In Situ X-ray Photoelectron Spectroscopy Study of Cu/ZSM-5 in the Selective Catalytic Reduction of NO by Propene

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The Cu $2P_{3/2}$ photoelectron spectra were acquired to study the coordination state and oxidation state of Cu in ZSM-5 in the NO reduction by propene in the presence of excess oxygen. Two peaks at higher binding energy (937 eV) and lower binding energy (934.3 eV) were found to be changed in intensity depending on the treatment under oxidizing/reducing conditions. The oxidizing condition obtained by the presence of O_2 or NO/O_2 induces the formation of the peak at higher binding energy, indicating that Cu ions are coordinated to extralattice oxygen. However, the Cu−oxygen species began to be decomposed by thermal heating in He above 673 K. During propene oxidation in the gas mixture of O_2 and C_3H_6, the coordination of Cu to oxygen is achieved at 623 K where the surface carbonaceous species is completely oxidized. The same result was also observed in the NO reduction by propene with excess oxygen. However, the increase of reaction temperature up to 773 K leads to the decomposition of the Cu−oxygen species even in the oxidizing condition, as shown by the significant decrease in the intensity of the higher binding energy peak. From these results, it is suggested that the dependence of the selective catalytic reduction activity of NO on the temperature is correlated with the thermal stability of the Cu−oxygen species on which the reaction intermediates such as nitro species are stabilized.

1. Introduction

Since the discovery by Iwamoto *et al.*[1] and Held *et al.*[2] of the high activity of Cu/ZSM-5 in the selective catalytic reduction (SCR) of NO in the lean burn condition, the characterization of this catalyst has been extensively studied. The oxidation state of Cu ions and its effect upon the reaction property has been one of the most interesting subjects in the direct decomposition and the reduction of NO over Cu/ZSM-5. The Cu/ZSM-5 prepared by excess ion exchange of copper ions has a characteristic redox property which is represented by the facile reduction of Cu^{2+} to Cu^+ during the thermal treatment. The redox chemistry of Cu ion in zeolite is rationalized by the extralattice oxygen which is introduced during the sample preparation.[3,4] The $Cu^{2+}-O-Cu^{2+}$ was proposed as an oxocation simultaneously satisfying the two-electron process of oxygen and the one-electron process of Cu during the reduction of Cu^{2+} to Cu^+. The redox properties of Cu are assumed to be essential both for NO decomposition and for NO reduction by hydrocarbon. It has been suggested that the dinitrosyl complex in the NO decomposition[5,6] and the nitro/nitrato species in the SCR reaction[7,8] are the possible reaction intermediates. These surface species may be stabilized on Cu^+ and Cu^{2+}, respectively, for the subsequent reaction to produce N_2. It is necessary to know the equilibrium oxidation state of Cu in strong oxidizing conditions for the study of the mechanism of NO reduction on Cu/ZSM-5. This can provide the information on the reaction intermediates linked on Cu ion in the SCR reaction containing both the reductant and excess oxygen. The stability of the reaction intermediate may strongly depend on the oxidation state change induced by the coordination and decomposition of the ligand on copper.

Electron spin resonance (ESR) has been extensively used to identify the oxidation state of Cu ion in zeolite. The ESR signal of Cu^{2+} decreased in the intensity after the evacuation of the Cu^{2+}/ZSM-5 above 373 K due to the spontaneous reduction of Cu ion.[9] This result was supported by the infrared spectroscopy and photoluminescence measurements. In contrast, the irreducible, isolated Cu^{2+} ions were identified in the Cu/ZSM-5 of low Cu content. It was observed in *in situ* ESR that this isolated copper ion was not reduced spontaneously and its oxidation state was 2+ in the presence of a strong reductant containing excess oxygen at high temperature.[10,11] However, ESR can not detect all kinds of Cu species present in Cu/ZSM-5 of high Cu content. X-ray photoelectron spectroscopy (XPS) has been used for the determination of the oxidation state of metal exchanged into zeolites.[12] *In situ* XPS is a useful method to clarify the oxidation state change of an active metal site in zeolite during the reaction. Although XPS was shown to give useful information on the oxidation state, coordination state, and location of Cu in zeolite matrix, there is relatively little XPS results on Cu/ZSM-5 without exposing the sample to air after the SCR reaction.

In this work, XPS was used to identify the oxidation state of copper and to observe the coordination change on copper in the SCR reaction. By using the XPS system directly connected to the high-pressure reactor, the catalyst was analyzed immediately after the SCR reaction. The variation of Cu $2P_{3/2}$ XPS peaks and satellite peaks after treatment under the oxidizing/reducing condition makes it possible to identify the state of Cu in ZSM-5. On the basis of these results, the change in the coordination state of Cu with the SCR reaction temperature was discussed to be correlated with the stability of the surface reaction intermediate in the SCR reaction.

2. Experimental Section

2.1. Preparation of Catalyst. Na/ZSM-5 zeolite (Si/Al = 15) was synthesized according to the open literature.[13] Crystallized zeolite was washed with distilled water, dried at 393 K for 24 h, and calcined at 823 K for 5 h. The crystallinity of Na/ZSM-5 was confirmed by powder X-ray diffraction.

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The sample was ion exchanged in an aqueous copper acetate solution at room temperature, washed with water, and dried at 393 K overnight. The procedure was repeated three times. The amount of copper ion in the zeolite was determined by ICP-AES (inductively coupled plasma−atomic emission spectroscopy) after the sample was dissolved in HNO_3 solution. The percent ion exchange of Cu was 95, *i.e.* Cu/Al = 0.48. 100% ion exchange corresponds to Cu/Al = 0.5. The catalyst was pretreated by heating in He at 773 K.

2.2. XPS Analysis. The X-ray photoelectron spectra were acquired with a surface analysis system (LHS10, SPECS GmbH) equipped with a multiplate channel detector using Mg Kα radiation (300 W). The pass energy was 100.6 eV. Samples were treated in the high-pressure reaction cell mounted directly to the preparation chamber. Catalyst powders were mounted on the sample holder. The reactant gases were introduced into the reaction cell through the mass flow controller (MFC). The reaction was carried out in the temperature range between room temperature and 773 K in the flow (20 mL/min) of various gas mixtures such as 20% O_2, 0.5% NO + 10% O_2, 0.5% C_3H_6 + 10% O_2, and 0.33% NO + 0.33% C_3H_6 + 6% O_2 in He. After the temperature was cooled down to room temperature in the pure He flow, the catalysts were pumped down to be transferred into the analysis chamber *via* the preparation chamber. During the X-ray exposure, the catalysts were cooled down to 100 K to avoid the reduction of Cu ions by X-ray radiation. Binding energies were referenced to Si 2p at 102.9 eV from ZSM-5 zeolite.[14] Data smoothing, subtraction of background, and curve fitting were performed with SPECTRA software from SPECS Co.

3. Results and Discussion

The Cu $2P_{3/2}$ core level peaks have been observed in copper-exchanged X- and Y-zeolite by Kevan *et al.*[15] The lower binding energy peak, peak I (933−934 eV), and higher binding energy peak, peak II (935−936 eV), were assigned to tetrahedrally and octahedrally coordinated Cu^{2+}, respectively. It was observed that peak II was transformed to peak I during the acquisition of XPS. This result was explained by the fact that octahedrally coordinated Cu^{2+}, which was coordinated by three framework oxygen and three water molecules, was dehydrated by either heating or X-ray radiation while its oxidation state was maintained.[15] Haack and Shelef[16] reported that the heating in Ar at 773 K following the oxidation at 773 K for 6 h did not change the XPS spectrum of Cu/ZSM-5 acquired after the oxidation at 773 K. It was suggested by them that the change in intensity of XPS peaks was induced by the change of the population of Cu^{2+} ions in different spatial coordination rather than the change of oxidation state of Cu. However, the XPS study of Cu/ZSM-5 and Cu−Y-zeolite by Jirka and Bosacek[17] showed different results from those mentioned above. Peak II disappeared after heating *in vacuo* and during the XPS measurement, where the Auger parameter of Cu was the closest to that for cuprous ion in Cu_2O, indicating that Cu^{2+} was reduced to Cu^+ through the decomposition of water. These controversial XPS results give rise to questions about the coordination state and oxidation state change of Cu ion, especially the reducibility of Cu ions in Cu/ZSM-5 during the SCR reaction.

In our work, Cu/ZSM-5 having the exchange level of 95% was sequentially treated in the flow of the various reactants. After the treatment, the sample was transferred immediately to an analysis chamber for XPS. As shown in Figure 1, the parent peak of the Cu $2P_{3/2}$ transition was deconvoluted into two peaks of peak I and peak II as designated by the same manner as Kevan *et al.*[15] However, the satellite peaks were too weak to
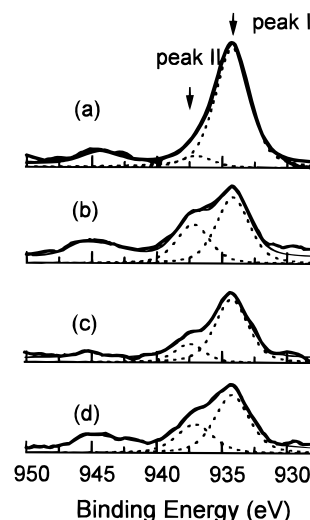
Figure 1. XPS Cu $2P_{3/2}$ core level spectra: (a) after the reaction with propene at 623K, (b) after the reaction with oxygen for 1 h at 623 K, (c) after the heating in He for 1 h at 673 K, and (d) after the reaction with NO/O_2 for 1 h at 623 K on Cu/ZSM-5, which was treated by heating in He at 773 K followed by the calcination in O_2 at 773 K. (The catalyst was sequentially treated from (a) to (d).)

be deconvoluted. At first, the effect of the oxidation treatment on Cu ions was examined by the interaction of either O_2 or NO/O_2 with Cu/ZSM-5. Cu/ZSM-5 prereduced by propene at 623 K was selected as the starting sample. Therefore, the catalyst, which was treated by heating in He followed by calcination at 773 K, was heated in the flow of 1% propene in He at 623 K. Figure 1a shows the Cu $2P_{3/2}$ core level spectrum of this catalyst. Peak I at 934.3 eV with a weak peak at 937.0 eV is observed, and a broad satellite peak is observed at around 944.0 eV. After the reaction with oxygen for 1 h at 623 K, the intensity of peak II and the satellite peak increased and the intensity of peak I decreased, as shown in Figure 1b. Subsequent heating in He at 673 K decreased the intensity of peak II and the satellite peak. Finally, the reaction with the mixture of NO/O_2 at 623 K increased the intensities of peak II and the satellite peak again. It is clear from these results that peak II is formed by the treatment under the oxidizing condition of either O_2 or NO/O_2. This suggests that the formation of the higher binding energy peak is caused by the increase in the coordination number of Cu arising from the coordination with oxygen. The variation of peak II illustrates the coordination state change of Cu ion resulting from the oxygen linkage to Cu and the decomposition of the Cu−oxygen species. The calcined Cu/ZSM-5 is reduced by the propene treatment at 623 K.[11] In our spectrum, Cu ions were not completely reduced as shown by the weak satellite peak (Figure 1a). The introduction of O_2 to this sample at 623 K causes the Cu ions to be oxidized to Cu^{2+}. Cu cation is coordinated by extralattice oxygen (ELO). At the same time, the carbonaceous species, which was formed on the catalyst during the reaction with propene, is expected to be oxidized to CO_2 on the surface. This Cu−oxygen species partially decomposes during the heating in He at 673 K. This leads to the decrease in the intensity of peak II (Figure 1c). The intensities of peak II and the satellite peak increase after treatment under the oxidizing condition and are reduced after treatment under the reducing condition (He and propene). This implies that redox cycle between the 2+ state and 1+ state is accomplished on Cu ion of which the coordination state can be changed by the adsorption/desorption of oxygen. The shake-up satellite is associated with only the Cu^{2+} because the filled 3d shell of Cu^+ prevents the ligand−metal charge transfer shake-up transition.[18] Although the quantification of the satellite effect

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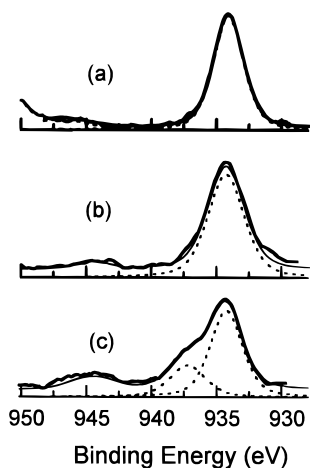
Figure 2. XPS Cu $2P_{3/2}$ core level spectra: (a) after the reaction with propene at 623 K, (b) after the reaction with C_3H_6 and O_2 at 523 K, and (c) after the reaction with C_3H_6 and O_2 at 623 K on Cu/ZSM-5, which was pretreated by heating in He at 773 K. (The catalyst was sequentially treated from (a) to (c).)

Figure 3. XPS Cu $2P_{3/2}$ core level spectra after the SCR reaction at (a) 523 K, (b) 623 K, and (c) 773 K on Cu/ZSM-5, which was pretreated by heating in He at 773 K. (The catalyst was sequentially treated from (a) to (c).)

is not clear at present, the oxidation states of Cu might be estimated indirectly by the satellite peak.[15] Recently, the redox behavior of Cu cation in ZSM-5 was observed by Cu $2P_{3/2}$ photoelectron spectra and Cu L3VV Auger spectra acquired by Shipiro *et al.*[19] Even though their $2P_{3/2}$ XPS peaks were not resolved to peak I and peak II, the variation of the satellite peak and the shift of the Auger parameter showed that Cu^{2+} was reduced to the state below 2+ by calcination followed by heating in He at 713 K. Furthermore, the structure of these Cu species was identified to be a small cluster containing ELO by X-ray absorption spectroscopy (XANES, EXAFS) studies. However, in Cu/ZSM-5, XPS spectra did not show the binding energy shift of peak I, which would be accompanied by the change of oxidation state, even if the intensity of the satellite peak changed. This has been shown from XPS spectra obtained after X-ray radiation on Cu/ZSM-5 by others.[16] It seems that the binding energies of the peaks corresponding to isolated Cu^{2+} and Cu^+ are not distinguishable in XPS spectra on Cu/ZSM-5 because of the X-ray-induced reduction of isolated Cu^{2+} ions.

Figure 2 shows the variation of Cu $2P_{3/2}$ XPS spectra with temperature in the propene oxidation reaction. The catalyst, pretreated in He at 773 K, was heated in the flow of propene at 623 K before the mixture gas of propene and oxygen was introduced (Figure 2a). XPS spectra in parts b and c of Figure 2 were acquired from the sample sequentially treated in the gas mixture of 0.5% C_3H_6 + 10% O_2 at 523 and 623 K, respectively. The enhancement of peak II shown in Figure 2c indicates that Cu ions begin to be oxidized at 623 K, while the oxidation of Cu is negligible in the reaction at 523 K (Figure 2b). Kucherov *et al.*[11] reported by ESR measurement that Cu^{2+} ions were significantly reduced and coke was formed by the interaction of CuH−ZSM-5 with 0.26% C_3H_6 + 2.7% O_2 below 573 K. It has been seen that the carbonaceous species was deposited to Cu sites by the interaction of propene with Cu/ZSM-5 below 600 K and the carbonaceous species on Cu ions was oxidized completely to CO_2 by oxygen above 600 K during the temperature programmed oxidation.[20] From these results, it is suggested that in the propene oxidation, Cu^+ is oxidized to the Cu−oxygen species at 623 K where the complete oxidation of the carbonaceous species to CO_2 is achieved on Cu ions. In our separate experiment, the steady state NO conversion as a function of temperature has been measured for this catalyst. The catalyst exhibited the maximum activity at 623 K, and its conversion of NO decreased with increasing temperature. The temperature dependence of activity like this has been reported
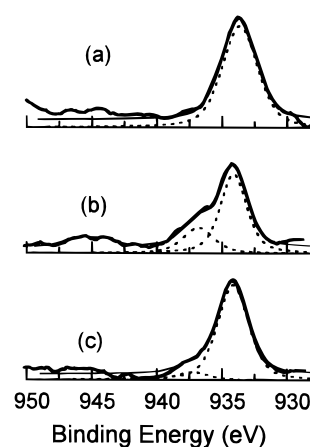
by others.[21,22] These results indicate that oxygen plays the role to remove the carbonaceous deposits on Cu ions and to oxidize Cu^+ ions to Cu^{2+}−oxygen species at 623 K, at which the SCR activity is the highest. Figure 3 shows Cu $2P_{3/2}$ XPS spectra of Cu/ZSM-5 as a function of temperature in the SCR reaction. It should be pointed out that the SCR reaction proceeded in the strongly oxidizing condition (NO/C_3H_6/O_2 = 3300 ppm/3300 ppm/6%). XPS spectra of Cu/ZSM-5 obtained after SCR reaction at 523 and 623 K as shown in parts a and b of Figure 3 are identical with those of parts b and c of Figure 2, respectively. This shows that the oxidation of Cu^+ ions is achieved at 623 K in the SCR reaction as well as that in the propene oxidation reaction. However, peak II at 937.0 eV significantly decreases in the SCR reaction at 773 K as shown in Figure 3c. This indicates that the Cu−oxygen species decomposes at high temperature even in oxidizing condition. At 773 K, the SCR activity is small, indicating that the Cu−oxygen species must be correlated with the catalytic activity of the SCR reaction.

Liu and Robota[23] observed in *in situ* X-ray absorption near edge structure spectroscopy studies that the proportion of Cu^+ increases with the reaction temperature in the NO decomposition reaction. This showed that Cu cation is reduced by the desorption of oxygen even in the oxidizing condition. In contrast, ESR results of Shelef *et al.* showed that the cupric state was dominant in Cu/ZSM-5 with an ion exchange level of 67% in the SCR reaction with excess oxygen at 773 K and isolated copper ions were not reduced even by the reductant in the SCR reaction with excess oxygen at high temperature.[11] The complexity of the reducibility of Cu ion can be explained by the fact that the structure of the Cu species is variable in highly loaded Cu/ZSM-5. Shelef[24] proposed that this discrepancy of the reducibility of Cu ions resulted from the difference of the ion exchange level between overexchanged Cu/ZSM-5 and the low-loaded one. It was pointed out that the spontaneous thermal reduction occurred only when the exchange level (EL) approaches 100%. Recently, Sachtler *et al.*[25] have identified the isolated Cu^{2+} ions, oxo-cations such as [Cu−O−Cu]$^{2+}$, and the CuO particle in calcined Cu/ZSM-5 (EL =100) using Fourier transform infrared spectroscopy, electron paramagnetic resonance, temperature-programmed reaction, and extended X-ray absorption fine structure spectroscopy. It was shown by them that [Cu−O−Cu]$^{2+}$, which was EPR silent, was reduced to Cu^+ through thermal decomposition by heating in Ar and was essential in NO decomposition. Bell and co-workers have used LSDFT (local spin density functional theory) to determine the
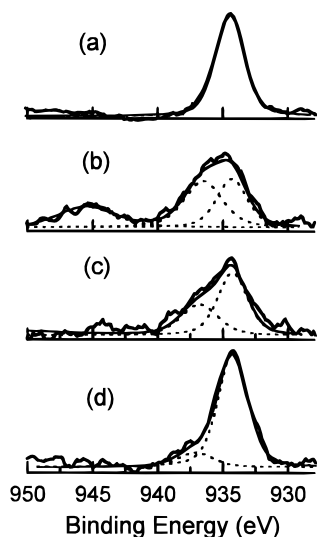
Figure 4. XPS Cu $2P_{3/2}$ core level spectra on Cu/ZSM-5: (a) after the reduction in CO at 573 K, (b) after the exposure to NO for 30 min at room temperature, (c) after heating *in vacuo* for 1 h at 523 K, and (d) after the exposure to NO for 30 min at room temperature followed by the heating *in vacuo* for 1 h at 773 K. (The catalyst was sequentially treated from (a) to (c).)

electronic and structural properties of various Cu species in ZSM-5, and their calculated structures have been compared with ESR results.[26,27] It was suggested that Cu^+ is asymmetrically coordinated to two lattice oxygen atoms and Cu^{2+} is coordinated to two lattice oxygen atoms and one extralattice oxygen. These sites, formed by the spontaneous desorption of oxygen from $Cu^{2+}OH^-$, were proposed to be responsible for redox process in NO decomposition. However, the reaction *via* superoxide

$$Cu^+ + O_2 \rightarrow Cu^{2+}O_2^-$$
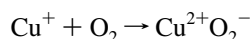
was suggested as the redox process for Cu/ZSM-5 in the oxygen.

We carried out XPS measurements on Cu/ZSM-5 exposed to NO to study the redox process of Cu ions. The catalyst was reduced by CO at 573 K and subsequently exposed to 99.999% NO for 30 min at room temperature. The decomposition temperature of the formed Cu species was estimated by XPS acquired after heating *in vacuo* at the specific temperature. After the reduction in CO, a peak attributable to Cu^+ is located at 934.3 eV. As shown in Figure 4b, a peak of higher binding energy (936.4 eV) appears after NO adsorption. The intensity of the peak decreases a little and the binding energy shifts to 947.0 eV after heating *in vacuo* at 523K for 1 h (Figure 4c). Finally, the peak nearly disappears after heating at 773K (Figure 4d). The structure of the sites corresponding to the higher binding energy peak can be speculated from the NO decomposition mechanism. According to the previously suggested mechanism, Cu−oxygen species such as $[Cu-O-Cu]^{2+}$ or $ZCu^{2+}O^-$ are produced by the oxidation of Cu^+ ions by O atom, which is left after the desorption of N_2O from Cu^+ dinitrosyl complex and are, subsequently, adsorbed by NO during NO adsorption on Cu/ZSM-5.[5,28,29] Hence, a peak at the higher binding energy in Figure 4b can be assigned to this Cu−oxygen species carrying NO. NO desorbs from Cu^{2+} ions in ZSM-5 below 523 K, which has been shown in NO temperature-programmed desorption (TPD).[30] The binding energy shift occurring after heating at 523 K indicates that the difference of about 0.6 eV observed between parts b and c of Figure 4 is arising from NO adsorbed on Cu^{2+} ions. The electron transfer from the adsorbed NO to Cu^{2+}−oxygen species shifts the binding energy of the peak to

low binding by 0.6 eV. The higher energy peaks, peak II, in Figure 1b and Figure 4c are observed at same position, indicating that the natures of the corresponding sites are closely similar. These Cu−oxygen species decompose at 773 K, as illustrated by the significant decrease of the higher energy peak in Figure 4d. From these results, it is concluded that peak II observed in this work is attributable to Cu^{2+} ions coordinated to ELO and decomposes at 773 K and that the large shift of the binding energy from that of Cu^+ is due to the change of oxidation state of Cu ions and the high ionic nature of Cu−O.

The amount of Cu ion on which the redox cycle proceeds by the adsorption/desorption of oxygen has been estimated by the detailed work of Li and Hall.[31] In their microbalance experiments, about 25% of total Cu ions in their sample (Si/Al = 26 and Cu/Al = 0.83) was found to be spontaneously reduced by the desorption of oxygen as evidenced by the weight loss after oxidation in O_2 followed by flushing in He at 773 K. Using ESR, Larsen *et al.*[27] showed that the ESR signal intensity attributable to the Cu^{2+} species decreased by 40−60% upon heating the sample (Si/Al = 18 and Cu/Al = 0.55) to 700−773 K for 1−3 h in flowing He. The ESR silent Cu species such as Cu^+, $Cu^{2+}O^-$, and $Cu^{2+}O_2^-$ were explained to be responsible for the redox process in NO decomposition or the adsorption/desorption of oxygen. The fraction of Cu ions corresponding to the higher binding energy peak in our sample (Si/Al = 15 and Cu/Al = 0.48) is approximately 40% as estimated by the relative intensity of peak I and peak II in Figure 1.

Since it is difficult to determine the structure of the Cu−oxygen species in ZSM-5 by XPS, the structural details of this species are not defined by the present work. However, our XPS study on the effect of oxidation/reduction on Cu/ZSM-5 suggests that the change of oxidation state of Cu is accompanied by the adsorption/desorption of oxygen. It has been reported by Valyon and Hall[32] that the apparent binding energy of oxygen in Cu/ZSM-5 (Si/Al =14 and Cu/Al = 0.52), calculated using the Clausius−Clapeyron equation and the slope of equilibrium pressure as a function of $1/T$, was 11 kcal/mol on sample evacuated below T_{ev} = 573 K, while it increased to 24 and 54 kcal/mol on samples evacuated at T_{ev} = 673 and 773 K, respectively, indicating ELO desorbs above 673 K. The measured equilibrium pressure on the catalyst calcined at 573 K and then evacuated at the same temperature was $10-1$ Torr at 773 K, implying that the pressure of $10-9$ Torr in our XPS system is low enough to release oxygen from Cu/ZSM-5 at 773 K. This result agrees with our XPS results, illustrating the depletion of the Cu−oxygen species corresponding to the higher energy peak after the evacuation at 773 K. O_2 can be released *via* a process in which ELO reacts with oxygen in the zeolite lattice at 773 K as suggested by Hall and co-workers.[32]

In addition, it is suggested that Cu−oxygen species identified by XPS take part in the reaction route in the SCR. The nitro/nitrato species as possible candidates of the reaction intermediate for the NO reduction can be produced by the NO and NO_2 adsorption on this Cu−oxygen species. It has been found that IR bands at 1630, 1613, and 1577 cm^{-1} appeared after the adsorption of NO as well as NO_2 and NO + O_2 on Cu/ZSM-5.[33] These bands can be assigned to the nitro/nitrato species.[34] TPD results showed that the operating temperature of the catalysts in the SCR reaction was strongly dependent on the thermal stability of surface NO_y species and the stability of these species was dependent on that of surface oxygen.[35] Hence, the fact that the activity in the SCR reaction decreases above 623 K where Cu/ZSM-5 gives the maximum activity might be

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explained by the depletion of nitro/nitrato species arising from the desorption of oxygen from these sites at the elevated temperature.

4. Conclusions

XPS Cu $2P_{3/2}$ core level spectra were acquired after reaction in various gas mixtures containing O_2, NO, and C_3H_6. The variation of intensity in a peak at 937 eV is sensitive to the oxidation treatment on Cu/ZSM-5, showing that extralattice oxygen is coordinated to Cu ions. In the SCR reaction, this species is produced simultaneously with the complete propene oxidation at 623 K but decomposes by the desorption of oxygen at 773 K even in oxidizing condition. Thermal stability of the nitro/nitrato species as a candidate for the reaction intermediate is dependent on the thermal stability of the Cu−oxygen species. The SCR catalytic activity is well-correlated with the existence of the Cu−oxygen species.

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