, C_2H_6, and C_3H_8, respectively.

When CH_4 was used, no reaction occurred with O_2 (1000 or 6000 ppm) over Fe-ZSM-5 and most of CO and CO_2 was formed by the reaction between CH_4 and N_2O (2000 or 12,000 ppm). The total amounts of CO_x (CO and CO_2) were slightly increased by addition of O_2 (5000 ppm), while the amount of CO_2 formation increased apparently according to the oxidation of CO by O_2. Actually the contribution of N_2O obtained in the reduction of N_2O by CH_4 in the absence of O_2 is almost unity, while it slightly decreased to 0.79 in the presence of O_2. This suggests that most of CO and CO_2 was formed by the reaction between CH_4 and N_2O (2000 or 12,000 ppm) in the absence of O_2 and CO_2 was further formed by the oxidation of CO with additional O_2.

On the other hand, when C_2H_4, C_2H_6, and C_3H_8 were used, N_2O and O_2 were well reacted over Fe-ZSM-5 with hydrocarbons and produced equivalent amount of gaseous carbon oxides. However, when only N_2O was used as oxidant, the amount of gaseous carbon oxides was less than that of hydrocarbons consumed and the differences of carbon species could be due to the formation of carbonaceous deposits. When C_3H_6 was used, considerable amounts of carbon species remained on the catalyst even in the presence of O_2. Actually the contribution of N_2O obtained for the reduction of N_2O by C_2 and C_3 hydrocarbons in the absence of O_2 is 1.83–2.95, and only 0.13–0.18 in the presence of O_2. This suggests that significant amounts of carbonaceous de-
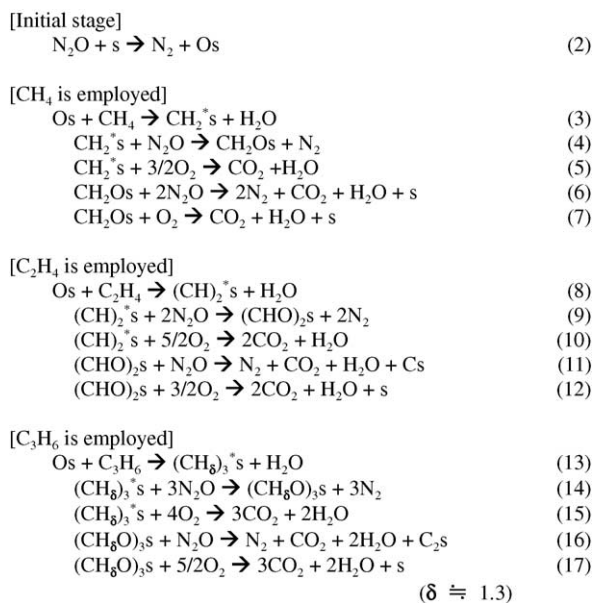
posits may be formed on the surface of catalyst when C_2 and C_3 hydrocarbons were used for the reduction of N_2O in the absence of O_2.

3.7. Reaction scheme for SCR of N_2O by hydrocarbons over Fe-ZSM-5

On the basis of the findings mentioned above, hydrocarbon reductants are phenomenologically divided into three groups, namely CH_4, C_3H_6, and others (C_2H_4, C_2H_6, C_3H_8), referred to as the C_2H_4 group and we propose the possible reaction scheme for each group as shown in Scheme 1.

In the initial stage, N_2O decomposes to produce N_2 and Os, active nascent oxygen, Eq. (2). When CH_4 is employed, CH_4 is hardly adsorbed on Fe-ZSM-5. Kunimori and his co-workers [17–19] have reported that nascent oxygen originating from N_2O decomposition could play an important role in the activation of methane. In this case, Os is thus reduced by CH_4 to produce CH_2^*s and H_2O, Eq. (3), and CH_2^*s may be very active and reacted instantaneously with N_2O or O_2 to produce CH_2Os and N_2 or CO and H_2O, respectively, Eqs. (4) and (5). As shown in Fig. 1, the steady state conversion of N_2O to N_2 decreased from about 95 to 75% by addition of O_2, while no reaction occurred between CH_4 and O_2 over Fe-ZSM-5, as shown in Table 4. For these reasons, it is presumed that the active CH_2^*s species may react partially with O_2 to produce CO_2 and H_2O. Nobukawa et al. [17,18] has reported that the reaction intermediates of methoxy and formate species were observed over Fe-BEA during the SCR of

[Initial stage]

$$N_2O + s \rightarrow N_2 + Os \qquad (2)$$

[CH$_4$ is employed]

$$Os + CH_4 \rightarrow CH_2{}^*s + H_2O \qquad (3)$$
$$CH_2{}^*s + N_2O \rightarrow CH_2Os + N_2 \qquad (4)$$
$$CH_2{}^*s + 3/2O_2 \rightarrow CO_2 + H_2O \qquad (5)$$
$$CH_2Os + 2N_2O \rightarrow 2N_2 + CO_2 + H_2O + s \qquad (6)$$
$$CH_2Os + O_2 \rightarrow CO_2 + H_2O + s \qquad (7)$$

[C$_2$H$_4$ is employed]

$$Os + C_2H_4 \rightarrow (CH)_2{}^*s + H_2O \qquad (8)$$
$$(CH)_2{}^*s + 2N_2O \rightarrow (CHO)_2s + 2N_2 \qquad (9)$$
$$(CH)_2{}^*s + 5/2O_2 \rightarrow 2CO_2 + H_2O \qquad (10)$$
$$(CHO)_2s + N_2O \rightarrow N_2 + CO_2 + H_2O + Cs \qquad (11)$$
$$(CHO)_2s + 3/2O_2 \rightarrow 2CO_2 + H_2O + s \qquad (12)$$

[C$_3$H$_6$ is employed]

$$Os + C_3H_6 \rightarrow (CH_\delta)_3{}^*s + H_2O \qquad (13)$$
$$(CH_\delta)_3{}^*s + 3N_2O \rightarrow (CH_\delta O)_3s + 3N_2 \qquad (14)$$
$$(CH_\delta)_3{}^*s + 4O_2 \rightarrow 3CO_2 + 2H_2O \qquad (15)$$
$$(CH_\delta O)_3s + N_2O \rightarrow N_2 + CO_2 + 2H_2O + C_2s \qquad (16)$$
$$(CH_\delta O)_3s + 5/2O_2 \rightarrow 3CO_2 + 2H_2O + s \qquad (17)$$
$$(\delta \doteqdot 1.3)$$

Scheme 1. Reaction scheme for N$_2$O reduction by various hydrocarbons.

N$_2$O with CH$_4$. They observed by FT-IR experiments that the Fe-OH species is present on the Fe-BEA catalyst during the SCR of N$_2$O with CH$_4$ and it plays an important role in the reaction. In a similar manner to this, the oxygenated intermediate species, CH$_2$Os, further reacted with N$_2$O or O$_2$ to produce N$_2$, CO, H$_2$O, Eq. (6) and (7). Gaseous or adsorbed CO may be oxidized consecutively with Os or N$_2$O to CO$_2$ (Fig. 7, Table 4). In this case, CH$_4$ itself is scarcely oxidized with gaseous O$_2$ (Table 3).

When C$_2$H$_4$ is employed, a little amount of C$_2$H$_4$ is adsorbed on the catalyst without oxidant. Os, active nascent oxygen, reacts with gaseous or adsorbed C$_2$H$_4$ to produce (CHO)$_2$s, carbonaceous deposit precursor, H$_2$O and N$_2$, through very active hydrocarbon adsorbed species, (CH)$_2{}^*$s, Eqs. (8) and (9). (CHO)$_2$s may react with N$_2$O to produce N$_2$, CO, H$_2$O and carbonaceous adsorbed species, Cs, which may further accumulate as Cα in the absence of O$_2$, Eq. (11), while (CHO)$_2$s reacts with O$_2$ above the stoichiometric composition and an active site (s) is regenerated, Eq. (12) (Fig. 1, Table 1). The reaction scheme for C$_2$H$_6$ and C$_3$H$_8$ could be represented phenomenologically in a similar manner to C$_2$H$_4$.

On the other hand, the influence of O$_2$ is significantly different between C$_3$H$_6$ and the other hydrocarbons (Fig. 1). C$_3$H$_6$ is adsorbed readily on Fe-ZSM-5 without oxidants and Cα with one-half of the saturated value accumulated (Table 1). Furthermore, significant amounts of Cβ were formed on Fe-ZSM-5 during N$_2$O reduction by C$_3$H$_6$ even in the presence of O$_2$ (Table 1) as well as the reaction between C$_3$H$_6$ and O$_2$ (Table 3). Yamada et al. [12] suggested on the basis of the observations of FT-IR spectroscopy that the bands attributed to CH$_2$ group, CH$_3$ group, and hydrocarbon oligomers are obtained by the adsorption of C$_3$H$_6$ and SCR of N$_2$O by C$_3$H$_6$ occurs mainly on Lewis acid

sites generated by the ion-exchange. It can be presumed that significant amounts of Cβ are formed during the oxidation of the adsorbed propylene species with O$_2$. When C$_3$H$_6$ is employed for reductant, Os reacts with C$_3$H$_6$ to produce (CH$_\delta$O)$_3$s, H$_2$O and N$_2$, through very active hydrocarbon adsorbed species, (CH$_\delta$)$_3{}^*$s, Eqs. (13) and (14), where, δ is calculated at 4/3 = 1.33. In fact, Kameoka et al. [15] reported that carbon-, hydrocarbon- and/or oxygen containing species such as C$_x$H$_y$(a) and C$_x$H$_y$O$_z$(a) are produced on the Fe-ZSM-5 surface by the reaction of the N$_2$O–O$_2$–C$_3$H$_6$ mixture and the average composition ratio of C$_x$H$_y$(a) and C$_x$H$_y$O$_z$(a) on the Fe ion site is roughly estimated to be FeC$_3$H$_4$O$_3$. Then, (CH$_\delta$O)$_3$s may react with N$_2$O to produce N$_2$, CO, H$_2$O, and carbonaceous species, and carbonaceous species, C$_2$s, which may further accumulate as Cα in the absence of O$_2$, Eq. (16). In the presence of O$_2$, (CH$_\delta$O)$_3$s partially reacts with O$_2$ to produce CO$_2$, H$_2$O and an active site (s), Eq. (17), while considerable amount of O$_2$ need to promote Eq. (17), and thus carbonaceous species may remain as Cβ.

On the basis of the findings from XPS as described in Section 3.3, the chemical nature of Cα obtained from C$_3$H$_6$ and C$_2$H$_4$ may be similar, while that of Cβ is significantly different and Cβ from C$_3$H$_6$ can be regarded as carbide rich carbonaceous species. The reactivity of Cβ with O$_2$ should be different and this may be responsible for the difference in the effects of O$_2$ addition on the reduction of N$_2$O between C$_3$H$_6$ and C$_2$H$_4$.

4. Conclusions

The nature and reactivity of carbonaceous deposits have been studied over Fe-ZSM-5 in the catalytic reduction of dinitrogen monoxide by various hydrocarbons (CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_3$H$_8$) in the absence and presence of O$_2$.

The hydrocarbon reductants used are phenomenologically divided into three groups, namely CH$_4$, C$_3$H$_6$, and others (C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_8$), referred to as the C$_2$H$_4$ group. Two types of carbonaceous deposits (Cα and Cβ) as classified by TPO are formed on the catalyst during the reduction of N$_2$O in the absence of O$_2$ irrespective of the kind of hydrocarbons used except for CH$_4$. The Cα species is formed on Fe sites and the Cβ is mainly accumulated on the support.

In both cases of C$_2$H$_4$ and C$_3$H$_6$, the catalytic activity of Fe-ZSM-5 decreases with an increase in the amount of Cα, while it is not affected by the presence of Cβ. The chemical nature and the amount of Cα obtained from the C$_2$H$_4$ group and C$_3$H$_6$ is similar, while those of Cβ is significantly different and Cβ from C$_3$H$_6$ can be regarded as carbide rich carbonaceous species. The formation of Cα is suppressed by the presence of O$_2$, and this promotes the catalytic reduction of N$_2$O. The reactivity of Cβ with O$_2$ should be different and this may be responsible for the difference in the effects of O$_2$ addition on the reduction of N$_2$O between the C$_2$H$_4$ group and C$_3$H$_6$.

In the case of CH_4, a stable high conversion of N_2O is obtained irrespective of the presence and absence of O_2 because the carbonaceous deposits are scarcely accumulated on the catalyst. It is concluded that CH_4 is the most effective reductant for the selective reduction of N_2O.

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