IR Investigation of Selective Reduction of NO by Ethene on Cu-ZSM-5

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Adsorbed species during the reaction of selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) on Cu ion-exchanged ZSM-5 (Cu-ZSM-5) were investigated by in situ FT-IR using isotopes as well as gas phase analysis. No oxygen-containing species was observed by IR and no reaction proceeded in the presence of gaseous O_2 and C_2H_4 below 473 K, at which HC-SCR occurs. However, an extra NO_x species (tentatively assigned to organic nitrite or nitrate species), other than inorganic NO_x species derived from O_2 and NO, appeared very rapidly in IR at 1670 cm^{-1} at room temperature, in the presence of adsorbed NO_2 species, gaseous C_2H_4 and NO. Afterwards, a carbonyl species (1677 cm^{-1}) was formed gradually at room temperature. When the extra NO_x species was observed, N_2 and N_2O evolved even at room temperature, therefore, the extra NO_x species is considered to be related to HC-SCR. In the $O_2+C_2H_4+NO$ reaction at 473 K, no nitrogen-containing species, except for quite a small amount of nitrile (2168 cm^{-1}), was observed in IR. At 473 K, N_2, and CO evolved very rapidly with a steep increase in the IR intensity of carboxylate (1574 and 1375 cm^{-1}), while CO_2 and carbonyl species increased more slowly.

NO_x emissions from diesel engines cause increases in NO_x concentration in urban areas, and so the removal of NO_x in the presence of excess oxygen is an important problem. Recently, it has been reported that selective catalytic reduction by hydrocarbon (HC-SCR) occurs on Cu ion-exchanged zeolite,[1—5] H-form zeolite,[6] and Al_2O_3.[7] Till now, various kinds of metal-loaded zeolite, metal oxide, and metal-loaded metal oxide catalysts have been reported as catalysts for HC-SCR.[8] However, in the case of HC-SCR, reductant hydrocarbons react not only with NO_x but also with oxygen. Therefore, besides high catalytic activity, high selectivity of NO_x reduction by hydrocarbon is required to put this reaction into practical use. Understanding the intermediate path of HC-SCR reaction is very important to improve selectivity and activity.

Among the HC-SCR catalysts, Cu ion-exchanged ZSM-5 (Cu-ZSM-5) is the best investigated catalyst for HC-SCR, not only because Cu-ZSM-5 is the first catalyst found for HC-SCR but because the catalyst has a high activity under high SV conditions, which is essential for the automobile use. However, even on Cu-ZSM-5, various schemes explaining the reaction mechanism of HC-SCR have been proposed. Iwamoto et al. proposed for SCR using ethene that oxygen is required to produce partially oxidized intermediates derived from hydrocarbons and that the intermediate would react with nitrogen monoxide (NO) to form molecular nitrogen (N_2).[4,9] It was also reported by Bennett et al. that HC does not reduce NO directly because the activation energy of N_2 evolution is quite different from that of hydrocarbon consumption during SCR using propene.[10] On the other hand, there is a hypothesis in which NO_2 formation instead of partial oxidation is the first stage of the reaction in SCR using C_3H_6 and C_3H_8.[11] Ansell et al. reported that deposited carbon is possibly an intermediate of SCR using propene,[12] while Burch et al.[13,14] and Inui et al.[15,16] claimed a redox mechanism in which hydrocarbons react with several surface oxygen atoms and nitrogen oxide is decomposed on the reduced surface.

Thus, to obtain information concerning the mechanism of HC-SCR, we studied the adsorbed species during HC-SCR using IR. It has been briefly reported that a nitrogen-containing species other than inorganic NO_x species was observed on Cu-ZSM-5 in the presence of gaseous NO, O_2, and ethene followed by an increase in the intensity of carbonyl species at room temperature, suggesting a nitrogen-containing intermediate derived from the NO_2 addition to olefin as an initial intermediate.[17,18] Tanaka et al. recently reported that organic nitro and nitrite species were also formed on Pt/SiO_2 in the presence of gaseous NO, O_2, and propene.[19] Ukisu et al. reported that an organic NO_x species was observed at room temperature in the presence of gaseous NO, O_2, and propene on $Cu–Cs/Al_2O_3$ and that isocyanate species was observed at elevated temperature after evacuation of the gas phase.[20—22] Yahiro et al. reported that isocyanate species was also observed on Cu-ZSM-5 after the reaction of $NO+O_2+C_3H_6$ at an elevated temperature under a net reducing atmosphere.[23] However, the formation process of isocy-

anate is still obscure. Heating a catalyst that adsorbs hydrocarbons in the absence of oxygen is a likely condition to lead to carbon formation, and so, it is questionable that the experimental conditions in Refs. 20, 21, 22, and 23 agreed with the actual reaction conditions containing abundant oxygen. In fact, it has also been suggested that isocyanate or nitrile species is formed on Pt/Al_2O_3 by the reaction between deposited carbon derived from propene and NO,[24] so that it is still unclear whether isocyanate was actually formed under actual reaction conditions in which carbon deposition was not observed.

Hence, in this report, we investigated the adsorbed species during the SCR reaction by propane or ethene on Cu-ZSM-5 using in situ FT-IR technique, because ethene is considered to be less active to form carbonaceous deposits and more selective than propene.[25]

Experimental

Materials. Na-ZSM-5 (N. E. Chemcat Corp., $SiO_2/Al_2O_3=25$) powder was suspended and ion-exchanged in a copper nitrate aqueous solution at about pH 7, washed with water, and dried overnight. The ion exchange rate was 150%, assuming that one Cu^{2+} is exchanged with two Na^+. The obtained Cu-ZSM-5 catalyst powder was pressed into a self-standing thin disk and calcined at 773 K in a vacuum.

The isotopic purity of the isotopic labeled gases (Isotec Inc.; ^{15}NO, $^{15}N^{18}O$, $^{18}O_2$, $^{13}C_2H_4$, C_2D_4) was more than 99%.

IR Measurement. A thin disk catalyst sample (about 0.05 g of Cu-ZSM-5) was placed in an IR cell with KBr windows. The cell, which can be heated by an external heater, was connected to a closed circulation system, and in situ measurements in a reaction atmosphere were done using an FT-IR. The experiments were mainly done using a system made of glass and an FT-IR (JASCO FT/IR 8900, MCT detector, resolution=2 cm^{-1}), but a system made of stainless steel with an FT-IR (Nicolet 60SX, MCT detector, resolution=2 cm^{-1}), was also used for the experiments in which the gas phase was not analyzed. It was confirmed that the same spectra were obtained by both sets of apparatus. The sample was heated in a vacuum at 773 K for 30 min as a pretreatment before each batch of experiment, and the spectrum taken just after the pretreatment at the temperature of measurement was used as the background.

To predict wavenumbers by isotopic shifts, ab initio molecular orbital calculation was done using the GAUSSIAN 92/DFT program with the BP86 method.[26] For the stretching modes of two atoms, isotopic shifts were calculated from the ratio of the square roots of the reduced masses assuming diatomic molecule.

General Procedure and Gas Phase Analysis. Reactant gas was introduced in the form of pure gas or mixed gas and another gas was sequentially added to the circulating gas after an appropriate time. During the reaction, the catalyst was investigated by FT-IR in the presence of the gas phase at the reaction temperature. The gas phase during the reaction was sampled at appropriate intervals to analyze its composition by a quadrupole mass spectrometer (QMS; Nichiden Anelva AQA-200). The mass spectrum (MS) profile for each molecule and the sensitivity of MS ion current for each ion species were measured using pure and mixed gas. The gas composition was analyzed as follows. After each background ion current was subtracted, the partial pressures of $^{15}N_2O$ and CO_2 in the QMS chamber were determined using previously obtained sensitivity data from the ion current at $m/z=46$ and 44 respectively. The ion currents for the branch channels, i. e. $m/z=32$, 31, 30, 28, 16, 15, and 12, were calculated from the previously obtained profile data and subtracted from the ion currents for those channels, though these branch currents to be subtracted were lower than the principal channel current by more than one order. Subsequently, the partial pressures of O_2, ^{15}NO, $^{15}N_2$, and C_2H_4 were determined from the subtracted ion currents at $m/z=32$, 31, 30, and 27 respectively, followed by a subtraction of the ion currents for those channels as well as the branch channels. Finally, the partial pressure of CO was calculated from the ion current at $m/z=28$ followed by subtraction of its branches. It was then confirmed that these quantifications were consistent and that the residual ion current summed over all channels was less than 3% of the total ion current just after subtraction of the background. Thus, the gas composition was derived from each partial pressure in QMS. The water produced as a result of the reaction could not be detected exactly, because water remains in the QMS chamber and the analyzer lines for a long time causing it to be counted as a background signal. The signal of $m/z=47$ corresponding to $^{15}NO_2$ was negligible because NO_2 was readily decomposed in the QMS chamber and counted as NO. On the other hand, the total pressure of the gas phase was measured by a capacitance manometer (MKS Baratron 127), and the partial pressure of each gas was calculated from the total pressure and the gas composition.

Results

Observed IR Absorption Peaks on Cu-ZSM-5 in the Presence of Gas Phase. First, IR spectra on Cu-ZSM-5 at room temperature were measured in the presence of various combinations of gas species, and the results are summed up in Table 1. When a single gas was exposed to the catalyst, adsorbed species reported previously[27] were observed as shown in the upper part of Table 1. Although the total pressure was around 2×10^3 Pa, the contribution of the gas phase was not observed except for the CH stretching of propane and ethene. When NO coexisted with O_2, NO_2 was formed and adsorbed on Cu-ZSM-5 at room temperature; as a result, the total gas pressure decreased below its stoichiometric value based on the gas phase reaction of $NO+1/2\ O_2\rightarrow NO_2$. The peaks at 1630 cm^{-1} (hereinafter referred to as Peak A′) and 1570 cm^{-1} (hereinafter referred to as Peak B) were first formed as shown in Fig. 1a, followed by formation of the peak at 1604 cm^{-1} (hereinafter referred to as Peak A). The final spectrum after 1 hour's exposure is shown in Fig. 1b. Peak A and A′ seem to be split into several peaks in Fig. 1b because of extremely strong absorption and of influence of atmospheric water, but the peak centers

Table 1. IR Peaks Observed in the Presence of Each Gas Phase

Gas phase	Major peaks/cm^{-1}
NO	1910 (NO^+), 1732 & 1825 (twin NO^-), 1811 (NO^-)[a]
O_2	None
NO + O_2	1630 (NO_2), 1604 (NO_3^-?), 1570 (NO_2?)
C_3H_8	2900—3000 (CH str.; gas phase), ca. 1500 (CH bend.; gas phase)
C_2H_4	ca. 3000 (CH str.; gas phase), 1422 (CH bend.)
C_3H_8 + O_2	2900—3000, 1625[b] (H_2O), ca. 1500
C_3H_8 + NO	2900—3000, 1910, 1811, ca. 1500
C_3H_8 + NO + O_2	2900—3000, 1630, 1604, 1570, ca. 1500
C_2H_4 + O_2	ca. 3000, 1422
C_2H_4 + NO	ca. 3000, 1910, 1811, 1422
C_2H_4 + NO + O_2	ca. 3000, 1670, 1630, 1604, 1570, 1422

Temperature range: room temperature—473 K. a) Assigned according to Ref. 27. b) Total pressure $=1.3\times10^4$ Pa.

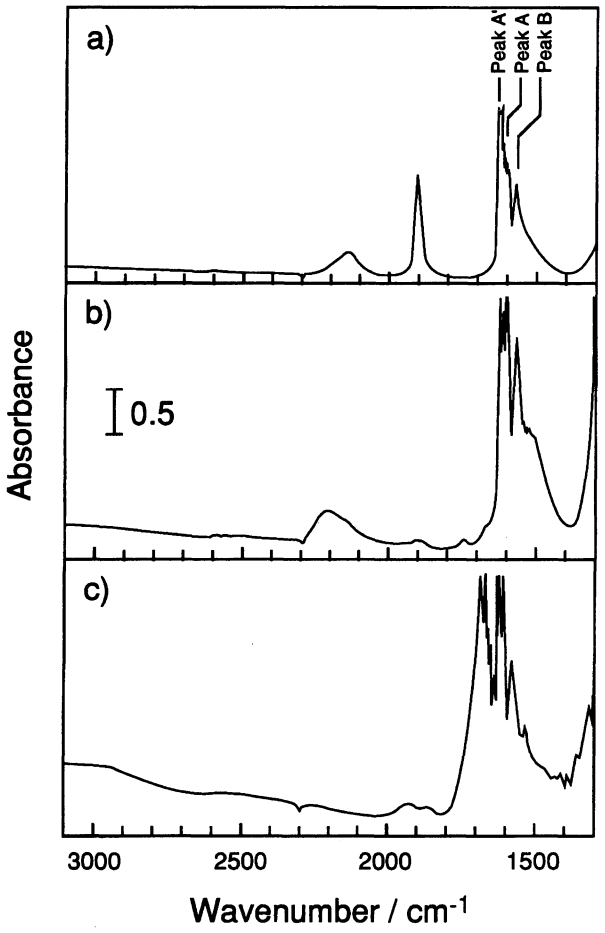

Fig. 1. IR spectral change on Cu-ZSM-5 by introduction of C_2H_4 into NO+O_2 gas phase. T=310 K. a) 5 min after NO+O_2. b) 1 h after NO+O_2. Initial partial pressure: NO=4.0×10^2 Pa, O_2=2.0×10^3 Pa. c) 1 h after introduction of C_2H_4 after b). C_2H_4=2.7×10^2 Pa. 1/4 of NO+O_2 gas was replaced for C_2H_4 at the introduction of C_2H_4.

were defined to 1604 and 1630 cm^{-1} from many other spectra. These peaks were not easily decreased by evacuation even at elevated temperatures below 473 K.

Second, the catalyst was exposed to various combinations of reactant gases. Using propane as a hydrocarbon, no extra peak, except for a small H_2O absorption, was observed below 473 K during the experiment for about 1 h, even in the co-exsistence with O_2, NO, or both. In contrast, in the case of ethene, new peaks were observed in the presence of gaseous ethene with both O_2 and NO even at room temperature, while no extra peak was observed in the presence of ethene with either NO or O_2 below 473 K. Figure 1c shows the spectra on Cu-ZSM-5 1 h after the addition of ethene into the gas phase: NO and O_2. A very strong peak around 1670 cm^{-1} was observed in the figure along with many small peaks below 1600 cm^{-1}. These peaks were not easily diminished by evacuation at room temperature, and therefore, they are not contributions of the gas phase.

Reaction of $^{15}NO+O_2+C_2H_4$ at Room Temperature. To confirm the relationship of the new peak at 1670 cm^{-1} to the reaction of SCR by ethene, in situ FT-IR measurement associated with gas phase analysis was made during the reaction using ^{15}NO. ^{15}NO was first circulated and exposed to the catalyst for 1 h. Then a part of the gas phase (about 1/4 of the total volume) was replaced by oxygen. The mixed gas, continuously exposed to the catalyst, was circulated for 1 h, followed by the addition of ethene by a similar partial replacement. The IR spectral changes before and after the addition of ethene are shown in Fig. 2. The initial partial pressures in the caption are the converted values at the addition of ethene after accounting for the losses of the gas phase by replacement and sampling. Figure 2 clearly shows that the peak at 1670 cm^{-1} in Fig. 1c, observed using unlabeled NO, consisted of at least two different species: Peak I at 1625 cm^{-1} in the case of ^{15}NO and Peak II at 1677 cm^{-1}. Peak I was

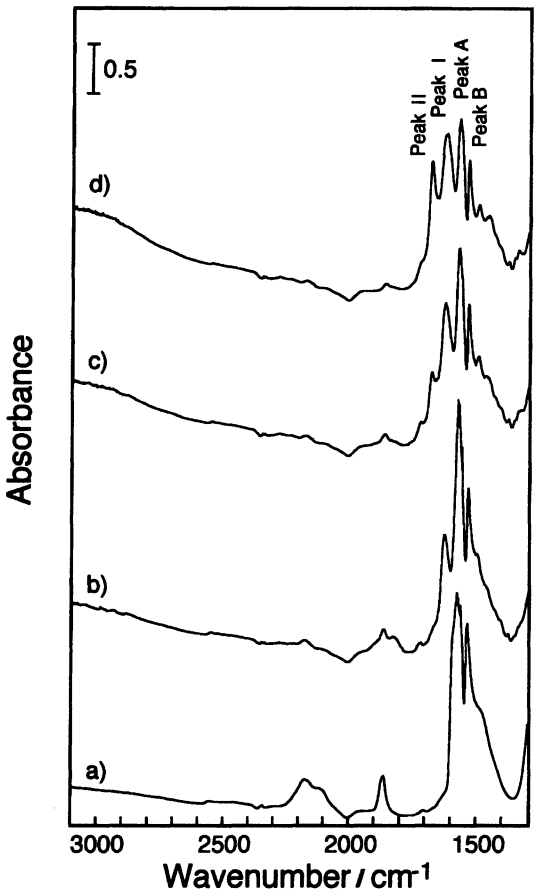

Fig. 2. IR spectral change during the reaction of $^{15}NO+O_2+C_2H_4$ on Cu-ZSM-5 at room temperature. a) $^{15}NO+O_2$, just before the addition of C_2H_4. b) 5 min, c) 55 min, d) 145 min after the addition of C_2H_4 into gas phase: $^{15}NO+O_2$. T=310 K. Initial partial pressure (at the addition of C_2H_4; see text): $^{15}NO=4.2\times10^2$ Pa, $O_2=1.0\times10^3$ Pa, $C_2H_4=2.2\times10^2$ Pa.

shifted by isotopic substitution with ^{15}N, while Peak II was not shifted. Further, Peak I appeared immediately after the addition of ethene, while Peak II grew gradually. It was also confirmed that the intensity of Peak II was never reduced by evacuation while Peak I was a little decreased.

The gas phase composition during the reaction shown in Fig. 2 was measured. After the addition of ethene, N_2 and N_2O increased with time, and finally the amount of gaseous N_2 and N_2O reached 19 and 18%, respectively, in conversions of the raw material NO. Although traces of CO and CO_2 were observed at the same time, the concentrations of CO and CO_2 did not seem to increase over the time of the reaction.

The conditions for the appearance of Peak I were investigated. First, it was confirmed that Peak I is observed in the presence of gaseous NO, O_2, and ethene at room temperature and that the appearance of the peak is independent of the order of the addition of the gases. Second, to find whether the existence of all the gaseous molecules is essential, the measurement after NO or NO_2 preadsorption was done. The result is summed up in Table 2. Peak I appeared when C_2H_4 and NO were introduced to the catalyst on which NO_2 species were once formed by NO and O_2 exposure followed by evacuation of the gas phase. That is, the existence of gaseous oxygen is not essential if surface NO_2 species exist. On the other hand, when surface NO_2 species exist, the existence of gaseous ethene and NO_x (NO or NO_2) is essential, as shown in Table 2.

Reaction of $^{15}NO+O_2+C_2H_4$ at Elevated Temperature. After the reaction of $^{15}NO+O_2+C_2H_4$ on Cu-ZSM-5 was done at room temperature for 2 h (2 h after the addition of ethene), the catalyst was heated at a rate of 10 K min^{-1} in the presence of the gas phase. The changes in IR peak intensities during the heating are shown in Fig. 3. The intensities of 1578 cm^{-1} (Peak A) and 1628 cm^{-1} (Peak I) decreased, while 1677 cm^{-1} (Peak II) increased with temperature and reached a maximum around 523 K. The intensities of 1578 and 1628 cm^{-1} involve another contribution, as mentioned below, and so they do not completely dis-

Table 2. Condition of Appearance of Peak I

Adsorbate phase	Gas phase							
	C_2H_4 +NO + O_2	C_2H_4 +NO	C_2H_4 + O_2	C_2H_4	NO + O_2	NO	O_2	None
NO	+	−	−	−	−	−	−	−
NO_2	+	+	−	−	−	−	−	−

+: observed, −: not observed. T=310 K.

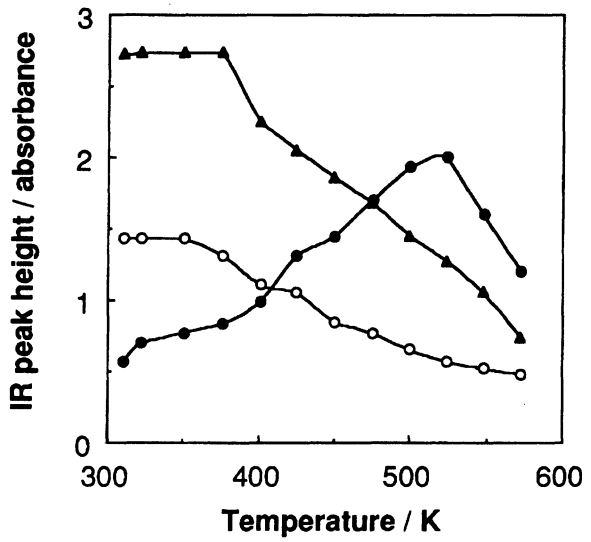

Fig. 3. Change in IR peak intensities of $^{15}NO+O_2+C_2H_4$/Cu-ZSM-5 with ascending temperature. Initial partial pressure: $^{15}NO=2.7\times10^2$ Pa, $O_2=6.7\times10^2$ Pa, $C_2H_4=4.0\times10^2$ Pa. Heating rate=10 K min^{-1}. ○: around 1628 cm^{-1} (Peak I), ●: around 1677 cm^{-1} (Peak II), ▲: around 1578 cm^{-1} (Peak A).

appear at high temperatures. During the heating, increases in the amounts of N_2, CO, and CO_2 were observed in the gas phase. Therefore, SCR by ethene reaction undoubtedly occurred during the heating.

To discuss the relationship between gas phase composition and the adsorbate phase, the reaction of $O_2+C_2H_4+^{15}NO$ was also done at a constant temperature: 473 K, at which the decrease in gas phase pressure due to adsorption can be minimized. In this experiment, the addition of ethene to O_2 was followed by the addition of ^{15}NO to $O_2+C_2H_4$, and neither additional peak in IR spectra nor change in gas composition were observed before the addition of ^{15}NO in the experiment. However, extra peaks other than Peak II (1677 cm^{-1}) were observed after the addition of ^{15}NO as shown in Fig. 4. First, peaks at 1631 and 1574 cm^{-1} (hereinafter referred to as Peak III) and 1375 cm^{-1} (hereinafter referred to as Peak IV) rapidly increased (Fig. 4 a and b), but Peak II took their place afterwards (Fig. 4c). Around 2128 cm^{-1}, a very small peak (hereinafter referred to as Peak V) was observed at the initial stage after the addition of ^{15}NO (Fig. 4 a and b), but Peak V was hidden in the shoulder of the growing peak at 2158 cm^{-1} (hereinafter referred to as Peak C) afterwards (Fig. 4c), and so its intensity cannot be quantitatively discussed.

The change in the gas phase composition and in the intensities of Peak II, Peak III, and Peak C, during the reaction in Fig. 4 is shown in Fig. 5 with the evolution rate of the products. It should be noted in Fig. 5 that the sum of ^{15}N at the end of the experiment apparently exceeded the initial partial pressure of ^{15}NO. This inconsistency is considered to be caused by the neglect of H_2O. H_2O might evolve with CO or CO_2 and must exist at the end of the experiment. However, the H_2O concentration was assumed to be zero when the partial pressures of gases were calculated by multiplying the concentration of each gas by total pressure, therefore, the partial pressures of the shown gases are overestimated when H_2O exists. Even so, it is considered that Fig. 5 still describes an actual qualitative relationship among the reactants and products, assuming the evolution of H_2O is not very different from that of N_2, CO, and CO_2.

Figure 5 clearly shows that $^{15}N_2$, CO, and CO_2 started to evolve as soon as ^{15}NO was added, while not so much $^{15}N_2O$ was formed. The evolution rates of N_2

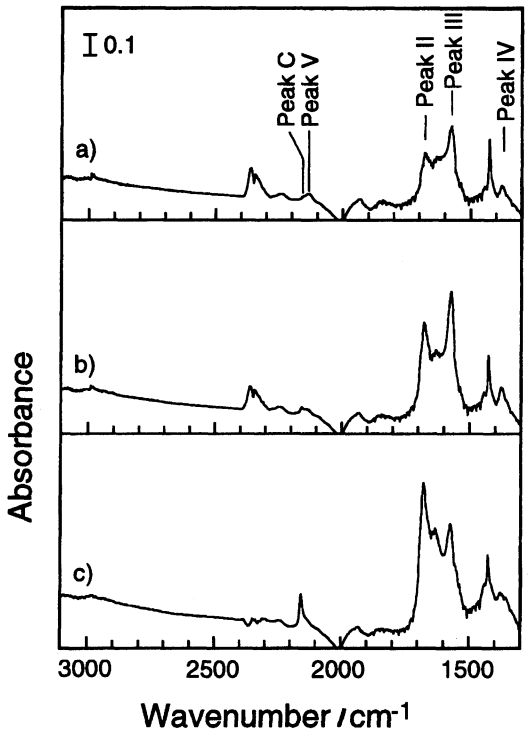

Fig. 4. IR spectral changes during $O_2+C_2H_4+^{15}NO$ reaction on Cu-ZSM-5 at elevated temperature. T= 473 K. a) 5 min, b) 15 min, c) 100 min after the addition of ^{15}NO to $C_2H_4+O_2$. Initial partial pressure (at the addition of C_2H_4; see text): $O_2=9.8\times10^2$ Pa, $C_2H_4=2.8\times10^2$ Pa, $^{15}NO=4.4\times10^2$ Pa.

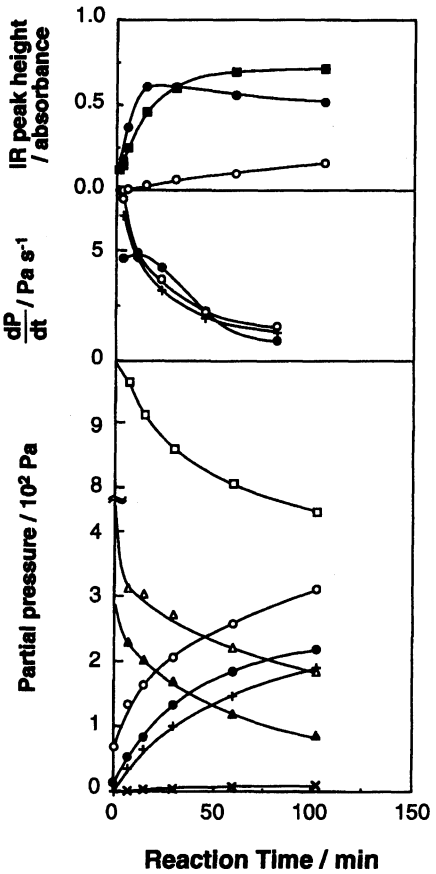

Fig. 5. Changes in IR intensity, evolution rate of products and gas phase composition during $O_2+C_2H_4+^{15}NO$ reaction on Cu-ZSM-5 at 473 K. Reaction condition is the same as Fig. 4. ^{15}NO was added at the reaction time=0. Upper part, ●: 1574 cm^{-1} (Peak III), ■: 1677 cm^{-1} (Peak II), ○: 2158 cm^{-1} (Peak C). Middle part, +: N_2, ○: CO, ●: CO_2. Bottom part, +: N_2, ○: CO, ●: CO_2, ×: N_2O, □: O_2, △: NO, ▲: C_2H_4.

and CO are quite similar to each other and decreases monotonously with time from the start of the reaction. The evolution rate of CO_2 shows a different feature. That is, the rate increased once before 15 min and then decreased. On the other hand, the IR intensity of Peak III increases with time and shows a maximum at 15 min, and subsequently Peak II rises. Peak C increases with the decline of the intensity of Peak III. When the initial O_2 concentration was changed, the reaction rate and the maximum peak intensity of each peak shown in Fig. 5 were changed with the initial O_2 concentration. However, the same pattern of gas evolution and change in IR intensity was observed as shown in Fig. 5.

Isotopic Shift of IR Peaks. To clarify what contributes to the IR peaks, the isotopic shift of the IR absorption was measured using ^{15}N, ^{18}O, ^{13}C, and deuterium. No significant isotopic shift was observed for the major peaks (Peaks A, A′, B, C, I, II, III, IV, and V) using C_2D_4. The spectra at room temperature around 1600 cm^{-1} after 1 h reaction were shown in Fig. 6 for unlabeled $NO+O_2+C_2H_4$, $^{15}NO+O_2+C_2H_4$, $^{15}N^{18}O+^{18}O_2+C_2H_4$, and $NO+O_2+^{13}C_2H_4$. On the other hand, the spectra at 473 K around 1600 cm^{-1} after 30 min and around 2150 cm^{-1} after 5 min of reaction are shown in Figs. 7 and 8, respectively, for unlabeled gases, ^{15}NO, and both ^{15}NO and $^{13}C_2H_4$.

From Fig. 6, Peaks A and B were shifted by ^{15}N (from 1604 to 1578 cm^{-1} and from 1570 to 1535 cm^{-1}, respectively) and by the additional isotopic substitution with ^{18}O (from 1578 to 1540 cm^{-1} and from 1535 to 1515 cm^{-1}, respectively). Peak I was also shifted by ^{15}N (from 1670 to 1625 cm^{-1}) and by the additional substitution with ^{18}O (from 1625 to 1600 cm^{-1}). On the other hand, Peak II was shifted only by ^{18}O (from 1677 to 1638 cm^{-1}) and by ^{13}C (from 1677 to 1637 cm^{-1}). The isotopic shifts of Peak I and II by ^{13}C were determined from the difference in growing rate of these two peaks, as shown in Fig. 6d. However, the contribution of ^{13}C to the shift of Peak I is obscure (from 1670 to 1666 cm^{-1}) because Peak II may partially overlapped and the shift by ^{13}C may perturb the peak wavenumber of Peak I. Although the results were not described in the figure except for Fig. 6d, the spectra at room temperature after 5 min of reaction corresponding to Fig. 6 were also obtained. From the results, Peak A′ was shifted by ^{15}N (from 1630 to 1596 cm^{-1}) and by the additional substitution with ^{18}O (from 1596 to 1564 cm^{-1}).

In Fig. 7, there is no peak shifted by ^{15}N; Peaks C, II, III, and IV were shifted by ^{13}C. On the other hand, as shown in Fig. 8, Peak V showed an isotopic shift both by ^{15}N and ^{13}C. The peak wavenumber cannot easily be read from raw spectra b) and c), because of the overlap with Peak C. However, the difference spectrum between b) and c) clearly shows the existence of a species which shows any isotopic shift, by subtracting Peak C which does not show isotopic shift by ^{15}N.

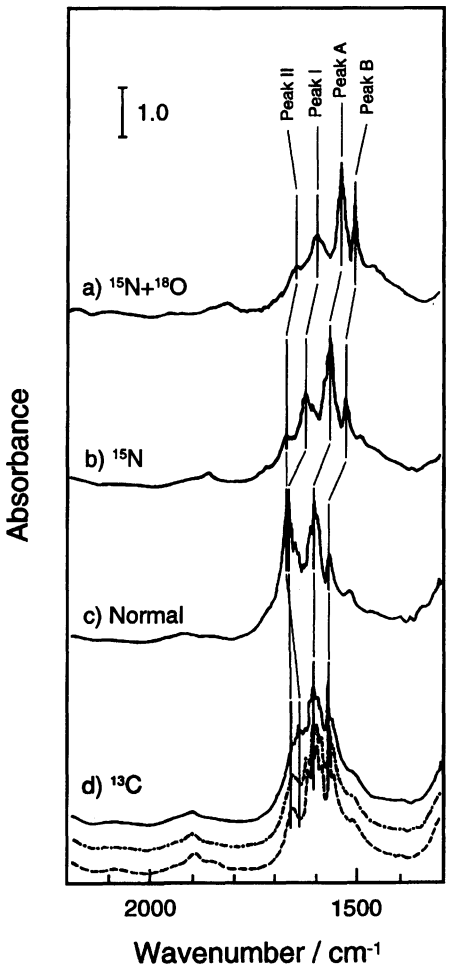

Fig. 6. Isotopic shift of IR spectra of $NO+O_2+C_2H_4$/Cu-ZSM-5 at room temperature. $T=310$ K. a) $^{15}N^{18}O+^{18}O_2+C_2H_4$, b) $^{15}NO+O_2+C_2H_4$, c) $NO+O_2+C_2H_4$, d) $NO+O_2+^{13}C_2H_4$. Initial partial pressures are the same as Fig. 2. Each spectrum was obtained 1 h after the addition of C_2H_4 except for d): --- 5min, –·– 1 h, and — 2 h after the addition of C_2H_4.

In Fig. 8a, Peak V is identified as the peak at 2089 cm^{-1} because no band was observed around 2120 cm^{-1} except for Peak C at 2107 cm^{-1}. Peak V behaved identically in each spectrum, therefore, this identification is considered reasonable.

Discussion

Assignment of IR Peaks. The isotopic shifts of the IR peaks are summarized in Table 3 with tentative assignments. Peaks A′, A, and B are the peaks observed in the presence of NO and O_2, and shifted by both ^{15}N and ^{18}O, therefore, they are assigned to surface inorganic NO_x species derived from NO and O_2. Further, the amplitudes of the shifts of Peak A′ and B by ^{15}N exceeded those by ^{18}O. It means that the nitrogen atom mainly vibrates in the mode of these peaks. The wavenumbers of Peak A′ agree well with the

Table 3. Isotopic Shifts and Tentative Assignment of IR Peaks

Peak	Peak wavenumber/cm^{-1}					Tentative assignment
	Gas phase composition	NO + O_2 + C_2H_4	^{15}NO + O_2 + C_2H_4	$^{15}N^{18}O$ + $^{18}O_2$ + C_2H_4	NO + O_2 + $^{13}C_2H_4$	^{15}NO + O_2 + $^{13}C_2H_4$	
A′		1630	1596	1564	1630	—[a]	weakly bound NO_2 (asym.)
A		1604	1578	1540	1604	—[a]	NO_3^- ? (inorg.)
B		1570	1535	1515	1570	—[a]	NO_2 ? (inorg.)
C		2158	2156	—[a]	—[a]	2107	–C=O (inorg.)
I		1670	1625	1600	1666	—[a]	–ONO, ONO_2 ? (org.?)
II		1677	1677	1638	1637	1633	>C=O
III		1574	1574	—[a]	—[a]	1530	$-CO_2^-$ (asym.)
IV		1375	1375	—[a]	—[a]	1356	$-CO_2^-$ (sym.)
V		2168	2128	—[a]	—[a]	2089	–CN

All peak data were derived from Figs. 6, 7, and 8. a) Experiment was not performed.

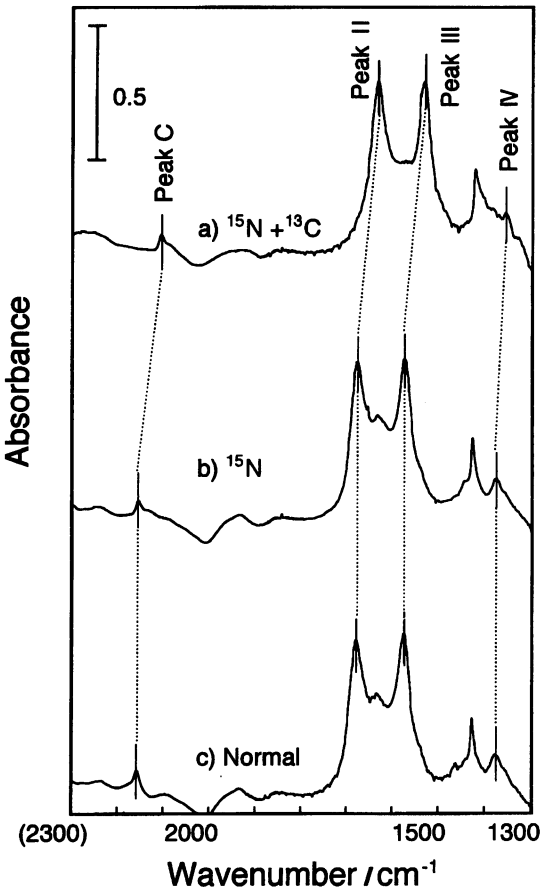

Fig. 7. Isotopic shift of IR spectra of $O_2+C_2H_4+NO$/Cu-ZSM-5 at 473 K. Initial partial pressures are the same as Fig. 4. Each spectrum was obtained 30 min after the addition of NO. a) $O_2+^{13}C_2H_4+^{15}NO$, b) $O_2+C_2H_4+^{15}NO$, c) $O_2+C_2H_4+NO$.

predicted values by the molecular orbital calculation of the asymmetric mode of a free NO_2: 1636 cm^{-1} for NO, 1599 cm^{-1} for ^{15}NO, and 1567 cm^{-1} for $^{15}N^{18}O$.

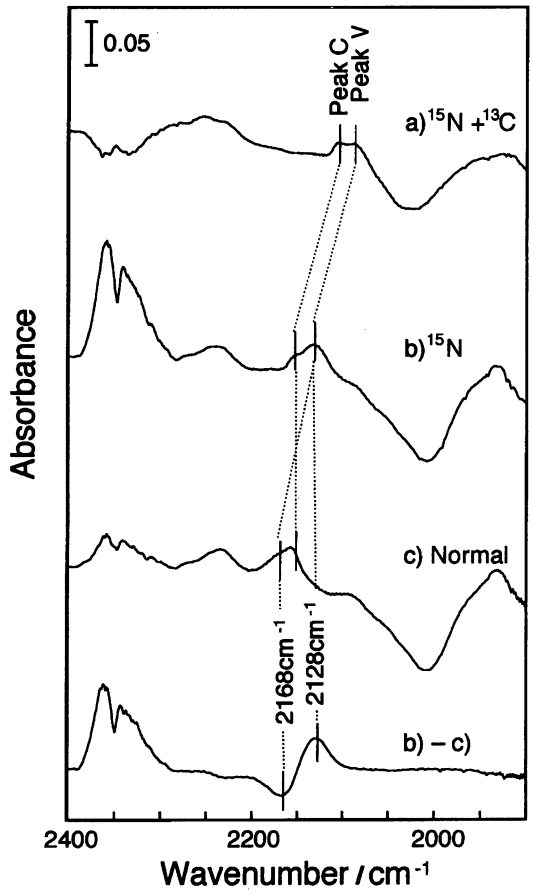

Fig. 8. Isotopic shift of IR spectra of $O_2+C_2H_4+NO$/Cu-ZSM-5 around 2150 cm^{-1}. T=473 K. Initial partial pressures are the same as Fig. 4. Each spectrum was obtained 5 min after the addition of NO. a) $O_2+^{13}C_2H_4+^{15}NO$, b) $O_2+C_2H_4+^{15}NO$, c) $O_2+C_2H_4+NO$. The bottom is a difference spectrum between b) and c) without any fitting.

Combined with the results that Peak A′ was the first observed species after the addition of O_2 to NO and that the wavenumber of Peak A′ is quite similar to that in the CO_2 matrix (1624 cm^{-1}),[28] it is considered that Peak A′ can be assigned to the asymmetric vibration of a weakly bound NO_2 molecule. Peaks A and B are more strongly adsorbed species than Peak A′. The isotopic shift pattern of Peak B is a little different from Peak A′. It is thought that Peak B is NO_2 or a more oxidized form of NO_x species with an alternative coordination in which the interaction between the species and surface is stronger than Peak A′. The isotopic shift pattern of Peak A is a little different from Peaks A′ and B. It may be thought that Peak A is NO_3^- rather than associative N_2O_x ($x \geq 3$) species[29,30] since Peak A was very stable even under evacuation at temperatures up to 473 K. However, more experimental data are required to identify the structure of these species.

Peak C was observed in the presence of gaseous carbon monoxide, and was not shifted by ^{15}N but by ^{13}C. Peak C is assigned to CO on Cu^+, because the wavenumber is similar to CO on CuO (2140 cm^{-1}),[29] and because the wavenumber of Peak C for ^{13}C agrees well with the calculated value of ^{13}CO by reduced mass: 2108 cm^{-1}.

Peak I showed an isotopic shift by ^{15}N and ^{18}O. The shift by ^{13}C was little, and so, Peak I is not due to the $\rangle C{=}N-$ species described in Refs. 20 and 31. The isotopic shift pattern and the wavenumber are roughly similar to those of Peaks A, A′, and B, therefore, the basic structure which contributes to Peak I is considered to be NO_x ($x>1$) group. The isotopic shift of Peak I by ^{15}N is extraordinarily large because the vibration of the nitrogen atom contributes much more than to Peak A′. Such a large contribution of N and the high wavenumber suggest that the surface species of Peak I may contain an $O{=}N{=}O^+$ like structure, because a higher order bond increases the frequency of the vibration and because the wide bond angle of O–N–O increases the contribution of the N atom in an assymmetric stretching mode. Such a structure is found in N_2O_5 in the form of $NO_3^-NO_2^+$. However, Peak I was not observed in the absence of ethene, therefore, it is difficult to assume that a more oxidative species such as N_2O_5 was formed by introducing reductant hydrocarbon. Another possibility for the species of Peak I is an organic NO_x group. If Peak I is an organic NO_x species, some changes may be observed in the CH stretching region (around 3000 cm^{-1}) with the appearance of Peak I. Unfortunately, few very weak peaks due to adsorbed species were observed in the region even in the absence of NO_x, and the background changed with the evolution of water during the reaction, therefore, it was not possible to discuss the changes in this region. However, it is well-known that N_2O_4 adds to alkene very rapidly even at room temperature,[32] and so it is reasonable that the addition of NO_x to ethene occured on Cu-ZSM-5 forming organic NO_x species. Organic nitrite or nitrate molecules have strong absorption around 1650—1620 cm^{-1} in IR spectra.[33] Tanaka et al. reported that butyl nitrite on Pt/SiO_2 gave a strong absorption peak at 1658 cm^{-1} due to ONO stretching.[19] Therefore, Peak I in this study may be assigned to an organic nitrite or nitrate, although the shift by ^{13}C is not obvious.

On the other hand, Peak II is easily assigned to a carbonyl species because the isotopic shift agrees well with the calculated value by reduced mass assuming C=O stretching: 1640 cm^{-1} for ^{13}CO and 1637 cm^{-1} for $C^{18}O$. Peaks III and IV are assigned to the asymmetric and symmetric modes of carboxylate, respectively, since the behaviors of Peak III and Peak IV were the same and since the wavenumbers and the intensity ratio between Peak III and IV were consistent with those of carboxylate species.[33,34] Further, the isotopic shift pattern agrees well with the value predicted by the molecular orbital calculation of CH_3COO^-, even though the wavenumbers are slightly different; the wavenumbers are shifted by ^{13}C from 1303 to 1286 cm^{-1} for the symmetric mode and from 1608 to 1564 cm^{-1} for the asymmetric mode.

Peak V was the only absorption shifted by ^{15}N during the reaction at 473 K. The isotopic shifts by ^{15}N and ^{13}C roughly agree with the calculated values by reduced mass assuming CN stretching: 2134 cm^{-1} for $C^{15}N$ and 2088 cm^{-1} for $^{13}C^{15}N$. On the other hand, the asymmetric mode of isocyanate may be observed around this region. However, the central carbon atom mainly vibrates in the mode, and so the wavenumber would not be shifted so much by ^{15}N as in the case for Peak V. In fact, molecular orbital calculations of the mode for HNCO and NCO^- show little isotopic shifts by ^{15}N: from 2273 to 2265 cm^{-1} and from 2126 to 2109 cm^{-1}, respectively. Besides, isocyanate species must be observed at a higher wavenumber: 2234 cm^{-1} on $Cu–Cs/Al_2O_3$[20] and 2189 and 2251 cm^{-1} on Cu-ZSM-5.[23] Thus, Peak V can be assigned to nitrile species.

Relationship of Adsorbed Species with Selective Reduction of NO_x by Ethene on Cu-ZSM-5. From the fact that the formation of N_2 and N_2O in gas phase was observed when Peak I was observed at room temperature, it is likely that Peak I appears with the reaction of HC-SCR, even though it is not readily concluded whether Peak I is an intermediate species of HC-SCR or not. When surface NO_2 (or a more oxidized form of inorganic NO_x compounds) existed, Peak I was observed in the presence of ethene and NO, and in the absence of oxygen. This result suggests that oxygen is not required for HC-SCR if sufficient NO_2 or more oxidized inorganic NO_x exists on the surface. Further, no change was observed in IR spectra and gas composition in the presence of ethene and oxygen even at 473 K, at which the HC-SCR reaction proceeds. These results suggest that oxygen does not contribute to generate partially oxidized hydrocarbon but rather to oxidize NO to

NO_2 under these experimental conditions (below 473 K). Therefore, as Petunchi et al. mentioned,[35] at least at a lower temperature or high SV, NO_2 formation is considered to be the first step of HC-SCR even on Cu-ZSM-5.

The intermediacy of the species of Peak I cannot be concluded from these results. However, in these experiments, a carbonyl species, which was not observed in the presence of oxygen and ethene, was formed with the coexistence with NO after the formation of Peak I species at room temperature. Therefore, the oxygen in the carbonyl species must originate in NO_x. That is, the carbonyl species is the product of the reaction between ethene and inorganic NO_x, and so, it is likely to assume an organic NO_x species as an intermediate of the reaction. Tanaka et al.[19] recently reported that IR peaks were observed during the reaction of $O_2+NO+C_3H_6$ on Pt/SiO_2 at 1655 and 1565 cm^{-1}, and assigned to organic nitrite and nitro species, respectively, and that those organic NO_x compounds might be an intermediate of HC-SCR. Therefore, organic nitrite or nitrate may be an intermediate of HC-SCR using ethene on Cu-ZSM-5, but more detailed kinetic studies are required to identify it.

On the other hand, the carbonyl species (Peak II) can be also a candidate for an intermediate of HC-SCR[36] because acetone is also reported as an effective reductant for HC-SCR.[37] However, this scheme is unlikely from the result shown in Fig. 5. If the carbonyl species were the intermediate, the rate of N_2 formation would positively depend on the concentration of the carbonyl species and reactant gases: NO, ethene, and O_2. However, the rate of N_2 formation rapidly dropped within 15 min though the reactant gases existed abundantly and the concentration of the carbonyl species increased. Peak II grew after the evolution of N_2, CO, and CO_2, and so the carbonyl species was not an intermediate but a product of the HC-SCR reaction in this case. The carboxylate species formed more rapidly than carbonyl species as shown in Fig. 5. Although it is unlikely that the carboxylate species is an intermediate of HC-SCR because carboxylate itself is considered to be too oxidized to contribute to NO_x reduction, the carboxylate species may be more closely related to HC-SCR reaction than the carbonyl species.

The nitrile species (Peak V) was also observed from the early stage of the reaction at 473 K, but the intensity was too weak to discuss its intermediacy. However, hydrogen cyanide formation was reported during the reaction of $C_2H_4+O_2+NO$ on Cu-ZSM-5 around 550—600 K,[38] and therefore, there is at least a path to form CN species during HC-SCR under these conditions, though HCN was not detected in gas phase because of the overlap with a branch of ethene. On the other hand, no isocyanate species was observed even after the evacuation of the gas phase after the reaction for some minutes at 473 K. It has been reported that isocyanate species adsorbed on zeolite was observed on Cu-ZSM-5 at 2251 cm^{-1} after the reaction of $C_3H_6+NO+O_2$ under a net reducing atmosphere above 473 K and the species was not so reactive.[23] Therefore, it is considered that the isocyanate species was not formed under these conditions, perhaps because ethene is less reactive to form carbonaceous deposits and because the reaction proceeded under a net oxidizing atmosphere at a relatively low temperature.

Concerning the products of HC-SCR, Yahiro et al. have suggested that N_2 and CO_2 evolve from a single intermediate on the catalyst during HC-SCR by propene on Cu-ZSM-5.[23] However, their suggestion is based on the changes in the partial pressures of N_2, CO, and CO_2 during the exposure of 1.3×10^4 Pa NO to C_3H_6-preexposed Cu-ZSM-5 at 573 K, while these results were obtained during HC-SCR by ethene at 473 K in the presence of all reactant gases. In fact, it was found that the evolution rate of CO_2 and the product CO_2/CO ratio increase at a higher temperature even under the same conditions as in this experiment. Therefore, under relatively mild conditions such as our experiments, it is considered that N_2 and CO evolve together as carboxylate forms as the products of HC-SCR by ethene at 473 K, although the intermediate and the reaction path are still unclear.

Conclusion

The following results have been obtained about HC-SCR reaction on Cu-ZSM-5 by IR investigation:

1) No oxygen-containg species was observed and no reaction proceeded in the presence of gaseous O_2 and C_2H_4 in IR below 473 K, at which HC-SCR occurs.

2) An extra NO_x species (tentatively assigned to organic nitrite or nitrate species), other than inorganic NO_x species derived from O_2 and NO, immediately appeared in IR at 1670 cm^{-1} at room temperature, in the presence of adsorbed NO_2 or more oxidized NO_x species, gaseous C_2H_4 and NO. Afterwards, a carbonyl species (1677 cm^{-1}) was formed gradually at room temperature.

3) When the extra NO_x species was observed, N_2 and N_2O evolved even at room temperature. That is, HC-SCR occurs even at room temperature. With the above-mentioned result, it is considered that O_2 is not essential for HC-SCR except for NO_2 formation.

4) In the $O_2+C_2H_4+NO$ reaction on Cu-ZSM-5 at 473 K, no nitrogen-containing species, except for quite a small amount of nitrile (2168 cm^{-1}), were observed in IR. At 473 K, N_2 and CO evolved very rapidly together with a steep increase in the IR intensity of carboxylate (1574 and 1375 cm^{-1}), while CO_2 and carbonyl species increased more slowly, although the reaction path is unclear.

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