

In-Situ Observation of Reaction Intermediate in the Selective Catalytic Reduction of N₂O with CH₄ over Fe Ion-Exchanged BEA Zeolite Catalyst for the Elucidation of Its Reaction Mechanism Using FTIR

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The selective catalytic reduction (SCR) of N₂O with CH₄ in the absence and presence of excess O₂ has been studied over ion-exchanged Fe–BEA catalyst by the combination of an activity test with in-situ infrared spectroscopy to understand the nature of the surface species involved in the SCR of N₂O with CH₄. From the results of flow reaction studies, the Fe–BEA catalyst exhibited high activity in the SCR of N₂O with CH₄, even in the presence of excess oxygen, which demonstrates that the active Fe species for the SCR are formed on the ion-exchanged Fe–BEA catalyst. In the FTIR spectra of fresh catalysts, the OH band on Fe ion species (Fe–OH) was observed on the Fe–BEA catalyst, and the Fe–OH species can be involved in the SCR of N₂O with CH₄. Furthermore, the reaction intermediates of methoxy and formate species over the Fe–BEA catalyst were observed during the reaction. We measured the oxidation rates of these surface species with N₂O and O₂, and found that the methoxy species were oxidized with N₂O more rapidly than O₂, while the formate species were oxidized with both N₂O and O₂ at almost the same rate. On the basis of these results, we discuss the reaction mechanism of the SCR of N₂O with CH₄.

1. Introduction

Nitrous oxide (N₂O) and methane (CH₄) are strong greenhouse-effect gases with a global warming potential (GWP) per molecule of about 300 and 30 times that of carbon dioxide (CO₂), respectively.¹ N₂O is also identified as a contributor to the destruction of ozone in the stratosphere.^{1,2} From the point of view of environment, therefore, it is important to study the selective catalytic reduction (SCR) of N₂O with CH₄, which can lead to simultaneous removal of N₂O and CH₄ in the emission gases. Recently, we reported that the SCR of N₂O with CH₄ over an Fe ion-exchanged BEA zeolite catalyst (Fe–BEA) took place effectively at low temperatures (ca. 523 K–623 K) even in the presence of excess O₂.^{3,4} In infrared study, we observed adsorbed intermediates (methoxy and formate species) in the SCR of N₂O with CH₄.⁵ During the course of study, it was found that the reaction temperature of the oxidation of CH₄ by N₂O is much lower than that by O₂ during the SCR of N₂O with CH₄. However, the oxidation process of CH₄ by N₂O in the SCR of N₂O with CH₄ over the Fe–BEA zeolite catalyst is not sufficiently understood.

The present paper is devoted to the systematic in-situ FTIR study on the formation and reaction of adsorbed species in N₂O reduction by CH₄ over Fe–BEA catalyst. The transient and pulse reaction techniques followed by FTIR were employed to examine the reactivity and dynamic behaviors of surface species. In particular, our study focused on the reactivity of adsorbed methoxy and formate species with N₂O and/or O₂. In the previous study, we have proposed that N₂O plays an important

role in the initial steps (reaction with CH₄ to form methoxy species) on the SCR of N₂O with CH₄.⁵ However, there has been little information for the kinetics study of the SCR of N₂O with CH₄. In this study, we observed the behaviors of reaction intermediates and evaluated the reactivity using FTIR. The mechanism of the SCR of N₂O with CH₄ based on in-situ FTIR study is discussed.

2. Experimental Section

The H–BEA zeolite support (SiO₂/Al₂O₃ = 25) was supplied by PQ Co. Fe–BEA catalyst was prepared by ion-exchange with a dilute solution of FeSO₄·7H₂O (Wako Pure Chemical Industries, Ltd., >98.0%) at 323 K for 20 h, and calcined for 12 h at 773 K.^{6,7} For comparison, Fe/BEA catalyst was prepared by an impregnation method using a Na–BEA support with a dilute solution of Fe(NO₃)₃·9H₂O (Wako Pure Chemical Industries, Ltd., >99.0%), and calcined for 3 h at 773 K.⁸ The loading amount of Fe of Fe–BEA and Fe/BEA was 1.5 wt % and 1.6 wt %, which was determined by an ICP chemical analysis, respectively. All reactant gases with the research grade were purchased from Takachiho Trading Co. Ltd. and were used without further purification.

The activity test was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of N₂O (950 ppm), CH₄ (500 ppm), and O₂ (10%) in a He flow at a total flow rate of 50 cm³ min^{−1} over 50 mg of catalyst [total pressure: 0.1 MPa; space velocity (SV): 60000 h^{−1}]. The samples were pretreated at 773 K with O₂ for 0.5 h in the reactor just before the test, followed by a He purge at the initial reaction temperature. The activity tests of four kinds of reaction were performed and the details are listed in Table 1. The effluent gas was analyzed with a TCD on-line gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5A (N₂) and Porapak Q (N₂O, H₂O)

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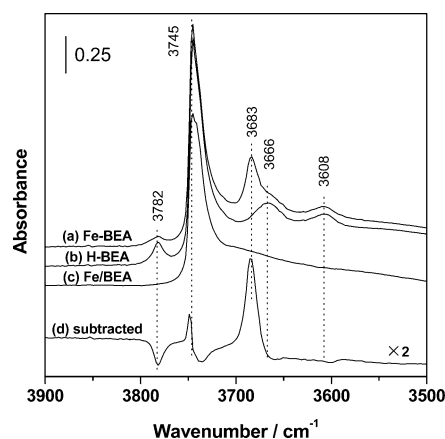


Figure 1. FTIR spectra of the OH stretching bands over (a) Fe-BEA, (b) H-BEA, (c) Fe/BEA, and (d) the subtracted spectrum from (a) to (b). Reaction conditions: measurement temperature = 300 K, He flowing, SV = 60000 h⁻¹, total pressure = 0.1 MPa. Pretreatment: 100% O₂, 773 K, 0.5 h.

TABLE 1: Feeding Composition of the Reactant Gases for the Activity Tests

reaction	feeding composition of the reactants		
	N ₂ O (ppm)	CH ₄ (ppm)	O ₂ (%)
N ₂ O decomposition	950	0	0
CH ₄ /O ₂	0	500	10
N ₂ O/CH ₄	950	500	0
N ₂ O/CH ₄ /O ₂	950	500	10

columns^{3,4,6} and an FID GC equipped with a methanator for CH₄, CO, CO₂.

In-situ FTIR spectra were recorded by a Magna 550 spectrometer (Nicolet) with a resolution of 4 cm⁻¹ (16 and 64 scans) in a transmission mode, using a quartz glass IR cell equipped with a sample holder, electric heater, and CaF₂ windows. The sample for the IR measurements was prepared by pressing catalyst powder ground in an agate mortar into a wafer of ca. 16 mg/cm² (50 mg, 20 mm ϕ). Pretreatment was carried out by O₂ (30 cm³ min⁻¹) at 773 K for 0.5 h. The FTIR measurements were carried out under various reaction conditions with space velocity (SV) of 60000 h⁻¹, and details are described in each result. In the case of pulse reaction, the injection of N₂O pulse (0.31 μ mol) was carried out under CH₄ (500 ppm) or CH₄ (500 ppm) + O₂ (10%) flowing conditions (SV = 60000 h⁻¹) at 473 K. The FTIR spectra of methanol adsorption were obtained by exposing methanol vapor (13.3 Pa, 40.3 μ mol) to the samples after O₂ treatment at 423 K for 0.5 h, followed by evacuating at the same temperature. To evaluate the reactivity of adsorbed intermediate species, N₂O or O₂ containing gas was introduced to the sample with surface species. The details are shown in each result.

3. Results and Discussion

3.1. Catalyst Performance and FTIR Observation of Fresh Catalysts. Figure 1 shows FTIR spectra of Fe-BEA, Fe/BEA and H-BEA after O₂ treatment. The spectra were collected at 300 K in He flowing. The spectra have been normalized on the basis of the intensities of the zeolite framework overtone bands at around 2000 cm⁻¹. Five peaks (3782, 3745, 3683, 3666 and 3608 cm⁻¹) were observed over these samples. The peaks at 3782, 3745, 3666 and 3608 cm⁻¹ were also observed over the H-BEA zeolite support. The detail of the peak assignment was listed in Table 2. These peaks at 3745, 3666 and 3608 cm⁻¹ could be assigned to OH stretching mode of the terminal silanols

TABLE 2: Assignment of the Stretching of Surface OH Species on the Catalysts in Figure 1

wavenumber/cm ⁻¹	species	references
3782	tri Al-OH (VHF)	10, 11
3745	Si-OH	9-11
3683	Fe-OH	5
3666	ex Al-OH	10
3608	Si-OH(Al) Brønsted acidic site	9-11

(Si-OH), a hydroxyl group associated with extraframework aluminum (ex Al-OH) and bridging OH group (i.e., Brønsted acidic site, Si-OH (Al)) of BEA zeolite, respectively.⁹⁻¹¹ The 3782 cm⁻¹ band has already been assigned to $\nu(\text{OH})$ of a hydroxyl group attached to a tricoordinated aluminum atom linked to the network via two oxygen bonds (tri Al-OH).^{10,11} The Fe-BEA catalyst showed a new band at 3683 cm⁻¹, which was also observed on Fe-BEA catalyst with a different H-BEA support.⁵ This band was observed only on the ion-exchanged Fe-BEA catalyst. We have reported that the intensity of this band decreased with increasing temperature of H₂ treatment.⁵ The decrease of the band intensity at 3683 cm⁻¹ started above 523 K, and completed at 723 K. This behavior corresponded well to the reduction from Fe³⁺ to Fe²⁺ in the profile of temperature programmed reduction. In addition, Mauvezin et al.¹² also have reported in the IR study of a similar catalyst that a band appeared at 3670 cm⁻¹ after O₂ and N₂O treatment; however, the band disappeared after H₂ treatment. They suggest that this band likely corresponds to OH groups on Fe³⁺ species on the basis of the density functional theory calculations of small iron-hydroxo clusters.¹² Although the peak position was a little different from that observed in the present study (3683 cm⁻¹), it is thought that this difference was caused by the different temperature of collected spectra (673 K in the previous report and 300 K in the present study). It has been reported that the hydrogen bonds shift due to their thermally excited state when temperature is high.¹³ In addition, similar behavior after H₂ reduction was also observed. Therefore we can assign the band at 3683 cm⁻¹ to the Fe-OH species. The subtracted spectrum from Fe-BEA to H-BEA in Figure 1 shows the increasing area in the peak at 3683 cm⁻¹ and the decreasing area in that of the OH peaks at 3782 and 3666 cm⁻¹. This suggests that some OH group is consumed by ion-exchange procedure and some Fe-OH group is formed. At present, the structure of Fe ion species is not clear; however, various kind of structural models have been proposed. Prins et al.¹⁴ have reported that the binuclear iron clusters are the active species in the SCR of NO_x and in the decomposition of N₂O. They have proposed the formation pathway of the binuclear iron clusters. The isolated [FeCl₂]⁺ ion formed by sublimation of FeCl₃ was aggregated upon hydrolysis into hydroxide clusters by washing, and finally converted to the binuclear iron clusters after calcination. They also proposed that two Fe ions in these binuclear iron clusters seem to be connected through two (hydr)oxo bridges on the ion exchange positions. Panov et al.¹⁵ have reported that α -oxygen formation was related to the presence of binuclear Fe complex. However, their model of binuclear Fe complex did not require two neighboring Al atoms in the lattice because the probability of such Al pairs occurring in the high-silica zeolites is very small. Mauvezin et al.¹² also claimed that Fe is mainly present as binuclear oxocations of the type [(OH)FeOFe-(OH)]²⁺ in an Fe-BEA catalyst system. These studies suggest that the observed Fe-OH species correspond to the ones in the binuclear [(OH)FeOFe(OH)]²⁺ ion species. In the present paper, however, we assign the peak at 3683 cm⁻¹ simply to the Fe-OH species, because we have no direct information about the detailed structure of the Fe ion species in our Fe-BEA catalyst.

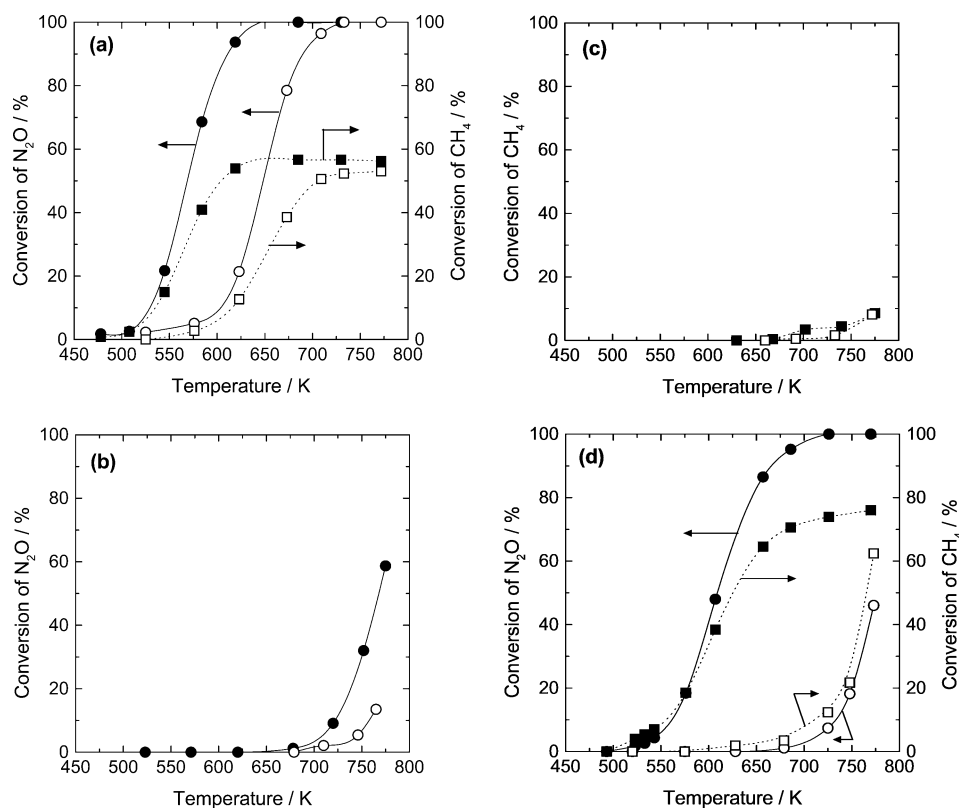


Figure 2. Reaction temperature dependence of N₂O and CH₄ conversion over Fe-BEA and Fe/BEA catalysts. (a) N₂O (950 ppm) + CH₄ (500 ppm) system, (b) N₂O (950 ppm) system, (c) CH₄ (500 ppm) + O₂ (10%) system, (d) N₂O (950 ppm) + CH₄ (500 ppm) + O₂ (10%) system. ●, ○: N₂O conversion (full lines), ■, □: CH₄ conversion (dotted lines), closed symbol: Fe-BEA, open symbol: Fe/BEA. Reaction conditions: SV = 60000 h⁻¹, total pressure = 0.1 MPa. Pretreatment: 100% O₂, 773 K, 0.5 h.

The spectrum of the impregnated Fe/BEA catalyst is also shown in Figure 1. The band at 3745 cm⁻¹ (Si-OH) was only observed because of the Na-BEA support. The intensity of this band was a little decreased. These results indicate that the state of the supported iron is very different between the Fe/BEA and Fe-BEA catalysts. We have reported that the iron in the ion-exchanged Fe-BEA catalyst exists in ionic form on the ion exchange sites of zeolite, whereas the iron in the impregnated Fe/BEA catalyst exists as oxide (Fe₂O₃) on zeolite support.⁶

Figure 2 shows the conversion of N₂O and CH₄ as a function of the reaction temperature. In the N₂O/CH₄ system (Figure 2(a)), the activity over the Fe-BEA catalyst was much higher than that over the Fe/BEA catalyst. In this reaction, N₂, CO₂, CO, and H₂O were formed. CO was mainly formed in the low-temperature region (<550 K; CO/CO₂ = 4), and gradually decreased in the high-temperature region (> 700 K; CO/CO₂ = 2/3). In this reaction, the plateau in the CH₄ conversion curve was observed when the N₂O conversion reached 100%. In the N₂O decomposition (Figure 2(b)), N₂O conversion was much lower than that in the case of N₂O/CH₄ reaction over both catalysts. Furthermore, CH₄ combustion (CH₄/O₂ system: Figure 2(c)) over both catalysts hardly proceeded even at 773 K. These results indicate that the coexistence of N₂O and CH₄ is an important factor to promote the N₂O/CH₄ reaction at the low-temperature regions.

On the other hand, the activity in the N₂O/CH₄/O₂ system exhibited different behavior. The composition of product gases over the Fe-BEA catalyst (Figure 2(d)) was similar to that in the N₂O/CH₄ system (Figure 2(a)), although CO/CO₂ ratio became about 3/7 in the high-temperature region. CH₄ conversion in the N₂O/CH₄/O₂ system was a little higher than that in the N₂O/CH₄ system. On the other hand, the plateau in the CH₄ conversion curve was also observed. It seems that CH₄ can be

converted only when N₂O is present. However, the higher CH₄ conversion of the plateau suggests that O₂ also can contribute to CH₄ oxidation. N₂O conversion in Figure 2(d) was a little lower than that in Figure 2(a). This can be interpreted by the inhibition of excess oxygen on the N₂O reduction with CH₄. It should be noted that the N₂O reduction with CH₄ over ion-exchanged Fe-BEA catalyst was promoted even in the presence of the excess oxygen (Figure 2(d)). We have observed a similar enhancement effect of the N₂O removal by adding CH₄ as a reductant.^{3,4,8} In addition, the catalytic activity over the impregnated Fe/BEA catalyst in the N₂O/CH₄/O₂ reaction drastically decreased compared with that in the N₂O/CH₄ reaction. This behavior is much different from that over Fe-BEA. It is thought that the tendency can be caused by difference of Fe species. In the SCR of N₂O with CH₄, redox ability of iron sites (Fe²⁺ ↔ Fe³⁺) is important for the high catalytic activity. Coq et al.¹⁶ have proposed that N₂O conversion occurs through the redox cycle Fe³⁺ ↔ Fe²⁺ with NN-O splitting mainly on the SCR of N₂O with NH₃ in the presence of O₂. Voskoboinikov and Sachtler et al.¹⁷ also have proposed the redox manner in the SCR of NO_x with hydrocarbons in the presence of O₂. As shown in Figure 2(a), the Fe-BEA catalyst, in which the iron exists in ionic form, is active for the N₂O/CH₄ reaction because the iron ion species on the Fe-BEA catalyst can be easily oxidized and reduced. On the other hand, the Fe/BEA catalyst, in which the iron exists as oxide, is also active for the N₂O/CH₄ reaction. Furthermore, iron oxide seems to have similar redox ability in the N₂O/CH₄ reaction (Figure 2(a)). However, the activity in the presence of excess oxygen is drastically different between the Fe-BEA and Fe/BEA catalysts (Figure 2(d)). It is considered that the redox ability of iron oxide in the presence of excess oxygen is less than that of iron ion species from the comparison of the activities of the N₂O/CH₄/O₂ reaction. The Fe-BEA

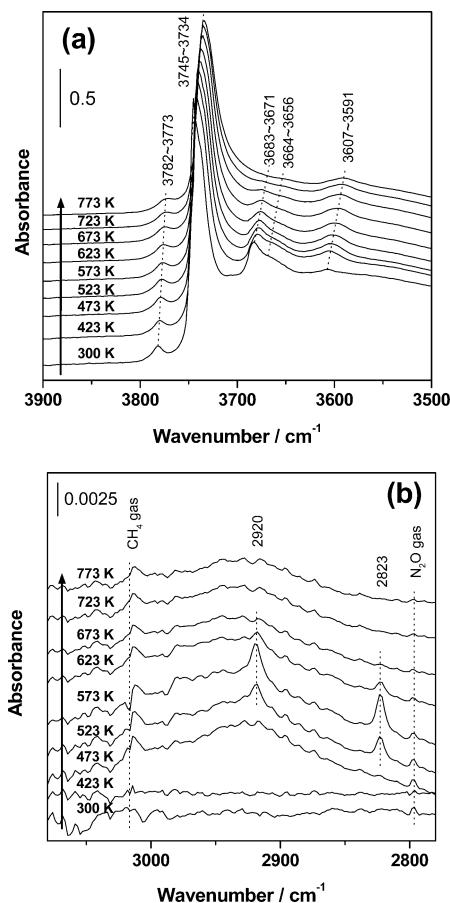


Figure 3. FTIR spectra of Fe-BEA catalyst in the $\text{N}_2\text{O} + \text{CH}_4$ flowing. (a) OH stretching band region, (b) CH stretching band region. Reaction conditions: reaction temperature = 300–773 K, $\text{N}_2\text{O}/\text{CH}_4 = 1000 \text{ ppm}/500 \text{ ppm}$, $\text{SV} = 60000 \text{ h}^{-1}$, total pressure = 0.1 MPa. Pretreatment: 100% O_2 , 773 K, 0.5 h.

catalyst has high activity because iron ion species can be readily reduced even in the presence of excess oxygen. This strongly suggests that the Fe-OH species (3683 cm^{-1}) is related to the high activity, especially under the condition containing excess oxygen.

3.2. In-Situ Observation of the Catalyst Surface during the SCR of N_2O with CH_4 . In the previous study,⁵ we have shown that the intensity of the Fe-OH species (3683 cm^{-1}) was not changed when the catalyst was exposed with CH_4 only, but it was changed when the catalyst was exposed with the mixture of N_2O and CH_4 . The coexistence of N_2O and CH_4 in the gas phase was needed for the reaction. Figure 3 shows FTIR spectra of the Fe-BEA catalyst, which was exposed to $\text{N}_2\text{O}/\text{CH}_4$ at 300 K after O_2 pretreatment and the sample was heated stepwise up to 773 K. The negative shifts in Figure 3(a) were due to the thermally excited state of hydrogen bonds.¹³ The bands at 3016 (noisy) and 2796 cm^{-1} (Figure 3(b)) were assigned to the CH_4 and N_2O gases, respectively. As shown in Figure 3(a) and (b), raising the temperature to 773 K led to the decrease of the Fe-OH species (3683 cm^{-1}) and simultaneous appearance of new bands at 2920 and 2823 cm^{-1} between 523 and 623 K. These bands at 2920 and 2823 cm^{-1} can be assigned to methoxy species ($\text{CH}_3\text{O}(\text{a})$) on Fe ion sites.¹⁸ This assignment is also supported by the experiment of methanol adsorption, as will be shown later. Considering from the behavior of the decreasing and increasing bands, the adsorbed species are formed on the Fe sites. In the high-temperature region from 673 to 773 K, the adsorbed and Fe-OH species could not be observed. It can be considered that the concentration of an

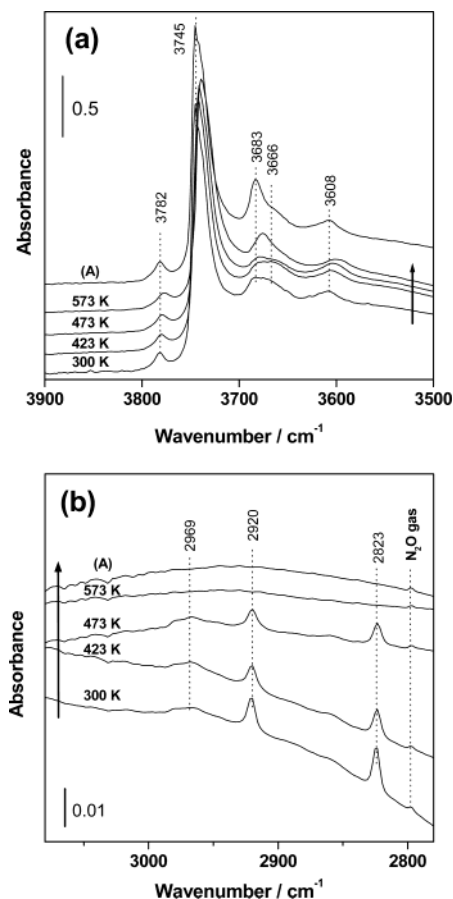


Figure 4. FTIR spectra of Fe-BEA catalyst in the N_2O flowing. (a) OH stretching band region, (b) CH stretching band region. Reaction conditions: reaction temperature range = 300–573 K, $\text{N}_2\text{O} = 1000 \text{ ppm}$, $\text{SV} = 60000 \text{ h}^{-1}$, total pressure = 0.1 MPa. Spectrum (A) was measured at 300 K after experiment. Pretreatment: N_2O (1.00%) + CH_4 (0.493%), 673 K, 0.5 h. Sample was slowly cooled to 300 K under flowing condition, followed by exposure to N_2O (1000 ppm, $\text{SV} = 60000 \text{ h}^{-1}$) at 300 K.

adsorbed intermediate is very low at high temperature under the steady-state condition. The observed $\text{CH}_3\text{O}(\text{a})$ species can be a reaction intermediate, and then we evaluated the reactivity of the adsorbed species with N_2O . Figure 4 shows FTIR spectra of the Fe-BEA catalyst with the adsorbed species, which formed under N_2O (1.00%) + CH_4 (0.493%) reaction, exposed to N_2O (1000 ppm) from 300 to 573 K. Three peaks at 2969, 2920 and 2823 cm^{-1} were observed in the CH stretching band region before N_2O introduction. As already mentioned, the two peaks at 2920 and 2823 cm^{-1} are assigned to $\text{CH}_3\text{O}(\text{a})$. The peak at 2969 cm^{-1} can be assigned to formate species ($\text{HCOO}(\text{a})$) on Fe ion sites,¹⁹ as will also be shown later. The peak of Fe-OH sites disappeared after the pretreatment. It should be noted that there was no difference in the infrared spectra between before and after the introduction of N_2O to the treated sample at 300 K. As shown in Figure 4, however, raising the temperature to 573 K led to a decrease of the ν_{CH} region peaks and an increase of the peak at 3683 cm^{-1} up to its original intensity. The behavior is in good agreement with the previous results using Fe-BEA catalyst with a different H-BEA support.⁵ These results indicate that the surface $\text{CH}_3\text{O}(\text{a})$ and $\text{HCOO}(\text{a})$ species are intermediate species of the $\text{N}_2\text{O}/\text{CH}_4$ reaction since they could react with N_2O . In addition, the Fe-OH sites play an important role in the formation of these intermediate species because the reaction of the surface $\text{CH}_3\text{O}(\text{a})$

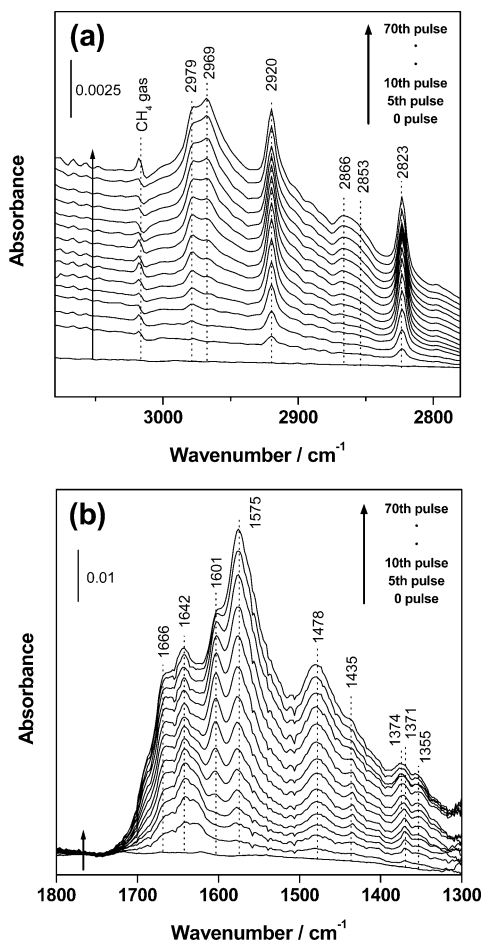


Figure 5. FTIR spectra of Fe-BEA during N₂O pulse under the CH₄ flowing over Fe-BEA. (a) CH stretching band region, (b) CO stretching and CH bending band region. Reaction conditions: reaction temperature = 523 K, N₂O pulse = 0.31 μ mol, CH₄ = 500 ppm, SV = 60000 h⁻¹, total pressure = 0.1 MPa. Spectra were shown every 5 pulses. Pretreatment: 100% O₂, 773 K, 0.5 h.

and HCOO(a) species with N₂O leads to regeneration of the Fe-OH sites.

3.3. In-Situ Observation during N₂O Reaction under CH₄ or CH₄ + O₂ Flowing and after Methanol Adsorption. The surface concentration of the reaction intermediate was rather low as shown above. Therefore, it is not so easy to obtain the kinetic parameters. To concentrate the intermediate species, we carried out the pulse reactions by injecting an N₂O pulse (0.31 μ mol) under the CH₄ (500 ppm) and CH₄ (500 ppm) + O₂ (10%) flowing at 523 K. In this experiment, 50 mg of catalyst was used and it contained 13.4 μ mol of Fe. These results are shown in Figure 5. As shown in the CH stretching band region (Figure 5(a)), six peaks at 2979, 2969, 2920, 2866, 2853, and 2823 cm⁻¹ were observed. In the initial step of the N₂O pulses (between the first and the 15th pulse), the bands at 2920 and 2823 cm⁻¹ grew, and then the band at 2979 cm⁻¹ appeared. In the next step (between the 15th and the 55th pulse), the bands at 2969 and 2866 cm⁻¹ grew, and then the band at 2853 cm⁻¹ appeared. In the final step (between the 55th and 70th pulse), although the bands at 2920 and 2823 cm⁻¹ were almost maintained, the band at 2969 cm⁻¹ (shoulder) and 2866 cm⁻¹ grew. The bands at 2866 and 2853 cm⁻¹ were indivisible, although the band at 2866 cm⁻¹ seems to have a shoulder. In this reaction, the peak of the Fe-OH site was decreased by injecting an N₂O pulse, and completely disappeared after the 70th pulse (not shown). The bands at 3782, 3745, and 3608 cm⁻¹ were hardly affected. This indicates that the adsorbed

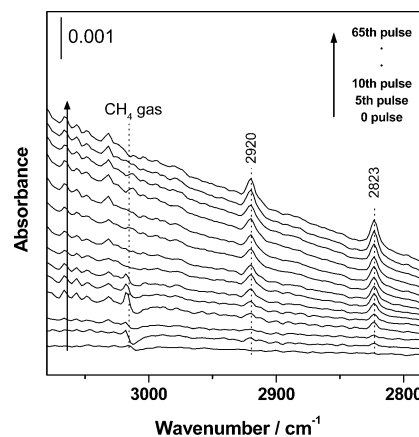
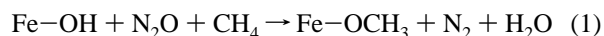


Figure 6. FTIR spectra of CH stretching band region during N₂O pulse under the CH₄ + O₂ flowing over Fe-BEA. Reaction conditions: reaction temperature = 523 K, N₂O pulse = 0.31 μ mol, CH₄/O₂ = 500 ppm/10%, SV = 60000 h⁻¹, total pressure = 0.1 MPa. Spectra were shown every 5 pulses. Pretreatment: 100% O₂, 773 K, 0.5 h.

intermediates such as methoxy species are formed on the Fe-OH sites, as shown below (eq 1):



We observed many peaks in the CO stretching and CH bending band region (Figure 5(b)). Almost all peaks became larger with injecting the N₂O pulse. The band at 1601 cm⁻¹ was increased and decreased with a maximum peak at the 40th pulse.

Figure 6 shows FTIR spectra of the N₂O pulse study under the CH₄ + O₂ flowing. In the CH stretching band region, we could only observe the bands at 2920 and 2823 cm⁻¹, which are assigned to the CH₃O(a) species. In the CO stretching and CH bending band region (not shown), very weak peaks at 1640, 1568, and 1478 cm⁻¹ were observed. The intensity of the bands was much smaller than that in Figure 5(a). This suggests that it is more difficult to store the reaction intermediate under the presence of O₂. When the bands of the CH₃O(a) species (2920 and 2823 cm⁻¹) were increased, the intensity of the Fe-OH peak decreased. From the comparison between Figures 5 and 6, it is shown that the N₂O pulse technique under CH₄ flowing is a suitable method for accumulating the reaction intermediate.

To assign the observed species, we carried out the studies on methanol adsorption over Fe-BEA and H-BEA. We also carried out the reaction of adsorbed methanol with N₂O and O₂. Figure 7 shows FTIR spectra of Fe-BEA and H-BEA before and after methanol adsorption. The spectra were obtained at 300 K. As shown in Figure 7(a), all OH band peaks of both catalysts except Si-OH (3745 cm⁻¹) were significantly decreased after methanol adsorption. This is due to the interaction of OH groups with methanol.

On the H-BEA sample, we observed some CH stretching bands of adsorbed methanol (Figure 7(b)). Campbell and Howe et al.²⁰ reported that the bands at 3007 (shoulder), 2957, and 2853 cm⁻¹ are assigned to $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{s}}(\text{CH}_3)$ of methanol hydrogen-bonded to Brønsted acid sites. They also observed an intense negative feature at 3610 cm⁻¹, indicating the interaction of Brønsted acid sites with methanol. On the other hand, Raskó et al.²¹ reported that the bands at 2956 and 2857 cm⁻¹ correspond to methoxy group chemisorbed onto silica, which can form on Pd/SiO₂ above 253 K. Fisher and Bell²² have also assigned the bands at 2998, 2961, and 2861 cm⁻¹ to methoxide on silica (Si-OCH₃). Therefore, we assigned the bands at 3004, 2959, and 2854 cm⁻¹ to the degeneracy of the $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_3)$, and $\nu_{\text{s}}(\text{CH}_3)$ of hydrogen-bonded methanol

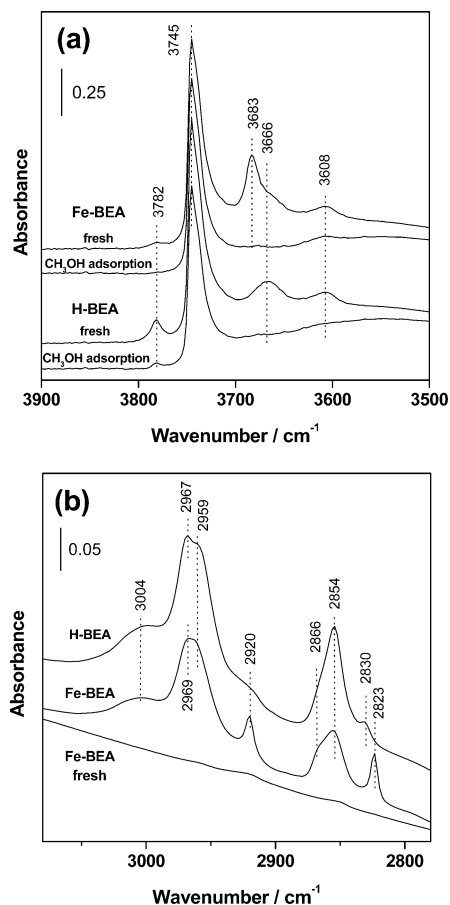


Figure 7. FTIR spectra of methanol adsorption on Fe-BEA and H-BEA. (a) OH stretching band region, (b) CH stretching band region. Reaction conditions: measurement temperature = 300 K, IR cell was evacuated in vacuo. Methanol adsorption: 13.3 Pa (40.3 μ mol), 423 K, followed by evacuation for 5 min at 423 K.

to Brønsted acid sites,²⁰ and the intensity of the same bands at 2959 and 2854 cm^{-1} was enhanced by the overlapping with the adsorption bands of Si-OCH₃.^{21,22} We confirmed the decrease of the Si-OH band after methanol adsorption, and high thermal stability of these bands (Figure 8). Thus these properties also support our assignment. The band at 2967 cm^{-1} can be assigned to $\nu_{\text{as}}(\text{CH}_3)$ of methoxy groups formed by the reaction of methanol with ex Al-OH.²⁰ The band at 2830 cm^{-1} can be assigned to the Fermi resonance $2\delta_{\text{s}}(\text{CH}_3)$ of methoxy groups in the nondissociated methanol.²³

In the Fe-BEA sample, the new bands at 2969, 2920, 2866, and 2823 cm^{-1} were observed. To assign these bands, we carried out the reaction between adsorbed methanol and N₂O (2.67 kPa) from 300 to 573 K. These results are shown in Figure 8. As shown in Figure 8(a), almost all OH bands recovered after the evacuation at 573 K. Increasing the reaction temperature, the intensity of the new bands decreased. In particular, the bands at 2969 and 2866 cm^{-1} disappeared completely at 523 K. According to Wang et al.,²⁴ the surface species of Fe-OOCH, Fe-OCH₃, and Si-OCH₃ are thermally stable even at 473 K. However, the iron redox capability is to primarily convert adsorbed methoxy species (Fe-OCH₃) to formate species (Fe-OOCH) and molecular H₂O even at the same temperature. In our recent study, we confirmed the redox ability of the Fe-BEA catalyst.⁵ Furthermore, we also observed the bending mode of adsorbed H₂O ($\delta(\text{H}_2\text{O})$) at 1621 cm^{-1} in both studies (not shown). Taking into account the reactivity of formate species, the bands at 2969 and 2866 cm^{-1} were assigned by formate species on Fe ion sites (Fe-OOCH), and the bands at 2920

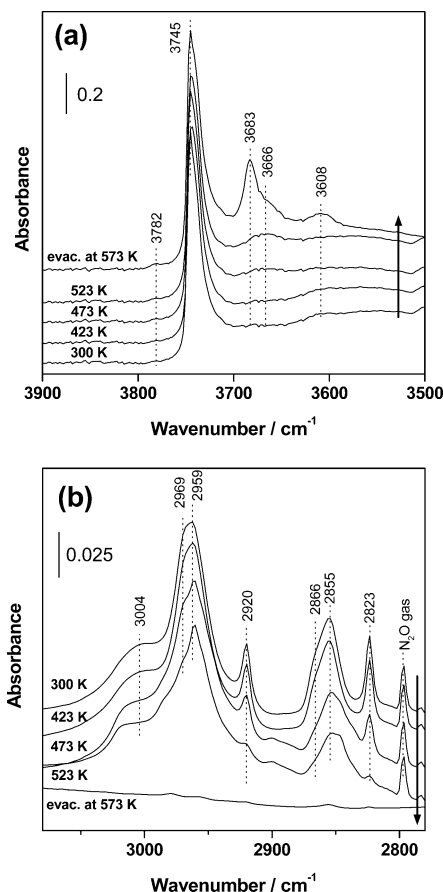


Figure 8. FTIR spectra of the reaction of adsorbed methanol with N₂O over Fe-BEA. (a) OH stretching band region, (b) CH stretching band region. Reaction conditions: reaction temperature range = 300–573 K, N₂O = 2.67 kPa (static). Methanol adsorption: 13.3 Pa (40.3 μ mol), 423 K, followed by evacuation for 5 min at 423 K.

TABLE 3: Assignment of IR Bands of CH₃OH Adsorbed at 423 K on Fe-BEA and H-BEA in Figures 7(b) and 8(b)

wavenumber/ cm^{-1}	species	interpretation	references
3004	hydrogen-bonded CH ₃ OH	$\nu_{\text{as}}(\text{CH}_3)^a$	20, 25
2969	Fe-OOCH	$\delta(\text{CH}) + \nu_{\text{as}}(\text{OCO})^b$	19, 26
2967	ex Al-OCH ₃	$\nu_{\text{as}}(\text{CH}_3)$	20
2959	hydrogen-bonded CH ₃ OH	$\nu_{\text{as}}(\text{CH}_3)$	20, 25
	Si-OCH ₃		21, 22
2920	Fe-OCH ₃	$\nu_{\text{as}}(\text{CH}_3)$	18
2866	Fe-OOCH	$\nu(\text{CH})$	19
2855, 2854	hydrogen-bonded CH ₃ OH	$\nu_{\text{s}}(\text{CH}_3)$	20, 25
	Si-OCH ₃		21, 22
2830	nondissociated CH ₃ OH	$2\delta_{\text{s}}(\text{CH}_3)^b$	23
2823	Fe-OCH ₃	$\nu_{\text{s}}(\text{CH}_3)$	18

^a Degeneracy of the asymmetric $\nu(\text{CH})$ mode. ^b These bands are assigned to a Fermi resonance between the $\delta(\text{CH})$ and $\nu_{\text{as}}(\text{COO})$.²⁶

and 2823 cm^{-1} were assigned by methoxy species on Fe ion sites (Fe-OCH₃). These assignments of methanol adsorption were shown in Table 3. These results support that the bands at 2920 and 2823 cm^{-1} , which we observed in Figures 3(b), 4(b), 5(a), and 6, are due to the Fe-OCH₃, and the bands at 2969 and 2866 cm^{-1} in Figure 5(a) are due to Fe-OOCH. The band at 2969 cm^{-1} in Figure 4(b) is also due to Fe-OOCH, although the peak at 2866 cm^{-1} was not observed because of very low intensity.

From these experiments and many other references on the methanol synthesis studies, we decided the assignment of the reaction intermediate species of the SCR of N₂O with CH₄ in Figures 5 and 6. The bands at 2969, 2920, 2866, and 2823 cm^{-1}

TABLE 4: Assignment of IR Bands of Pulse Reaction at 523 K on Fe-BEA in Figures 5 and 6

wavenumber/cm ⁻¹	species	interpretation	references
2979	CH ₃ OH	$\nu_{\text{as}}(\text{CH}_3)$	20, 25
2969	b-HCOO-Fe	$\delta(\text{CH}) + \nu_{\text{as}}(\text{COO})^a$	19, 26
2920	Fe-OCH ₃	$\nu_{\text{as}}(\text{CH}_3)$	18
2866	b-HCOO-Fe	$\nu(\text{CH})$	19
2853	CH ₃ OH	$\nu_{\text{s}}(\text{CH}_3)$	20, 25
2823	Fe-OCH ₃	$\nu_{\text{s}}(\text{CH}_3)$	18
1666	m-HCOO-Fe	$\nu_{\text{as}}(\text{COO})$	24
1642	Fe \cdots O=CH ₂	$\nu(\text{CO})$	24
1601	H ₂ O	$\delta(\text{H}_2\text{O})$	24, 30
1575	b-HCOO-Fe	$\nu_{\text{as}}(\text{COO})$	18, 24, 29
1478	Fe-OCH ₃	$\delta_{\text{as}}(\text{CH}_3)$	24, 28
1435	Fe-OCH ₃	$\delta_{\text{s}}(\text{CH}_3)$	28
1374	b-HCOO-Fe	$\delta(\text{CH})$	18, 24, 29
1371	CH ₃ OH	$\delta(\text{OH})$	20, 25
1355	b-HCOO-Fe	$\nu_{\text{s}}(\text{COO})$	18, 29

^a The band is assigned to a Fermi resonance between the $\delta(\text{CH})$ and $\nu_{\text{as}}(\text{COO})$.²⁶

in Figure 5(a) have behavior similar to that of the methoxy and formate species, which formed by the reaction of adsorbed methanol with N₂O. The detail of the peak assignment was listed in Table 4. It can be expected that the Fe-OOCH species readily reacts with N₂O in the N₂O/CH₄ and N₂O/CH₄/O₂ systems. In fact, the Fe-OOCH species (2969 and 2866 cm⁻¹) were not observed in the presence of excess oxygen systems in Figures 3(b) and 6. The reaction rates of these species with N₂O or O₂ will be compared later in section 3.4.

The bands at 2979 and 2853 cm⁻¹ can probably be assigned to $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{s}}(\text{CH}_3)$ of symmetrically adsorbed methanol.^{20,25} In addition, the band at 1371 cm⁻¹ can probably be assigned to the in-plane bending vibrations of OH groups of adsorbed methanol.^{20,25} This is because the bands at 2853 and 1371 cm⁻¹ (Figure 5) have different behavior compared with methoxy and formate species. However, some authors have assigned the 2961–2970 cm⁻¹ band to $\nu_{\text{as}}(\text{CH}_3)$ of an asymmetric Si-OCH₃ species²⁷ and of methoxy groups on V-Ti-O, TiO₂, and Al₂O₃.²⁸ However, we could not observe the decrease of Si-OH in the OH stretching band (not shown). Therefore, the assignment of Si-OCH₃ can be excluded.

As shown in Figure 5(b), the band at 1666 cm⁻¹ is assigned to $\nu_{\text{as}}(\text{COO})$ of the monodentate formate species (m-HCOO-Fe),²⁴ and the bands at 1575, 1374, and 1355 cm⁻¹ are assigned to $\nu_{\text{as}}(\text{COO})$, $\delta(\text{CH})$, and $\nu_{\text{s}}(\text{COO})$ of the bidentate formate species (b-HCOO-Fe),^{19,24,29} respectively. Unfortunately, no information on formate species was obtained in the 1700–1300 cm⁻¹ region in the adsorption experiment of methanol because of strong bands of CH₃O(a). However, to confirm the assignments of formate species, we carried out the CO₂ + H₂ pulse reaction (CO₂ + H₂ \leftrightarrow HCOOH \leftrightarrow CO + H₂O) at 523 K. In this experiment, we observed the major peaks at 1670 and 1570 cm⁻¹, which can be assigned to formate species. The CO stretching band of bidentate formate species should be observed in the low wavenumber regions compared to that of the monodentate formate species. Thus, we assigned the bands at 1666 and 1575 cm⁻¹ to the monodentate and bidentate formate species over Fe species. The bands at 1478 and 1435 cm⁻¹ are assigned to $\delta_{\text{as}}(\text{CH}_3)$ and $\delta_{\text{s}}(\text{CH}_3)$ of the methoxy species (Fe-OCH₃), respectively.^{24,28} Although the same band at 1478 cm⁻¹ can be assigned to Si-OCH₃ species (overlapping with the absorption bands of Fe-OCH₃),²⁴ the OH stretching vibration band on Si was hardly changed. Therefore the band at 1478 cm⁻¹ is not Si-OCH₃ species. The bands at 1642 cm⁻¹ are assigned to $\nu(\text{CO})$ of adsorbed formaldehyde Fe \cdots O=CH₂.²⁴ This species was formed by oxidation of methoxy species on

iron ion sites. The band at 1601 cm⁻¹ is assigned to $\delta(\text{H}_2\text{O})$ of the adsorbed water, which is formed by the oxidation of Fe-OCH₃ and Fe-OOCH species.^{24,30} All assignments of the pulse reaction are listed in Table 4.

It can be concluded that the N₂O + CH₄ reaction proceeds on the iron ion species Fe-OH (3683 cm⁻¹), and the methoxy species (Fe-OCH₃) is formed. The species is oxidized by N₂O to form formate species (Fe-OOCH) and water. However, some methoxy species reacts with hydroxyl groups or adsorbed water, followed by formation of physically adsorbed methanol species. Formate species on iron ion sites (Fe-OOCH) mainly exists as the bidentate formate species (b-HCOO-Fe), and a small part of formate exists as monodentate formate species (m-HCOO-Fe). It seems that this difference is ascribed to the different structure of adsorption sites such as mononuclear or binuclear iron ion species. On the other hand, only the methoxy species was observed in the presence of excess oxygen. Judging from the result of the pulse reaction study, the rate of the reaction of formate with O₂ is much higher than that of methoxy species oxidation.

3.4. Determination of Reaction Rate of the Intermediate Oxidation with N₂O or O₂. Reaction-temperature dependence of the oxidation rate of the reaction intermediate was investigated. Pretreatment was carried out under N₂O (1.00%) + CH₄ (0.493%) reaction. For the accumulation of reaction intermediates, the sample was slowly cooled to 300 K under flowing condition. After pretreatment, N₂O or O₂ was introduced to the sample with the reaction intermediate at reaction temperature. Figure 9 shows subtracted spectra of the reacted samples from that before the introduction of N₂O or O₂. The similar spectrum before subtracting is shown in Figure 4. The spectra were obtained each 20 s. As shown in Figure 9, we observed the interesting feature about the reactivity of intermediate species. The Fe-OCH₃ species (2920 and 2823 cm⁻¹) were readily oxidized by N₂O (Figure 9(a)), although these species were hardly oxidized by O₂. On the other hand, the Fe-OOCH species (2969 cm⁻¹) were easily oxidized by both N₂O and O₂. For the comparison of the reaction rate, we analyzed the change of the peak area with reaction time as shown in Figure 10. The normalized peak area proportionally decreased after about 60 s. This is because it takes about 60 s for the treatment gas to reach the sample. Therefore, we estimated the rate on the basis of the data after 60 s. In the case of Fe-OCH₃ (Figure 10(a)), the initial rate was obviously different between O₂ and N₂O. It should be noted that the reaction rate with N₂O was much faster than that with O₂, although the N₂O concentration (1000 ppm) was quite dilute compared to O₂ (10%). In the case of b-HCOO-Fe (Figure 10(b)), however, the reaction rate was almost the same value between N₂O and O₂. To investigate the decomposition rate of the Fe-OOCH species, we carried out a similar experiment in the inactive He gas flow (not shown). The result obviously indicates that the oxidation rate of Fe-OOCH species was much faster than the decomposition rate (about 500 times). This supports the finding that the results in Figure 10b showed the oxidation rate by N₂O or O₂.

Figure 11 shows an Arrhenius plot of the oxidation of Fe-OCH₃ (2920 cm⁻¹) and Fe-OOCH species (2969 cm⁻¹) by N₂O or O₂. The method of the initial rate determination was shown in Figure 10. According to Figure 11a, the oxidation rate of Fe-OCH₃ species by N₂O was higher than that by O₂. In particular, this tendency becomes more significant at higher temperatures. Considering that N₂O concentration (1000 ppm) was much lower than that of O₂ (10%), N₂O can rapidly oxidize Fe-OCH₃ species. These results strongly support that N₂O can

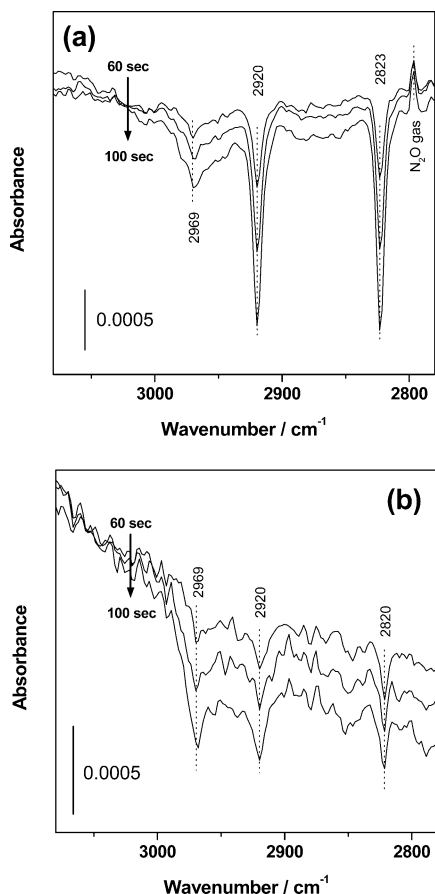


Figure 9. Subtracted FTIR spectra of the reaction of the intermediate with N_2O (a) or O_2 (b) over Fe-BEA (see text). Reaction conditions: (a) reaction temperature = 543 K, N_2O = 1000 ppm, SV = 60000 h^{-1} , total pressure = 0.1 MPa. (b) Reaction temperature = 543 K, O_2 = 10%, SV = 60000 h^{-1} , total pressure = 0.1 MPa. Pretreatment: N_2O (1.000%) + CH_4 (0.493%), 673 K, 0.5 h. Sample was slowly cooled to 300 K under flowing condition, followed by exposure to N_2O (1000 ppm, SV = 60000 h^{-1}) or O_2 (10%, SV = 60000 h^{-1}) at 543 K.

be utilized as the oxidizing agent, even in the presence of excess oxygen. And this is related to the selective catalytic reduction (SCR) of N_2O . From an Arrhenius plot of the oxidation of Fe-OCH₃ species in Figure 11(a), the activation energies E_a can be evaluated for the oxidation by N_2O and O_2 to be 192 kJ mol⁻¹ and 53 kJ mol⁻¹, respectively. On the other hand, the oxidation rate of b-HCOO-Fe species by N_2O is similar to that by O_2 . The activation energies E_a evaluated for the oxidation with N_2O and O_2 were 177 kJ mol⁻¹ and 238 kJ mol⁻¹, respectively.

These results from kinetics experiments correspond well to that of activity tests. To confirm the contribution of excess oxygen in the $\text{N}_2\text{O}/\text{CH}_4/\text{O}_2$ reaction (Figure 2(d)), we calculated the consuming ratio of oxidizing agents ($\text{N}_2\text{O}/\text{O}_2$ ratio) between 523 and 543 K. The O_2 consumption was estimated from the amount of N_2O consumption, H_2O , CO, and CO_2 production. From the calculation results, the $\text{N}_2\text{O}/\text{O}_2$ ratio is 0.70, 0.82, and 1.15 at 523, 533, and 543 K, respectively. Since the CO/ CO_2 ratio was 4, the $\text{N}_2\text{O}/\text{O}_2$ ratio indicates the contribution ratio of N_2O and O_2 against CH_4 conversion. Hence, these results indicate that the contribution of N_2O increased with increasing reaction temperature. This is in good agreement with the result in Figure 11(a). We clarified that the methoxy species (Fe-OCH₃) rapidly reacted with N_2O , and the formate species (Fe-OOCH) has similar reactivity with N_2O and O_2 .

3.5. Proposed Reaction Steps in the SCR of N_2O with CH_4 .

We propose the following possible reaction steps for the SCR

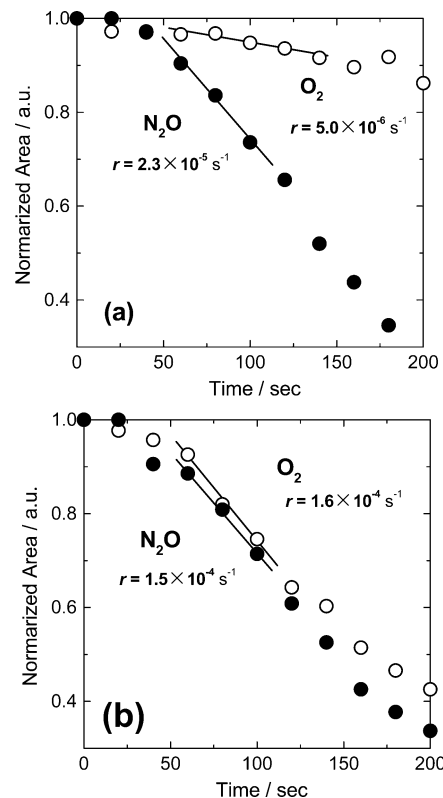


Figure 10. Reaction time dependence of the peaks of the intermediate during the reaction with N_2O or O_2 . (a) Methoxy species (2920 cm^{-1}), (b) formate species (2969 cm^{-1}). Reaction conditions: reaction temperature = 543 K, N_2O (closed symbol) = 1000 ppm, O_2 (open symbol) = 10%, SV = 60000 h^{-1} , total pressure = 0.1 MPa. Pretreatment: N_2O (1.000%) + CH_4 (0.493%), 673 K, 0.5 h. Sample was slowly cooled to 300 K under flowing condition, followed by exposure to N_2O (1000 ppm, SV = 60000 h^{-1}) or O_2 (10%, SV = 60000 h^{-1}) at 543 K. Intensities normalized to the value observed at the end of the transient for methoxy and formate species.

of N_2O with CH_4 in the presence of excess oxygen over Fe-BEA catalyst, as shown in Figure 12. First, CH_4 is activated by N_2O on the Fe-OH sites, followed by formation of the Fe-OCH₃ species (Figure 12(I)). In contrast, the reaction cannot proceed using O_2 , even under rather high partial pressure (Figure 12(II)). This reaction was completely dependent on the presence of N_2O , although the activity is a little hindered from the presence of excess oxygen as described in Figure 2. Second, the oxidation of Fe-OCH₃ species by N_2O readily proceeded (Figure 10(a)), followed by formation of the Fe-OOCH species (Figure 12(III)). Although there is a little contribution from O_2 for the oxidation of Fe-OCH₃ species in the low-reaction-temperature region (Figure 11(a)) (Figure 12(IV)), the oxidation of Fe-OCH₃ species by N_2O is predominant in the reaction temperature of the SCR. Finally, the oxidation of the Fe-OOCH species proceeds. Both N_2O and O_2 can contribute to this reaction (Figures 12(V) and (VI)). The decomposition rate of Fe-OOCH species is very low.

4. Conclusions

(1) The ion-exchanged Fe-BEA catalyst exhibited much higher activity in the $\text{N}_2\text{O}/\text{CH}_4$ and the $\text{N}_2\text{O}/\text{CH}_4/\text{O}_2$ reactions. On the other hand, the impregnated Fe/BEA catalyst exhibited low activity in the $\text{N}_2\text{O}/\text{CH}_4/\text{O}_2$ reaction, although it exhibited activity in the $\text{N}_2\text{O}/\text{CH}_4$ reaction. The difference of activity in the presence and absence of excess oxygen is due to the states of surface iron species. Only the iron ion species exhibits high

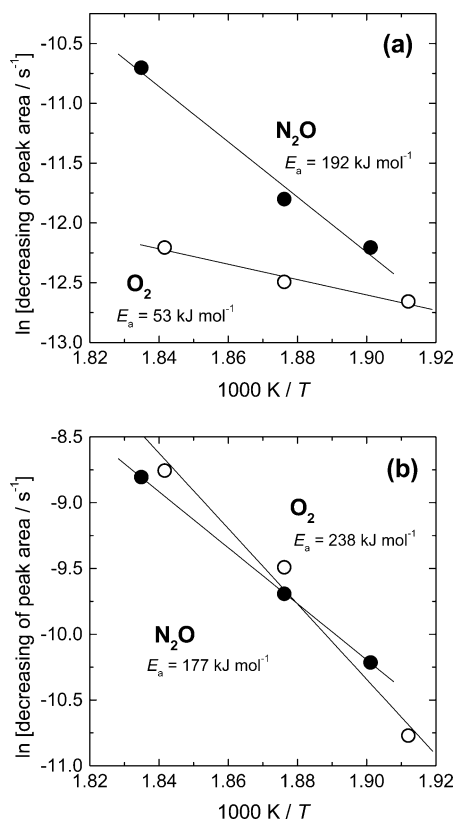


Figure 11. Arrhenius plot of the oxidation of intermediate by N₂O or O₂. (a) methoxy species (2920 cm⁻¹), (b) formate species (2969 cm⁻¹). Reaction conditions: reaction temperature range = 523–545 K, N₂O (closed symbol) = 1000 ppm, O₂ (open symbol) = 10%, SV = 60000 h⁻¹, total pressure = 0.1 MPa.

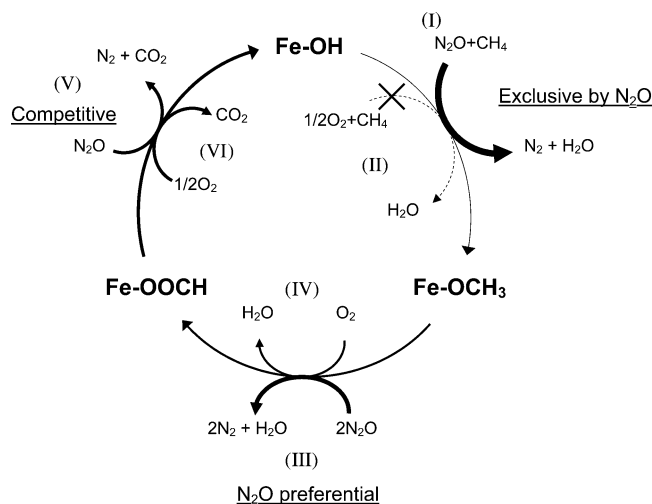


Figure 12. Proposed reaction scheme for the SCR of N₂O with CH₄ in the presence of excess oxygen over Fe-BEA catalyst. The arrow thickness represents relative reaction rate. The inside and the outside of this circle indicate the O₂ and N₂O reaction with CH₄ and/or intermediate species, respectively.

activity in the SCR of N₂O with CH₄, even in the presence of excess oxygen.

(2) The Fe–OH species (3683 cm⁻¹) was observed only on the Fe–BEA catalyst in FTIR experiments. This band was made to disappear by the SCR of N₂O with CH₄. It plays an important role in the SCR of N₂O with CH₄.

(3) Some intermediate species were observed on the Fe–BEA catalyst. These were assigned by using methanol adsorption results. The main intermediate species were methoxy and

bidentate formate species. They were only formed by coexisting of N₂O with CH₄. N₂O plays an important role in the initial steps on the SCR of N₂O with CH₄.

(4) The oxidation rate of the intermediate species by N₂O or O₂ was measured by IR experiments. The methoxy species were oxidized with N₂O more rapidly than with O₂. However, the formate species were oxidized with N₂O and O₂. These kinetics results, which were estimated by FTIR experiments, are in good agreement with activity test experiments.

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