Enhancement of C_2H_6 oxidation by O_2 in the presence of N_2O over Fe ion-exchanged BEA zeolite catalyst

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Selective catalytic reduction (SCR) of N_2O with C_2H_6 took place effectively over Fe ion-exchanged BEA zeolite catalyst (Fe-BEA) even in the presence of excess oxygen. The mechanism in the SCR of N_2O with C_2H_6 over Fe-BEA catalyst was studied by a transient response experiment and an *in situ* DRIFT spectroscopy. No oxidation of C_2H_6 by O_2 took place below 350 °C (in C_2H_6/O_2). In the $N_2O/C_2H_6/O_2$ system, however, it was found that the reaction of C_2H_6 with O_2 was drastically enhanced by the presence of N_2O even at low temperatures (200–300 °C). Therefore, it was concluded that N_2O played an important role in the oxidation of C_2H_6 (*i.e.*, activation of C_2H_6 at an initial step). On the basis of these findings, the mechanism in the SCR of N_2O with C_2H_6 is discussed.

KEY WORDS: SCR, N_2O; enhancement of C_2H_6 oxidation; mechanism; Fe-BEA zeolite.

1. Introduction

Nitrous oxide (N_2O), which also contributes to catalytic stratospheric ozone destruction, is a strong greenhouse-effect gas with a global warming potential (GWP) per molecule of about 300 times that of carbon dioxide (CO_2) [1,2]. From the point of view of environment, therefore, it is important to study removal of N_2O in the emission gases. Selective catalytic reduction (SCR) of N_2O with reductants such as hydrocarbons [3–11] and ammonia [12,13] have been proposed as the effective method of N_2O abatement. Recently, we reported that CH_4 reacted selectively with N_2O to produce N_2, CO_2 and H_2O even in the presence of excess O_2 over Fe-BEA zeolite [7,8]. The oxidation of CH_4 as one of inactive molecules by O_2 required high temperature (above 450 °C) over Fe-BEA zeolite. Nevertheless, the selective oxidation of CH_4 by N_2O over Fe-BEA zeolite readily occurred at much lower temperatures whether in the presence of O_2 or not [8]. On the other hand, the oxidation behavior of C_2H_6 in the SCR of N_2O was significantly different from that of CH_4 [10]. The reaction of C_2H_6 with O_2 was significantly enhanced by the presence of N_2O even at low temperatures (200–300 °C), while the oxidation of C_2H_6 by O_2 did not proceed at these temperatures (below 350 °C in C_2H_6/O_2).

The present study is devoted to an investigation of C_2H_6 oxidation in the SCR of N_2O with C_2H_6 over Fe-BEA catalyst by using a transient response reaction technique and an *in situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The role of N_2O as oxidant in the oxidation of C_2H_6 and the reaction mechanism in the SCR of N_2O are investigated.

2. Experimental

Fe-BEA catalyst was prepared by ion-exchange with a dilute solution of $FeSO_4$ at 50 °C for 20 h under nitrogen atmosphere, and calcined in air for 12 h at 500 °C [4,7,14]. The zeolite supports (H-BEA, $SiO_2/Al_2O_3 = 27.3$) were supplied by Tosoh Co. The loading weight of Fe on BEA support was 0.77 wt% (25% exchanged with Fe^{2+}, 1.3×10^{-4} mol Fe ion · g-cat^{-1}). The reaction was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of N_2O (0–2000 ppm), C_2H_6 (0–300 ppm) and O_2 (10%) in He flow at a total flow rate of 50 cm min^{-1} over 50 mg of catalyst (total pressure: 1 atm; space velocity (SV): 60 000 h^{-1}). The transient response experiment was carried out in the same apparatus as described previously [11], capable of rapid switching (ON–OFF) of the gases, using a mixture of N_2O (1300 ppm), C_2H_6 (1000 ppm) and O_2 (10%) in He flow (SV = 60 000 h^{-1}). Pretreatment of the samples and analysis of the products were carried out as described previously [11]. The catalytic activity for the reduction of N_2O with C_2H_6 was evaluated by the percentage conversion of N_2O and C_2H_6 to N_2 and CO_x (CO_2 and/or CO), respectively. It should be noted that there were no by-products such as NO_x and other N-containing compounds in the present work, which was confirmed by the mass balance of nitrogen atoms between the reacted N_2O and the produced N_2.

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The *in situ* DRIFT measurement was performed using the same set up and experimental procedures as in a previous paper [15]. A clean catalyst-surface spectrum was recorded at the reaction temperature and used as a background to which the measured spectra were corrected; the final spectra were presented in Kubelka–Munk form. The pretreatment and the exposure of the gaseous mixture (N_2O: 1500 ppm, O_2: 10%, C_2H_6: 1000 ppm) to the sample before the DRIFT measurements were carried out in the same way as in the transient response experiment described above (at 350 °C).

3. Results and discussion

3.1. Catalytic activities in various reaction systems

Figure 1 shows N_2O and C_2H_6 conversions in various reaction systems over Fe-BEA catalyst. The direct decomposition of N_2O and the oxidation of C_2H_6 by O_2 initiated above 370 °C and 350 °C, respectively. However, the catalytic activity of N_2O removal was drastically assisted by adding C_2H_6 as reductant even at the low temperatures (200–300 °C). Increasing of N_2O conversions correlated well with that of C_2H_6 conversions. This result indicates that SCR of N_2O with C_2H_6 takes place effectively even in the presence of excess oxygen. Similar SCR reactions of N_2O over Fe-zeolite catalysts have also been observed in other hydrocarbons such as CH_4 [3,7,8], C_3H_8 [4–6] and C_3H_6 [4–6,11].

The activities in the SCR of N_2O with CH_4 and the oxidation of CH_4 with O_2 over Fe-BEA are also shown in figure 1 for the comparison, which are taken from reference [8]. Although the oxidation of CH_4 ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) over Fe-BEA required high temperatures (above 450 °C), the oxidation of CH_4 in the SCR of N_2O readily occurred at much lower temperatures (figure 1). In the SCR of N_2O with CH_4 over Fe-BEA catalyst, we also reported that there was a plateau in CH_4 conversion after N_2O conversion reached 100% (*ca.* 350–450 °C) [7,8]. This is due to the fact that N_2O in the mixture gas was completely consumed by the reaction with CH_4 at these temperatures. N_2, H_2O and CO_2 were observed as products in this reaction system. These results clearly indicated that CH_4 reacted selectively with N_2O even in the presence of excess O_2. Therefore, overall reaction in the $N_2O/O_2/CH_4$ system was represented by [8]

$$4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O. \qquad (1)$$

On the other hand, the oxidation behavior of C_2H_6 in the SCR of N_2O was significantly different from that of CH_4. No plateaus in the C_2H_6 conversion were observed in the $N_2O/O_2/C_2H_6$ system, while the plateau in the C_2H_6 conversion curve was observed after the N_2O conversion reached 100% (in N_2O/C_2H_6 system). In the N_2O/C_2H_6 system (without O_2), it should be noted that N_2O in the mixture gas was completely consumed by the reaction with C_2H_6 at these temperatures. If C_2H_6 reacted selectively with N_2O (in $N_2O/O_2/C_2H_6$ system, equation (2)) in the same way as the $N_2O/O_2/CH_4$ system (equation (1)), a plateau should be observed at *ca.* 45% in the C_2H_6 conversion. Therefore, it was found that the oxidation of C_2H_6 by coexistent O_2 concomitantly occurred. As shown in figure 1, the oxidation of C_2H_6 by O_2 (in the C_2H_6/O_2 system) required much

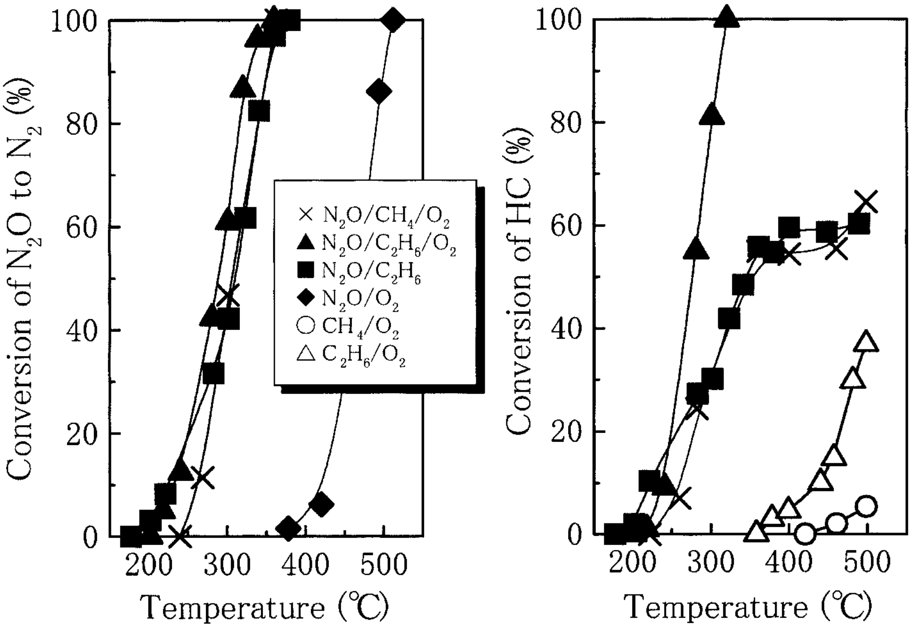


Figure 1. Conversion of N_2O and HC in various reaction systems over Fe-BEA catalyst.; N_2O (950 ppm), O_2 (10%) and HC (CH_4: 500 ppm, C_2H_6: 300 ppm).

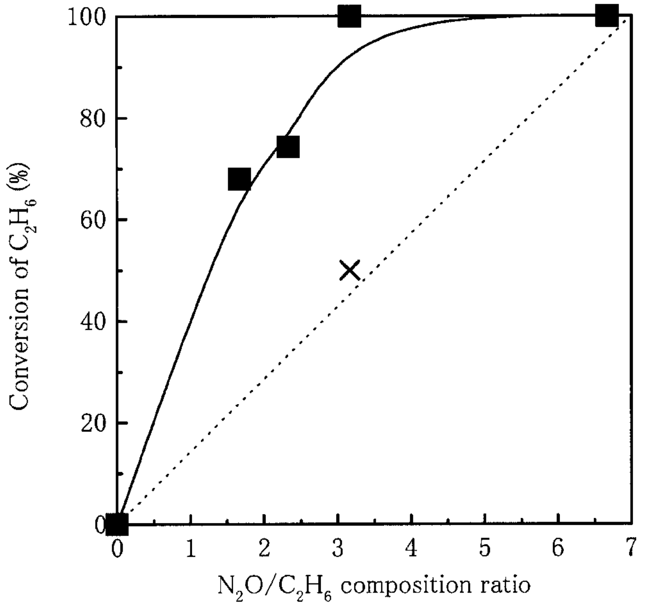


Figure 2. C_2H_6 conversion as a function of C_2H_6/N_2O composition ratio in the $C_2H_6/N_2O/O_2$ reaction system at 350 °C. ■: C_2H_6 300 ppm (constant), O_2 10% (constant) and N_2O (0, 500, 700, 950, 2000 ppm); ×: C_2H_6 300 ppm (constant) and N_2O (950 ppm).

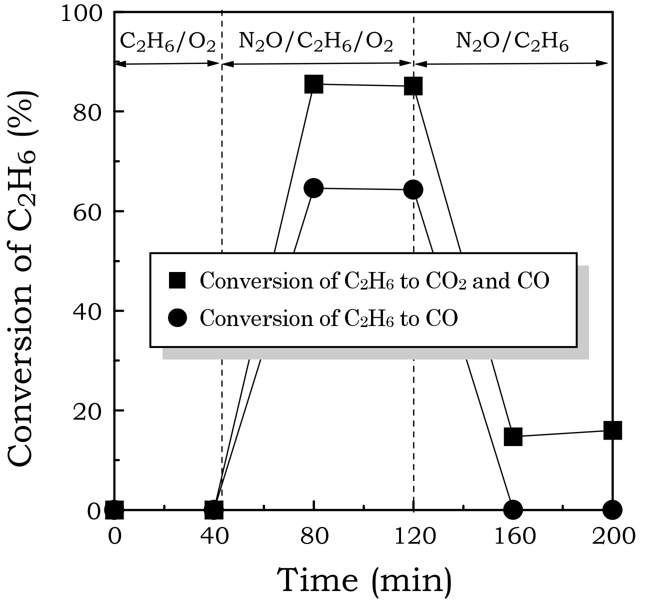


Figure 3. Transient responses for C_2H_6 oxidation on addition of N_2O (1300 ppm) to C_2H_6 (1000 ppm)/O_2 (10%) flow and on removal of O_2 (10%) from N_2O (1300 ppm)/C_2H_6 (1000 ppm)/O_2 (10%) flow at 350 °C over Fe-BEA catalyst.

higher temperatures (above 350 °C). This result indicates that the oxidation of C_2H_6 by O_2 in the SCR of N_2O is enhanced by the presence of N_2O, and that N_2O plays important roles at an initial step in the oxidation of C_2H_6 by O_2 (*i.e.*, activation of C_2H_6).

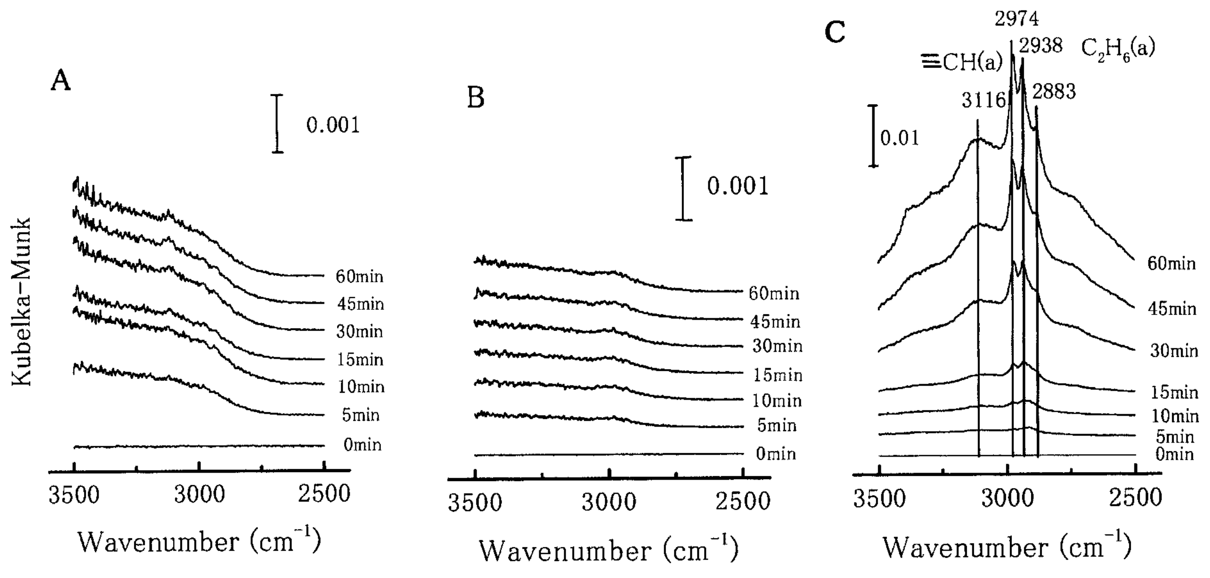
$$7N_2O + C_2H_6 \rightarrow 7N_2 + 2CO_2 + 3H_2O. \qquad (2)$$

Additionally, the enhancement of C_2H_6 oxidation by O_2 in the presence of N_2O was also confirmed by the catalytic experiments at the different N_2O/C_2H_6 composition ratio in the N_2O (0, 500, 700, 950, 2000 ppm)/O_2 (constant as 10%)/C_2H_6 (constant as 300 ppm) system. Figure 2 shows the dependence of the N_2O/C_2H_6 composition ratio (0, 1.67, 2.33, 3.17, 6.67) in the $N_2O/C_2H_6/O_2$ system for the C_2H_6 conversion at 350 °C. The plot of the N_2O/C_2H_6 system at 350 °C (in the absence of O_2, the N_2O/C_2H_6 ratio = 3.17) is also shown in figure 2 for comparison. If the ratio of N_2O conversion to C_2H_6 conversion was along the stoichiometry of equation (2), the plots should exist on the dotted straight line. The C_2H_6 conversions in the presence of O_2 exhibit large deviations from the straight line of stoichiometry over the whole range ($0 < N_2O/C_2H_6 < 7$).

3.2. Transient reaction experiments and DRIFT measurements

In order to examine in more detail the oxidation behavior of C_2H_6 in the SCR of N_2O, we performed the transient reaction experiments in the $N_2O/O_2/C_2H_6$ system over Fe-BEA catalyst. Figure 3 shows the transient responses for C_2H_6 oxidation on addition of N_2O (1300 ppm) to C_2H_6 (1000 ppm)/O_2 (10%) flow at 350 °C. C_2H_6 conversion was drastically increased by adding N_2O to C_2H_6/O_2 flow at 350 °C, while oxidation of C_2H_6 by O_2 hardly occurred. Figure 3 also shows the transient responses for C_2H_6 oxidation on removal of O_2 from $N_2O/C_2H_6/O_2$ flow at 350 °C. After changing to the N_2O/C_2H_6 flow, the C_2H_6 conversion decreased. In this case, the C_2H_6 conversion was small simply due to the depletion of the oxidant (*i.e.*, N_2O). These results directly demonstrate that the oxidation of C_2H_6 by O_2 is significantly enhanced by the presence of N_2O. The behaviors of these catalytic activities are in good agreement with the results in figure 1. In these experiments, CO, CO_2, H_2O and N_2 were observed as products. It should be noted that CO formation was observed only at the $N_2O/C_2H_6/O_2$ flow. As shown in figure 3, the formation of CO_2 occurred in the reaction of C_2H_6 with N_2O (in the N_2O/C_2H_6 flow). Therefore, this result apparently shows that the formation of CO occurred in the reaction of C_2H_6 with O_2 (in the $N_2O/C_2H_6/O_2$ flow).

In order to investigate the correlation between the enhancement of C_2H_6 oxidation by O_2 in the presence of N_2O and the formation of the adsorbed surface species, the DRIFT spectra were recorded at 350 °C on Fe-BEA under the similar condition of the transient response experiments shown in figure 3. Figures 4(A) and 4(B) show *in situ* DRIFT spectra during the reaction in the C_2H_6/O_2 and $N_2O/C_2H_6/O_2$ mixture gas at 350 °C over Fe-BEA, respectively. Clear peaks were hardly observed in exposing the C_2H_6/O_2 and $N_2O/C_2H_6/O_2$ mixture (figures 4(A) and 4(B)). This is due to the fact that the activation and/or adsorption of C_2H_6 hardly occur in the C_2H_6/O_2 system at 350 °C, and that



(A) C_2H_6/O_2 (B) $C_2H_6/O_2/N_2O$ (C) C_2H_6/N_2O

Figure 4. DRIFT spectra in the 3500–2500 cm^{-1} region during the reaction at 350 °C. Gas composition: C_2H_6 (1000 ppm), O_2 (10%), N_2O (1500 ppm) in He flow.

almost no adsorbed species were present in the $N_2O/C_2H_6/O_2$ system at 350 °C because of the steady-state reaction at high conversion.

Figure 4(C) shows *in situ* DRIFT spectra during the exposure of the N_2O/C_2H_6 mixture gas at 350 °C over Fe-BEA. Several absorption peaks were observed in exposing the N_2O/C_2H_6 mixture (figure 4(C)). All of these observed peaks increased in intensity with time during the reaction in the N_2O/C_2H_6 mixture. It should be noted that these observed peaks were hardly changed by the He purge at 350 °C for 15 min. In general, it could be admitted that the IR bands observed in the region of 3100–2800 cm^{-1} indicate the CH stretching (ν_{CH}) bands of alkanes or adsorbed C–H bond-containing species [16,17]. The peaks at 2974, 2938 and 2883 cm^{-1} were assigned to ν_{CH} of $C_2H_6(a)$ [17,18]. The increase in the intensities of the other broad band at around 3116 cm^{-1} was also observed (figure 4(C)). Similar broad band observed during the SCR of N_2O with C_3H_6 over Fe-MFI [11], which was assigned to $-C{\equiv}CH(a)$ and/or unsaturated carbonaceous species (*i.e.*, $C_xH_y(a)$) [11,19,20]. In our previous report [11], the partial oxidized species (*i.e.*, $C_xH_yO_z(a)$) as well as $C_xH_y(a)$ species, which were important active surface species, were observed during the SCR of N_2O with C_3H_6 over Fe-MFI. In the present work, however, the low-wavenumber region (1700–1400 cm^{-1}) of the $C_xH_yO_z$ species ($\nu_{C=O}$, $\nu_{C=C}$, ν_{COO}, etc.) bands could not be measured reliably because of the strong absorption band of Fe-BEA (below 1700 cm^{-1}). Therefore, we do not exclude the presence of $C_xH_yO_z(a)$ as intermediate surface species over Fe-BEA. These above results suggest that $C_xH_y(a)$ and/or $C_xH_yO_z(a)$ species may be the important active surface species of the C_2H_6 oxidation by coexistent O_2 in the $N_2O/C_2H_6/O_2$ system. Previously, we reported that $C_xH_y(a)$ and/or $C_xH_yO_z(a)$ species react with O_2 (and/or N_2O) to produce N_2, CO_x and H_2O at 350 °C [11].

3.3. Proposed reaction mechanism

On the basis of above mentioned findings, we propose the following possible reaction steps for the SCR of N_2O with C_2H_6 over Fe-BEA catalyst, as shown in figure 5. Firstly, adsorption and activation of C_2H_6 are initiated by the reaction with N_2O over the Fe ion sites on zeolite (*i.e.*, abstraction of H atom and oxidation to form $C_xH_y(a)$ and/or $C_xH_yO_z(a)$ species). At the low temperatures ($\leq$350 °C), the formation of $C_xH_y(a)$ and $C_xH_yO_z(a)$ species by the reaction of C_2H_6 with N_2O readily occurred, while the formation of $C_xH_y(a)$ and $C_xH_yO_z(a)$ species by the reaction of C_2H_6 with O_2 hardly occurred. Therefore, N_2O plays important roles in the formation of $C_xH_y(a)$ and/or $C_xH_yO_z(a)$ species as active surface species. Finally, $C_xH_y(a)$ and/or

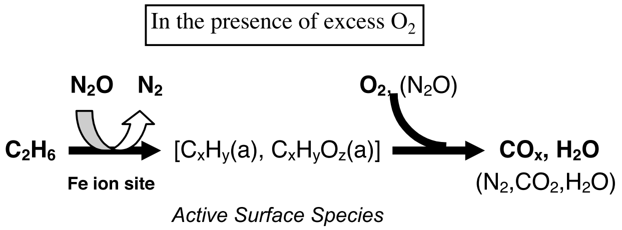


Figure 5. Proposed reaction steps for the SCR of N_2O with C_2H_6 over Fe-BEA zeolite catalyst.

$C_xH_yO_z$(a) species react with O_2 or N_2O to produce N_2, CO_x and H_2O.

In the oxidation behavior of alkane with O_2, the difference between the $N_2O/CH_4/O_2$ system and the $N_2O/C_2H_6/O_2$ system could be attributed to the reactivity of active surface species with O_2 (*e.g.*, CH_x(a) *versus* C_xH_y(a)). Previously, Panov *et al.* [21] reported that the O atom from the N_2O molecule (so-called α-oxygen), which cannot be produced by O_2, readily reacted with CH_4 or benzene to produce CH_3OH or phenol over Fe/ZSM5 catalyst. The O atom from the N_2O molecule is much more active than that from the O_2 molecule. In our experiment, therefore, both CH_4 and C_2H_6 molecules are readily activated by the O atom from the N_2O molecule to form active surface species. The reaction of CH_4 with N_2O presumably leads to the formation of CH_x(a) species etc., although no adsorbed species were detected by the DRIFT technique because of very low concentration of these species. However, the plateau in the CH_4 conversion (*ca.* 350–450 °C, in figure 1) means that the reaction rate of CH_x(a) etc. with O_2 is much lower than that with N_2O over Fe-BEA catalyst below 450 °C. Therefore, CH_4 reacts selectively with N_2O. On the other hand, the formation of C_xH_y(a) by the reaction of C_2H_6 with N_2O were observed by the DRIFT (figure 4(C)). The reaction of C_xH_y(a) species with O_2 as well as N_2O readily takes place, which leads to the enhancement of C_2H_6 oxidation.

4. Conclusion

The selective catalytic reduction of N_2O with C_2H_6 in the presence of excess O_2 took place efficiently over Fe-BEA catalyst. The present study demonstrates the enhancement of C_2H_6 oxidation by O_2 in the presence of N_2O. This result suggests that N_2O plays an important role in the oxidation of C_2H_6 (*i.e.*, activation of C_2H_6 at an initial step).

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