The existence of dual Cu site involved in the selective catalytic reduction of NO with propene on Cu/ZSM-5

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In order to establish the role of surface species in the selective catalytic reduction (SCR), in situ IR studies were carried out using a DRIFT (diffuse reflectance infrared Fourier transform) cell in gas mixtures of various C_3H_6/NO ratios containing excess oxygen. The location and mobility of Cu ions were investigated by recording the relevant bands of CO adsorbed on Cu/ZSM-5. The nitro species coordinated on Cu^{2+} and the –NCO surface complex as possible intermediates were observed in the reduction of NO with propene on Cu/ZSM-5 between 350 and 400°C. The reactivities of these species toward NO, O_2 and propene were examined. The nitro species can react with propene very rapidly to form N_2 without the formation of NCO species. NCO also reacts with NO_2 and/or NO at 350°C. IR spectra of CO adsorbed on cuprous ions show that two kinds of Cu ions, which are responsible for the activation of NO and propene respectively, exist on Cu/ZSM-5. From these results, a dual site mechanism involving nitro species and –NCO species as intermediates is suggested.

Keywords: SCR; NO; propene; Cu/ZSM-5; nitro species; –NCO species; reaction intermediates; DRIFT spectroscopy; IR

1. Introduction

During the past three years, many mechanistic studies on the selective catalytic reduction (SCR) of NO on Cu/ZSM-5 have been published [1–4]. These earlier works concentrated on the reaction intermediates and the nature of the active site. Very diverse observations were reported in the literature. It has been suggested that the oxidation of nitric oxide to nitrogen dioxide may be the first step in the reaction for many metal-exchanged ZSM-5 zeolites [5,6]. Even at high temperature, where equilibrium favors NO in the gas phase of $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$, the formation of NO_2 was enhanced by these catalysts [7]. It has been suggested that NO_2 reacts preferentially with hydrocarbon as a reducing agent [8]. Recently, the role of a surface nitro complex was emphasized by Sachtler et al. [9,10]. This complex was reported to be chemically reduced to N_2 upon exposure to propane. Cu/ZSM-5 has been proven to be a very active catalyst in direct NO decomposition. The high activity has been reported to be due to the redox properties that the Cu ion is easily reduced by desorbing oxygen, even below 500°C [11,12]. It has been suggested that the rapid redox process can be accomplished by the help of a hydrocarbon like ethene, even under reaction conditions containing excess O_2 [3,13]. However, this mechanism is not feasible on H/ZSM-5, which has no active sites for NO decomposition. On the other hand, it has been proposed that NO reduction proceeds via a derivative of the hydrocarbon, such as a carbonaceous residue [1] or partially oxidized hydrocarbon [14]. Although the formation of these compounds might not be the first step in the SCR, there is also evidence that these compounds take part in the reaction [15,16]. Moreover, it was reported that the isocyanate (NCO) compound, which was observed during the reduction of NO with propene on Cu/ZSM-5, was produced from these derivatives of hydrocarbon. Iwamoto et al. [17] and Yoshida et al. [18] suggested that NCO species may be a key intermediate for the reduction of NO on Cu/ZSM-5. However, when propene was substituted for either ethene or propane, this species was not detected [9,19]. These diverse results led to the proposal that the reduction of NO by hydrocarbons cannot be explained by one mechanism and the reaction routes are dependent on the kinds of reductant and catalyst.

The oxidation activity of Cu^{2+} ion exchanged zeolite has been studied by many workers [20,21]. The catalytic activity of CuH-ZSM-5 in the total oxidation reaction has been suggested to be correlated with the concentrations of Cu cations at the discrete ion exchangeable sites [22,23]. The location and reactivity of Cu^{2+} cations in H-ZSM-5 have been studied previously by the electron spin resonance (ESR) technique [24]. CuH-ZSM-5 has been reported to have two discrete types of isolated coordinately unsaturated Cu^{2+} cations. Kevan et al. [25] have studied the location and mobility of Cu ions by the interaction of adsorbates on Cu-NaHZSM-5 using ESR and electron spin echo modulation (ESEM) spectroscopy. It was suggested that the adsorption of molecules such as water, alcohol, pyridine and ammonia, causes the migration of the Cu^{2+} to the main channel. Masai et al. [26]

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have studied the redox behavior and mobility of the Cu ions in Cu-NaZSM-5 during the benzyl alcohol oxidation by recording IR bands of CO adsorbed on cuprous ions. The Cu ions have been suggested to migrate from the recessed site to a more open space, such as a channel intersection, by the adsorption of benzyl alcohol. The oxidation activity of benzyl alcohol was dependent on the location of the Cu ions. Joyner et al. [27,28] have suggested from XPS and XANES studies of the structure of Cu/ZSM-5 that there may be present Cu active sites which are responsible for the activation of NO and hydrocarbon, respectively, in the SCR reaction.

Motivated by these previous results, we studied the location and mobility of the Cu ions in correlation with the mechanisms involving the specific reaction intermediate. The IR spectra of CO adsorbed on Cu/ZSM-5 were used to investigate the location and mobility of Cu ions in ZSM-5. The characteristic bands of nitro species and –NCO species were identified by in situ DRIFT spectroscopy acquired under various reaction conditions. The relative reactivities of nitro species and NCO species with NO, O_2 and/or C_3H_6 were measured. Based on these results, a dual site mechanism was proposed for the NO reduction by propene.

2. Experimental

2.1. Preparation of catalyst

Na/ZSM-5 zeolite was synthesized according to the literature [29]. The crystallized zeolite was washed with distilled water, dried at 120°C for 24 h and calcined at 550°C for 5 h. The crystallinity of Na/ZSM-5 was confirmed by powder X-ray diffraction. The Si/Al ratio = 31 was calculated by the following equation, in which $I_{Si(n\mathrm{Al})}$ is the integrated intensity of the ^{29}Si MAS NMR peak:

$$\mathrm{Si/Al} = \sum_{n=0}^{4} I_{Si(n\mathrm{Al})} \Big/ \sum_{n=0}^{4} \frac{n}{4} I_{Si(n\mathrm{Al})} .$$

The Cu/ZSM-5 catalyst was prepared by the conventional ion exchange method. Na/ZSM-5 was stirred for one day in an aqueous solution of copper(II) acetate, ion-exchanged three times, filtered and dried at 120°C. The Cu/ZSM-5 dissolved in 3 wt% HNO_3 solution was analyzed to measure the degree of ion exchange by ICP-AES (inductively coupled plasma–atomic emission spectroscopy). The percent ion exchange of Cu was 80.

2.2. DRIFTS study

The DRIFT spectra were acquired using an in situ DRIFT cell (Spectra Tech. Inc.) equipped with a gas flow system, which consisted of mass flow controllers and four port valves with electric actuator. A Bomem model MB-102 FT-IR spectrometer was used. In the in situ cell, Cu/ZSM-5 was pretreated in He for 2 h at 500°C. After the sample was cooled to the specified temperature, the gas mixture was introduced. The SCR reaction was carried out in the flow of gas mixture ($NO/C_3H_6/O_2$ = 3300 ppm/3300 ppm/7%) in He balance. The total flow rate was 30 ml/min. In order to observe the change of surface species with the increase in C_3H_6/NO ratio (0.14, 0.36, 0.54, 0.72 and 1), C_3H_6 was added at a desired flow rate to the flow of NO/O_2 (NO/O_2=5000 ppm/10% and 20 ml/min) to vary the C_3H_6 concentration from 0 to 3300 ppm. The C_3H_6 flow rate was sequentially increased. After the reaction had reached steady state, the spectra were acquired under in situ conditions. During IR measurement, the gas compositions at the outlet of the in situ cell were analyzed by a mass spectrometer.

The feed gas was changed to He after the SCR reaction and 20% O_2 or NO (5000 ppm)/O_2 (10%) in He was subsequently introduced at specific temperature to examine the reactivity of surface species produced during the SCR reaction condition.

In the IR measurement of CO adsorbed on Cu/ZSM-5, the sample was cooled down to room temperature in He after the treatment at the specified temperature. CO was adsorbed for 5 min in 1% CO in He flow controlled by a mass flow controller. After the cell had been purged in He for 30 min, IR spectra were acquired in the flow of He.

3. Results

The NO and NO_y complexes adsorbed on Cu/ZSM-5 have been extensively studied by IR spectroscopy. The IR absorption bands of the surface species formed from NO on Cu/ZSM-5 were summarized by Valyon and Hall [30]. The bands between 1619 and 1630 cm^{-1} were assigned to the asymmetric NO_2 stretching. Recently, Adelman et al. [10] suggested that the band at 1628 cm^{-1} is due to a nitro group associated with a Cu^{2+} cation. The IR study of the NCO surface complex adsorbed on Cu/ZSM-5 has been carried out by Solymosi and Bansagi [31]. The adsorption of HNCO on Cu/ZSM-5 gave IR absorption bands between 2260 and 2180 cm^{-1} arising from NCO associated on either Cu ion or ZSM-5 zeolite.

Fig. 1 shows the gradual change of the band at 1624 cm^{-1} assigned to nitro species coordinated on Cu ion and the bands between 2100 and 2400 cm^{-1} arising from NCO species, CO and gaseous CO_2 at various C_3H_6/NO ratios. The C_3H_6/NO ratio was changed by increasing the flow rate of 1% C_3H_6 in He added to the flow (20 cm^3/min) of NO/O_2 = 5000 ppm/10%. The intensity of the band at 1624 cm^{-1} decreases with the increase in C_3H_6/NO ratio and the band disappears above C_3H_6/NO = 0.54. By contrast, the band at 2250 cm^{-1} is not

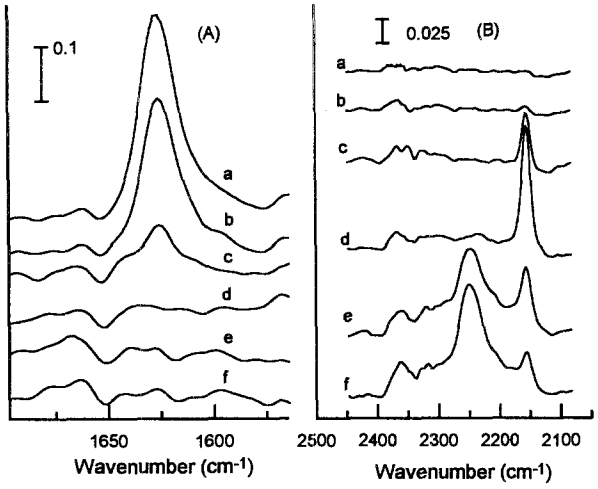

Fig. 1. Infrared spectra of Cu/ZSM-5 in the flow of reaction mixtures having different C_3H_6/NO ratios: (a) C_3H_6/NO = 0, (b) 0.14, (c) 0.36, (d) 0.54, (e) 0.72, and (f) 1 at 400°C. C_3H_6 was added to the mixture gas of 5000 ppm NO and 10% O_2 and the amount of addition was sequentially increased.

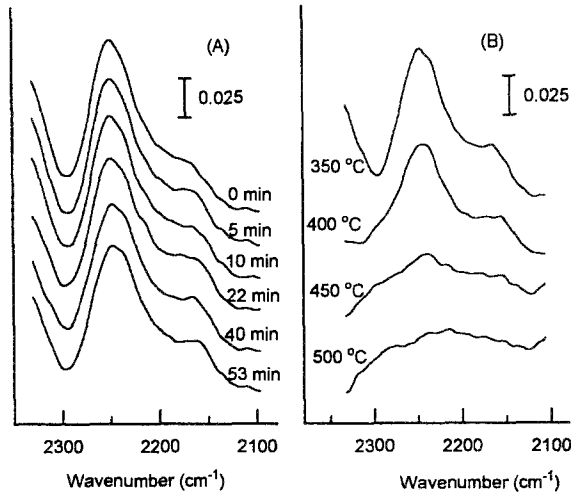

Fig. 3. (A) Infrared spectra of Cu/ZSM-5 as a function of time after O_2 is introduced at 350°C, (B) infrared spectra of Cu/ZSM-5 at 40 min after O_2 (20%/He) is introduced at various temperatures to Cu/ZSM-5 pre-treated with NO/C_3H_6/O_2 = 3300 ppm/3300 ppm/7% at 350°C. (All spectra were acquired by subtraction of the background spectrum of Cu/ZSM-5 from the original spectrum.)

observed until the C_3H_6/NO ratio increases to 0.54 but appears above C_3H_6/NO = 0.72. The gas composition at the outlet of the IR cell was analyzed by mass spectrometry during IR experiments corresponding to fig. 1. Mass signals of $m/e = 44$, 28 and 30 were detected. As shown in fig. 2, mass signals of $m/e = 44$ and $m/e = 28$ increase with increasing C_3H_6/NO ratio, while that of $m/e = 30$ decreases.

After Cu/ZSM-5 was treated in NO/C_3H_6/O_2 = 3300 ppm/3300 ppm/7% at 350°C, the catalyst was exposed to either 20% O_2/He or NO/O_2 = 5000 ppm/10% at various temperatures. After the treatment of Cu/ZSM-5 with the full gas mixture of NO/C_3H_6/O_2, a band at 2250 cm^{-1} having a shoulder at 2220–2160 cm^{-1} is developed, as shown in fig. 3A. The intensity of the band does not decrease even after prolonged exposure to O_2 at 350°C. This band is significantly weakened as the O_2 exposure temperature increases above 450°C as shown in fig. 3B. However, when Cu/ZSM-5 pre-reacted under SCR conditions is exposed to NO/O_2 at 350°C, the intensity of the band of the NCO species decreases markedly and is depleted after 90 min, as shown in fig. 4. At the same time, the band is observed at 1624 cm^{-1} and its intensity increases with exposure time (not shown). It was found that the depletion of NCO species was accompanied by the formation of nitro species on Cu/ZSM-5. The rate of increase in integrated inten-

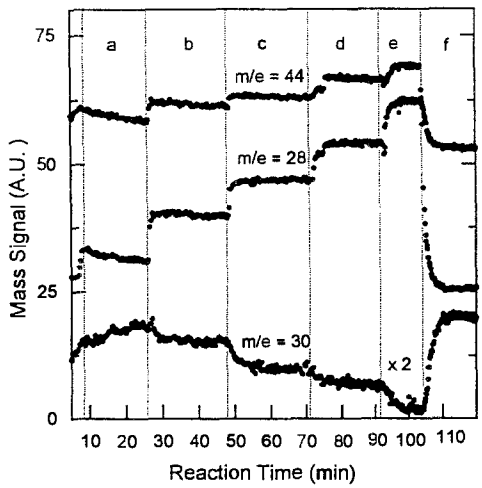

Fig. 2. Mass signals of $m/e = 44$, $m/e = 28$ and $m/e = 30$ detected at the outlet of the in situ IR cell in the SCR reaction at various C_3H_6/NO ratios at 400°C: (a) 0.14, (b) 0.36, (c) 0.54, (d) 0.72, (e) 1, and (f) 0.

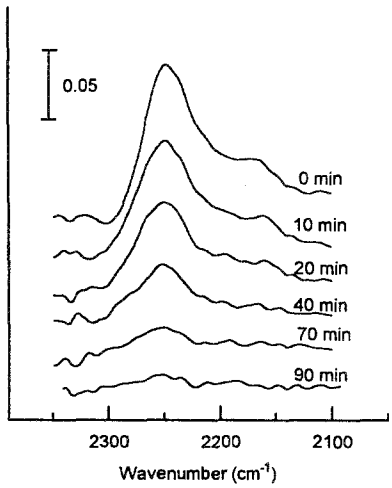

Fig. 4. Infrared spectra of Cu/ZSM-5 as a function of time after NO/O_2 = 5000 ppm/10% is introduced at 350°C to Cu/ZSM-5 pre-treated with NO/C_3H_6/O_2 = 3300 ppm/3300 ppm/7% at 350°C. (All spectra were acquired by subtraction of the background spectrum of Cu/ZSM-5 from the original spectrum.)

sity of the band at 1624 cm^{-1} with time is compared with that of the decrease in integrated intensity of the band at 2250 cm^{-1} (fig. 5). The rates of change in the intensities of both bands at 400°C are faster than those at 350°C. At 400°C, the intensity of the band at 1624 cm^{-1} is quickly increased and saturated within 40 min, while the band at 2250 cm^{-1} decreases slowly. However, the increase rate of the intensity of the band at 1624 cm^{-1} is similar to the decrease rate of the intensity of the band at 2250 cm^{-1} at 350°C.

Fig. 6 illustrates the effect of preadsorbed propene on the IR absorption band of CO adsorbed on Cu/ZSM-5. The IR spectrum of CO adsorbed at room temperature on Cu/ZSM-5 pretreated by heating in He at 500°C for 1 h shows a band at 2157 cm^{-1} with a shoulder near 2140 cm^{-1}. After the adsorption of propene on pretreated Cu/ZSM-5 in He at 500°C for 1 h followed by CO adsorption at room temperature, two resolved CO IR absorption bands are observed at 2153 and 2134 cm^{-1}. However, their intensities are very weak. The IR spectra of CO adsorbed on Cu/ZSM-5 on which the propene was preadsorbed at room temperature and subsequently heated in He at 350 and 500°C are shown in figs. 6c and 6d, respectively. The two bands shown in fig. 6b shift to 2157 and 2140 cm^{-1}, respectively. The intensities of both bands increase with increasing heating temperature. The band at 2140 cm^{-1} becomes sufficiently apparent to be distinguished from the shoulder in fig. 6a. After the treatment of fig. 6d, the catalyst was oxidized in O_2 at 500°C for 30 min and subsequently maintained in He at 500°C for 1 h. The IR absorption band of CO adsorbed on this catalyst (fig. 6e) is almost similar to that on Cu/ZSM-5 pretreated in He at 500°C for 1 h (fig. 6a). A band at 2140 cm^{-1} markedly decreases and is not well-resolved from the band at 2157 cm^{-1}.

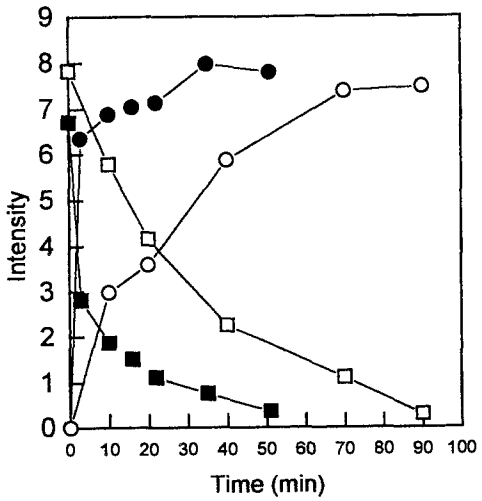

Fig. 5. The integrated intensities of bands at 2250 and 2220–2160 cm^{-1} (■, □) and at 1624 cm^{-1} (●, ○) as a function of time after NO/O_2 = 5000 ppm/10% is introduced at 350° (open) and at 400°C (solid) to Cu/ZSM-5 pre-treated with NO/C_3H_6/O_2 = 3300 ppm/3300 ppm/7% at 350°C.

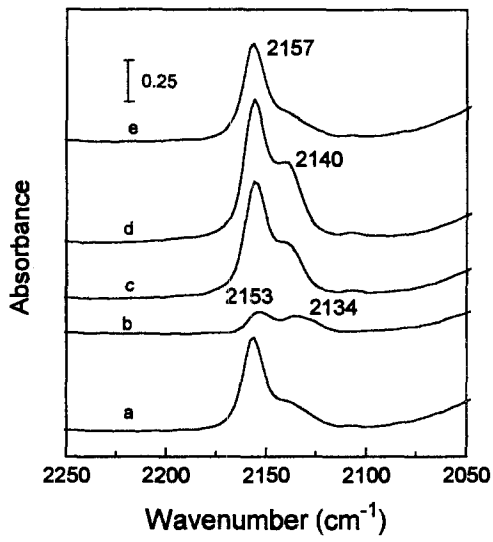

Fig. 6. IR spectra of CO adsorbed at room temperature for 5 min on Cu/ZSM-5 (a) heated in He at 500°C for 1 h, (b) exposed to propene at room temperature for 30 min followed by purging with He at room temperature for 30 min, (c) heated at 350°C in He for 1 h after adsorption of propene at room temperature, (d) heated in He at 500°C in He for 1 h after adsorption of propene at room temperature, and (e) subsequent to (d), oxidized in O_2 at 500° for 30 min followed by heating in He at 500°C for 1 h. (All samples were pretreated by the calcination in O_2 at 500°C for 30 min followed by the heating in He at 500°C for 1 h.)

The effect of the propene content in the SCR reaction on the IR absorption band of CO adsorbed on Cu/ZSM-5 was investigated and compared with the case of NO reduction using ethene as a reductant. The SCR reaction was carried out at 370°C for 30 min. After the reaction was quenched by sweeping the catalyst with He, the temperature was decreased to room temperature, the gas flow of He was changed to 1% CO/He and the sample was maintained for 5 min until it was flushed by pure He. Fig. 7a illustrates the IR spectrum of Cu/ZSM-5 which was treated in the flow of NO/O_2 and subsequently exposed to CO. Any CO IR absorption bands are not observed. During the reaction in the flow of NO/O_2, the nitro species associated on Cu ion was already shown to be present in Cu/ZSM-5 in fig. 1a. At C_3H_6/NO ratio of 0.2, a band of CO adsorbed on Cu/ZSM-5 appears at 2157 cm^{-1} with a very weak shoulder band at 2138 cm^{-1} (fig. 7b). No bands are observed in the region of 2300–2200 cm^{-1}. Increasing the C_3H_6/NO ratio to 0.6 induces the appearance of strong bands at 2157 and 2138 cm^{-1} (fig. 7c). The band at 2138 cm^{-1} becomes more dominant than that at 2157 cm^{-1} with C_3H_6/NO ratio increasing up to 1.2. The appearance of the strong band at 2138 cm^{-1} is shown to be accompanied by the evolution of the bands in the region of 2300–2200 cm^{-1} (fig. 7d). The bands at 2241 and 2267 cm^{-1} appear at C_3H_6/NO = 0.6 and a band at 2261 cm^{-1} is developed with the increase of C_3H_6/NO to 1.2. It was observed during this experiment that these bands shifted from 2235 and 2260 (C_3H_6/NO = 0.6) and 2251 cm^{-1} (C_3H_6/NO = 1.2)

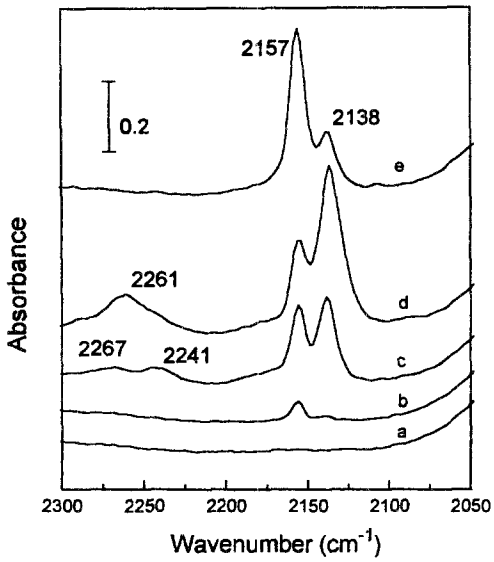

Fig. 7. IR spectra of CO adsorbed on Cu/ZSM-5 pretreated at 370°C: (a) in the flow of NO/O_2 = 5000 ppm/10%, (b) in the reaction mixture of $C_3H_6/NO = 0.2$, (c) in the reaction mixture of $C_3H_6/NO = 0.6$, (d) in the reaction mixture of $C_3H_6/NO = 1.2$, and (e) in the reaction mixture of $C_2H_4/NO = 1.2$, followed by the adsorption of CO at room temperature for 5 min. (The C_xH_y/NO ratio was controlled by increasing the flow rate of 1% C_xH_y/He to the flow of NO/O_2 = 5000 ppm/10% at 20 cm^3/min.)

after CO adsorption. These bands may be assigned to NCO species adsorbed on Cu/ZSM-5. When the ethene as a reductant was mixed at the C_2H_4/NO ratio = 1.2 instead of propene, the band at 2157 cm^{-1} is mainly developed and the formation of the band at 2138 cm^{-1} was much less than that at 2157 cm^{-1}. The bands in the 2300–2200 cm^{-1} region attributable to NCO species are not observed (fig. 7e).

The catalysts used in this work have the maximum yield of N_2 between 350 and 400°C.

4. Discussion

The possible reaction between adsorbed NO_y groups (nitro/nitrate species) and the hydrocarbon has been suggested to produce N_2 in the reduction of NO with propane [9,10] and NCO species have been found to be formed on Cu/ZSM-5 during the reduction of NO with propene as a reductant [17]. These species are considered as potential reaction intermediates in the SCR reaction. Recently, many experimental results indicate that the oxidation of nitric oxide to nitrogen dioxide may be the first step in the SCR. The light-off temperature for hydrocarbon combustion during the SCR catalyzed on Cu/ZSM-5 is lower than that for the homogeneous combustion in NO_2, indicating that this reaction occurs on the catalyst [32]. In Sachtler et al.'s work, it was shown that the intensities of the bands at 1628 and 1594 cm^{-1} assigned to nitro and nitrate complexes were decreased with the exposure time of propane to Cu/ZSM-5 which was saturated with NO/O_2/He. Mass spectrometric analysis of the released gases showed that N_2, CO_2 and H_2O were produced when nitro and/or nitrate complex presaturated Cu/ZSM-5 was exposed to the propane.

Our results indicate that stable nitro species identified by the band at 1624 cm^{-1} can be present on Cu ions in the flow of NO/O_2, even above 350°C (fig. 1a). The oxidation state of Cu which is coordinated to nitro species is 2+ [30]. With the increase in C_3H_6/NO ratio of the gas mixture for the SCR reaction, the band of nitro species decreased in intensity. This indicates that the surface nitro species reacts with propene. Since any bands corresponding to organic species on the catalyst were not observed at low C_3H_6/NO ratio ($\leqslant 0.54$), it is believed that the decrease in intensity of the band attributed to nitro species is not due to the occupation of Cu sites by propene but the reduction of surface NO_2 by the chemical reaction with propene. In addition, the intensities of mass signals of $m/e = 28$ and 44 increased with the increase of C_3H_6/NO ratio, as shown by the mass spectrometric analysis of the gases at the outlet of the IR cell. Based on Sachtler et al., the mass signals of $m/e = 28$ and 44 are considered to be contributed by N_2 and CO_2 yielded from the reduction of nitro species by the propene. Furthermore, the fact that NCO species is not formed under this condition ($C_3H_6/NO \leqslant 0.54$) strongly suggests that N_2 can be produced without the formation of –NCO. A strong band assigned to –NCO as organic species containing nitrogen was observed at $C_3H_6/NO = 0.72$. The yield of N_2 continuously increased with increase of C_3H_6/NO ratio above 0.72; the intensity of the –NCO band also increased. It is noticeable that NCO species begins to be formed after nitro species on Cu^{2+} is completely exhausted ($C_3H_6/NO = 0.72$). This indicates that the formation of NCO species does not result from the reaction of nitro species with propene but results from the adsorption of propene on Cu followed by the reaction of adsorbed propene with NO and/or NO_2. This is also supported by earlier IR studies. It was shown that the NCO species is produced by the interaction of adsorbed propene with NO and/or NO_2. An IR band (2249 cm^{-1}) corresponding to isocyanate species appeared after the addition of NO and O_2 to propene preadsorbed on CuH-ZSM-5 [16,17].

Based on the results described above, it can be proposed that there exist dual sites of Cu ions which are responsible for the activation of NO to nitro species and of propene to NCO, respectively. Our proposal was examined by IR measurement of CO selectively adsorbed on Cu^+. It has been reported that there are different sites in ZSM-5 on which Cu is ion exchangeable [24]. The location and adsorbate interaction of Cu cations in Cu-exchanged zeolite such as zeolite X, Y, L and ZSM-5 have been studied by Kevan et al. using ESR and ESEM [25,33]. It has been suggested that adsorption of polar molecules such as water and alcohol leads to the migration of Cu ions into the cation positions in the main

channels where adsorbate coordination occurs. Cu ions in CuNaH-ZSM-5 were suggested to migrate between the recessed sites and open sites, such as the channel intersections, by the adsorption of alcohol. Masai et al. [26] found different kinds of Cu ions in ZSM-5 during benzyl alcohol oxidation by IR absorption measurements of CO adsorbed on Cu-Na-ZSM-5. On the basis of Kevan et al.'s results, the Cu ions corresponding to the CO absorption bands at 2157 and 2137 cm^{-1} have been suggested to be located in a position inside the oxygen five-membered ring and in the intersection of the main channel of the ZSM-5 zeolite, respectively. In our results, the interaction of propene with Cu in Cu/ZSM-5 enhances the intensity of the band at 2140 cm^{-1} as shown in fig. 6. It has been suggested that Cu cations are located at different sites corresponding to the bands at 2157 and 2137 cm^{-1} in Cu/ZSM-5 evacuated at 500°C with high percentage of ion exchange [26] and the amount of Cu ions identified by the IR band at 2137 cm^{-1} is much smaller than that at 2157 cm^{-1}. CO IR absorption bands in fig. 6a show that Cu ions are mainly populated in the sites corresponding to the band at 2157 cm^{-1} after the standard pretreatment in He at 500°C. The decrease in band intensities and band shift occurring after the exposure of the catalysts to propene (fig. 6b) indicates that the Cu ions were blocked for CO adsorption due to the adsorption of propene. Heating at 350 and 500°C of Cu/ZSM-5 preadsorbed with propene at room temperature led to the increase of CO band intensities accompanied by the desorption of propene. It is noticeable that the intensity of the band at 2140 cm^{-1} increased after Cu/ZSM-5 preadsorbed with propene at room temperature was heated at 350 and 500°C (figs. 6c and 6d). Finally, the original IR spectrum was recovered by oxidation in O_2 at 500°C followed by heating in He at the same temperature (fig. 6e). These results suggest that the formation of the band at 2140 cm^{-1} is due to the site displacement of Cu ions which is induced by the interaction of propene with the Cu ions. The Cu ion, which was moved from one site to the other site by the adsorption of propene, was relocated to the original site by the oxidation in O_2 at 500°C for 30 min followed by the heating in He at same temperature for 1 h. Therefore, it can be concluded that CO IR absorption bands at 2157 and 2140 cm^{-1} arise from Cu ions located in the recessed site from the main channel and in the channel intersection in Cu/ZSM-5, respectively and that adsorbed propene migrates the Cu ions from the recessed site to the channel intersection.

On the basis of the assignment of CO IR absorption bands at 2157 and 2140 cm^{-1}, the variation of Cu sites involved in the NO reduction by propene was investigated by the IR measurement of adsorbed CO. Any CO IR absorption band was not found after the reaction in the flow of NO/O_2 followed by the adsorption of CO at room temperature (fig. 7a). Only the band at 2157 cm^{-1} appeared after the SCR reaction in excess oxygen with $C_3H_6/NO = 0.2$ (fig. 7b). As the C_3H_6/NO ratio increased, the intensities of the bands at 2157 and 2138 cm^{-1} increased. The intensity of the band at 2157 cm^{-1} was saturated, while the intensity of the band at 2138 cm^{-1} continued to increase. The band at 2138 cm^{-1} became dominant at C_3H_6/NO ratio = 1.2. This result shows that cuprous ions are produced in either and both of the recessed site and channel intersection during the NO reduction by propene and the relative amount of cuprous ions in these two sites is changed with the concentration of propene in the reaction mixture. This can explain which of the two Cu sites the depletion of the nitro species and the production of NCO species as shown in fig. 1 proceed on, respectively. The fact that a CO IR absorption band appears at 2157 cm^{-1} under the reaction condition of $C_3H_6/NO = 0.2$ (fig. 7b), where a part of nitro species on Cu ions were reduced by the propene as shown in fig. 1, may indicate that nitro species is associated on the Cu site corresponding to the band at 2157 cm^{-1}, that is, the Cu site in the oxygen five-membered ring. After the surface nitro species is completely depleted by the large concentration of propene ($C_3H_6/NO \leqslant 0.54$) as shown in fig. 1, the CO band at 2138 cm^{-1} significantly increases (figs. 7c and 7d). This indicates that Cu ions migrate to Cu sites in the channel intersection identified by the IR CO band at 2138 cm^{-1} due to the interaction of Cu ions with the propene. At the same time, NCO species began to be produced on the catalyst. These results lead to the proposal that Cu ions in the channel intersection mainly participate in the propene activation leading to the formation of NCO species.

It has been reported that ethene is a more efficient reductant than propene in the SCR over Cu/ZSM-5 [3]. The mechanism of NO reduction using ethene as a reducing agent has been suggested to be different from that in the case of using propene as a reductant. Cho argued a reaction mechanism which involves the NO decomposition accompanied by ethene oxidation [13]. The argument was based on the results that the formation of the partially oxidized hydrocarbon, gaseous NO_2 and the carbonaceous species as possible reaction intermediates were not observed or their amounts were negligible under his reaction conditions. Though this NO decomposition mechanism is controversial, it is agreed by us that the formation of organic components containing the nitrogen such as NCO species via hydrocarbon activation may be excluded from the mechanism of NO reduction by ethene. In addition, though NO reduction via surface nitro species is still not evidenced in case of ethene, surface nitro species as a reaction intermediate cannot be excluded from the mechanism in the case of the SCR by ethene [13]. Our IR result (fig. 7e) illustrates that the NCO species was not produced even during the reaction with the large concentration of ethene ($C_2H_4/NO = 1.2$). The IR absorption band of CO adsorbed on this catalyst indicates that Cu ions are mainly populated on the site corresponding to the band at 2157 cm^{-1}. This

result is contrast with the case of propene. Kevan and Anderson [25] have reported that the nonpolar nature of ethene does not facilitate the migration of Cu in ZSM-5 and Cu ions are residing in the recessed site from the main channel after the adsorption of ethene. According to this result, most of Cu ions are considered to be present at the sites in the oxygen five-membered ring during the NO reduction by ethene. We already showed that the reduction of nitro species by propene is carried out on the Cu site corresponding to the band at 2157 cm^{-1} as shown in fig. 7b. Therefore it can be suggested that NO reduction via the reaction of hydrocarbon with nitro species proceeds on the Cu ion inside the oxygen five-membered ring in ZSM-5.

IR spectra of Cu/ZSM-5 (fig. 3A) show that the band at 2250 cm^{-1} having a shoulder at around 2180 cm^{-1} was developed during the SCR reaction at 350°C. Solymosi and Bansagi [31] reported the IR bands of HNCO adsorbed on Cu/ZSM-5. The band at 2260 cm^{-1} was assigned to be –NCO adsorbed on Al^{3+} of ZSM-5, the band at 2180 cm^{-1} to –NCO adsorbed on Cu^{2+} and the band at 2200 cm^{-1} to –NCO on Cu^{+}. According to these assignments, the band at 2250 cm^{-1} can be assigned to be –NCO on ZSM-5 and the shoulder at around 2180 cm^{-1} to –NCO on Cu. Figs. 3A and 4 illustrate the reactivities of NCO with O_2 and NO/O_2 at 350°C, respectively. The decrease in intensity of the bands of NCO was observed only in the reaction with NO/O_2. This indicates that –NCO cannot react with O_2 but with NO/O_2 at 350°C. When Cu/ZSM-5 pre-treated in the SCR reaction was exposed to NO/O_2, the formation of Cu^{2+}–NO_2 was accompanied with depletion of –NCO species on the surface. In order to distinguish the vacant Cu site on which nitro species was expected to be formed from the Cu site previously occupied by the NCO species, the decrease rate in the integrated band intensity of –NCO species and the increase rate in the integrated band intensity of nitro species are compared, as shown in fig. 5. In our experiment, it was difficult to distinguish the formation of NO_2 on the original vacant Cu site from the vacant Cu site previously occupied by NCO species because NCO on Cu also reacts quickly with NO and/or NO_2 to produce vacant Cu sites. Moreover, the depletion rate of –NCO species is comparable to the formation rate of Cu^{2+}–NO_2 at 350°C, as shown in fig. 5. However, it was found that the amount of NCO species on the catalyst continued to decrease even after the formation of nitro species was completed on Cu sites at 400°C. This indicates that Cu^{2+}–NO_2 is formed on the Cu site previously occupied by –NCO species, which is being exhausted by the reaction with NO/O_2 and that NCO on zeolite slowly reacts with NO/O_2. NCO species produced on the Cu site in the channel intersection spills over zeolite and reacts with the gaseous NO and/or NO_2. From these results, it is concluded that the formation of NCO species on Cu in the SCR of NO by propene is as important as the formation of NO_2 species.

Although various mechanisms of SCR have been suggested on many catalysts using different reductants, all of the catalytic phenomena could not be explained by one mechanism. This led to the proposal that the SCR would proceed through several mechanisms depending on the catalyst and the hydrocarbon used as a reductant. Our results suggest that two kinds of copper sites are involved in the formation of surface nitro species and NCO species as potential intermediates to produce N_2 simultaneously on Cu/ZSM-5. The following mechanisms can be proposed based on the prevalent previous results.

The first Cu site (2157 cm^{-1}) produces nitro species reduced by hydrocarbon in the following manner.

(i) Nitric oxide is oxidized by surface oxygen to form nitrogen dioxide. The nitro species is present on the Cu^{2+} ion.

(ii) Propene is activated by surface nitro species. The hydrocarbon radical is produced in this step and forms a complex with NO and/or NO_2.

(iii) This compound subsequently reacts with NO and/or NO_2 to form N_2.

The second Cu site (2138 cm^{-1}) is involved in the mechanism in the following manner.

(i) Propene is adsorbed on the Cu site and then subsequently reacts with oxygen to make an oxygenated compound.

(ii) This compound reacts with NO to form a –NCO species on the Cu ion. In this step, the spillover of NCO from Cu to the zeolite occurs. NCO is accumulated on ZSM-5.

(iii) –NCO reacts with NO and/or NO_2 to form N_2.

When the propene is substituted by ethene, NCO is not observed and the Cu site at 2158 cm^{-1} is dominant in contrast with the case of propene. From the fact that the NCO species is produced only in the reaction with specified reductant and on the specified Cu site, the mechanism involving NCO species might not be accepted as a general one of the NO reduction over Cu/ZSM-5.

5. Conclusion

It is suggested that two catalytic cycles involving nitro species and –NCO species as reaction intermediates proceed simultaneously on Cu/ZSM-5 in the SCR of NO with propene. The first one proceeds by the formation of NO_2 associated on Cu, followed by the reaction with propene. In the second one, the propene is activated on Cu ions in a first step and subsequently reacts with NO and /or NO_2. Two kinds of Cu sites responsible for each cycle are present on Cu/ZSM-5. These Cu sites, which are assigned to the site inside the oxygen five-membered ring and to the channel intersection in ZSM-5 respectively, are identified by IR absorption bands of CO adsorbed on cuprous ion at 2157 and 2138 cm^{-1}.

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