ELSEVIER

Catalysis Today 44 (1998) 47–55

CATALYSIS TODAY

Role of oxygen on NO_x SCR catalyzed over Cu/ZSM-5 studied by FTIR, TPD, XPS and micropulse reaction

In Chul Hwang, Do Heui Kim, Seong Ihl Woo*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology 373-1, Kusong-dong, Yusong-gu, Taejon 305-701, South Korea

Abstract

Pulse reaction, TPO/TPD (temperature programmed oxidation/temperature programmed desorption), XPS (X-ray photoelectron spectroscopy) and DRIFT (diffuse reflectance infrared transform spectroscopy) have been used to investigate the role of oxygen on SCR (selective catalytic reduction) of NO over Cu/ZSM-5 zeolites, especially during the early stage. Pulse reaction shows that propene is deposited on Cu ions and inhibits the adsorption of NO on them. It is necessary for oxygen to make Cu sites clean by deep oxidation of propene. In the presence of O_2, SCR at 623 K is accompanied by coke deposition on the zeolite. This coke can be discriminated from carbonaceous species formed on Cu in the absence of O_2 from the result of TPO. XPS results implies that Cu(II)–O species play a crucial role in forming Cu(II)–NO_2 species, and subsequently are well correlated with the activity of NO SCR.

Keywords: Cu/ZSM-5; SCR; Oxygen; FTIR; Pulse reaction; TPD; XPS

1. Introduction

Since Iwamoto [1] and Held et al. [2] reported that the selective catalytic reduction (SCR) of NO_x by hydrocarbon over Cu/ZSM-5 proceeded even in a large excess oxygen, many researchers in the world have enthusiastically tried to find a catalyst with better activity. Though Cu/ZSM-5 is known to show a good activity, it is still not high enough to fulfill further stringent emission standards. Therefore, the understanding of the reaction mechanism is essential for the design of better catalysts.

During past several years, many mechanistic studies on the SCR of NO on Cu/ZSM-5 have been published [3–7]. There are very diverse observations. NO_2 intermediate formed by oxidation of NO was proposed [3,4]. Yokoyama and Misono [5] suggested that NO is oxidized to NO_2 by oxygen, which is accelerated by Ce ion in Ce/ZSM-5 catalyst. Shelef et al. [6] reported that the activity of Cu/ZSM-5 in the reaction of NO with O_2 to form NO_2 parallels the activity in SCR. On the other hand, Iwamoto and coworkers [7] proposed that the partial oxidation of hydrocarbon species react first with NO to form an isocyanate species (–NCO), which was suggested to be a key reaction intermediate. In addition to the proposed mechanisms, the role of oxygen is also still controversial. The reduction of NO by hydrocarbon is accelerated by the presence of oxygen. It was suggested that oxygen plays an important role in keeping the catalyst clean, maintaining the

---

*Corresponding author.

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0920-5861(98)00172-2

catalyst in an oxidized state and forming reactive reaction intermediates during SCR [5]. In this work, FTIR, TPD/TPO (temperature programmed diffusion/ temperature programmed, XPS (X-ray photoelectron spectroscopy) and micropulse reaction studies were performed to identify the steps of reaction and the types of reaction intermediate, especially focusing on the role of oxygen.

2. Experimental

Na/ZSM-5 was synthesized according to the open literature [8]. 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 X-ray diffraction. The Si/Al ratio was calculated by the integrated intensity of ^{29}Si NMR peak. Cu/ZSM-5 was prepared by conventional ion exchange method. Na/ZSM-5 was stirred for one day in an aqueous solution of copper acetate. The degree of Cu ion exchange was in the range between 80% and 100% which was analyzed by ICP–AES.

FTIR spectra were acquired using in situ diffuse reflectance infrared transform spectroscopy (DRIFT) cell equipped with gas flow system. In DRIFT cell, the catalyst was pretreated at 773 K in He for 2 h. In TPD/TPO experiments, catalysts (0.02 g) were pretreated at 773 K in He for 2 h. After stabilization of the MS signal of effluent gases at RT, the temperature was increased to 1073 K at the rate of 10 K/ min and the partial pressure of evolved gas was measured with quadrupole mass spectrometer (VG SX300).

XPS spectra were acquired with a surface analysis system (LHS-10, SPECS GmbH) equipped with a multichannel detector using Mg K_α 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. During the X-ray exposure, the catalysts were cooled down to 100 K to avoid the reduction of Cu ions by X-ray. The pulse reaction was performed at 623 K in a fixed bed reactor. Reactant was pulsed in 30 cm^3/min He flow to the reactor containing 0.02 g of the catalyst. The sample loops of 1, 2 and 5 cm^3 were used in proportion to the composition of the reactant. The products were analyzed by GC.

3. Results

The dynamic pulse experiment was performed to investigate the adsorption behavior of propene over Cu/ZSM-5 at 623 K. Fig. 1 shows the variation of the amount of propene consumption with the number of pulses. The amount of propene consumption monotonously decreased with the increase in the number of pulse but it drastically decreased from sixth pulse and reached nearly a constant value at about 20th pulse. The catalyst underwent transient state before arriving at the steady state. The chemisorption of alkenes on copper-exchanged ZSM-5 zeolite was studied briefly by Jen and Otto [9]. They indicated that the adsorption of propene at RT was strong enough to be judged as chemisorption and found the desorption peaks at 343 and 523 K from TPD. Because the propene chemisorbed on Cu ions desorbed completely above 523 K, the consumption of propene at 623 K must be originated from some kind of reaction and from the deposition of fragmented propene on the surface of Cu/ZSM-5, indicated by the decrease in the amount of consumption of propylene in early pulses.

To investigate the adsorption behavior of O_2 and propene on Cu/ZSM-5 during propene oxidation, the gas mixture of propene and O_2 with the stoichiometric ratio ($O_2/C_3H_6=4.5$) of reaction (1) was injected to Cu/ZSM-5:

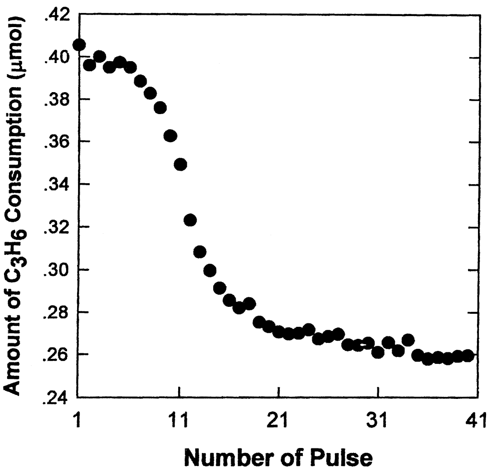

Fig. 1. The variation of amount of propene consumption with the number of pulses during the pulse reaction of C_3H_6 over Cu/ZSM-5 at 623 K.

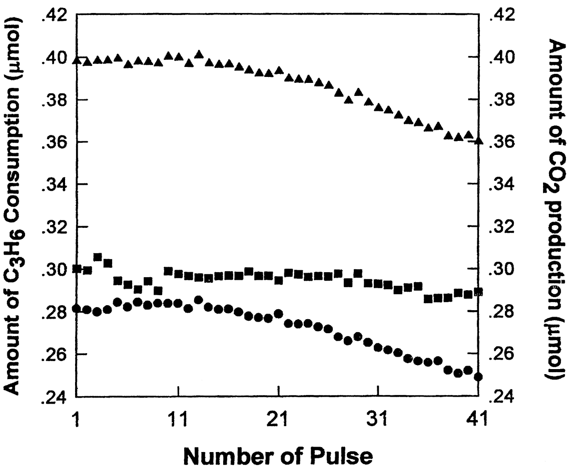

Fig. 2. Propene consumption over Cu/ZSM-5 during the pulse reaction of C_3H_6 and O_2 at 623 K: (▲) the amount of total propene consumption; (■) the amount of CO_2 production; (●) the amount of C_3H_6 consumption except for that oxidized to CO_2, which is calculated by subtraction of one-third amount of CO_2 production from total C_3H_6 consumption.

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O \qquad (1)$$

Fig. 2 shows the amount of total propene consumption, CO_2 production and propene consumption, which was not used to produce CO_2, calculated by subtraction of one-third of CO_2 production from total propene consumption. The amount of propene consumption monotonously decreased, while the consumption of propene decreases abruptly in the absence of O_2 as shown in Fig. 1. The amount of CO_2 production was nearly constant throughout the whole pulses. By comparing Fig. 2 with Fig. 1, the number of moles of consumed propene (0.1 μmol), which was calculated from CO_2 production in Eq. (1), was nearly the same as that calculated from the difference of propene consumption between the first pulse and the 21st one in Fig. 1 (0.13 μmol). This indicated that a part of propene, which is considered to interact with Cu sites, is oxidized to CO_2 and H_2O under O_2 at 623 K. The variation of the amount of O_2 consumption with the number of pulse during the pulsing with C_3H_6 and O_2 is shown in Fig. 3. We calculated the amount of O_2 retained on the catalyst in addition to O_2 used to produce CO_2 and H_2O. If the amount of CO_2 production was known, the amount of H_2O can be calculated according to Eq. (1) and then the amount of O_2 adsorbed on the catalyst can be calculated. This amount is arising from the oxygen which was retained on Cu/ZSM-5 during the propene oxidation at 623 K. The sequential pulse reaction followed. At first propene was injected over Cu/ZSM-5 at 623 K, and then the pulse of O_2 was injected, CO_2 production and O_2 consumption were measured. The same procedure was repeated one more time. The volume ratio of injected O_2 and propene was kept at the stoichiometry ratio of 4.5 according to Eq. (1). The results are shown in Fig. 4. After the injection of propene, it was consumed by the reaction with Cu/ZSM-5 at a nearly constant value. After five pulses of propene, O_2 was pulsed. The amount of O_2 consumption and CO_2 production exponentially decreased to zero after a few pulses. When propene was injected on this catalyst again, the same amount of propene was consumed in comparison with the first propene pulse. After second O_2 injection, the consumption of O_2 and production of CO_2 was observed again, however, it was slightly decreased. It is thought that a deactivation process occurs slowly due to the hydrocarbon fragments of C_3H_6 deposited on Cu ions which was not cleaned by O_2 completely. These results suggest that Cu ions blocked by hydrocarbon

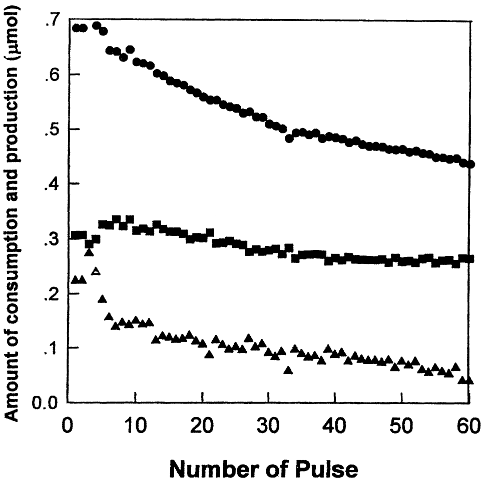

Fig. 3. O_2 consumption over Cu/ZSM-5 during the pulse reaction of C_3H_6 and O_2 at 623 K: (●) the amount of total O_2 consumption; (■) the amount of CO_2 production; (▲) the amount of O_2 consumption except for that used in the reaction of propene to CO_2 and H_2O, which is calculated by subtraction of CO_2 production and half of CO_2 production (calculated H_2O production) from total O_2 consumption.

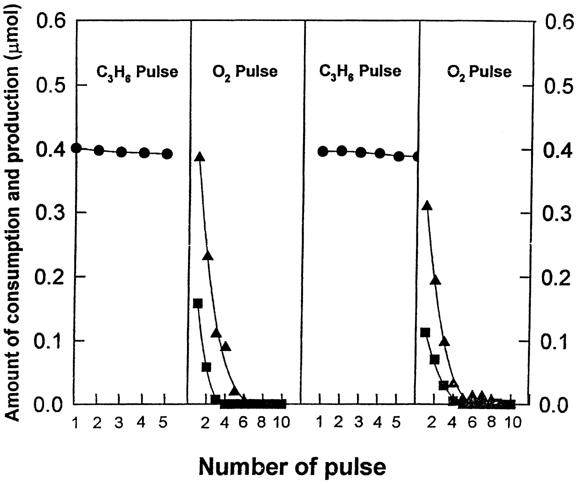

Fig. 4. The propene oxidation behavior over Cu/ZSM-5 during the sequential pulse reaction at 623 K consisted of C_3H_6 pulse followed by O_2 pulse: (●) C_3H_6, (▲) O_2 and (■) CO_2.

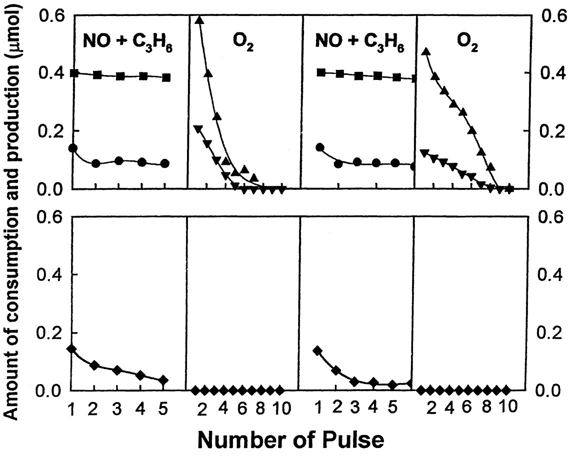

Fig. 5. The NO reduction behavior over Cu/ZSM-5 during the sequential pulse reaction at 623 K consisted of NO and C_3H_6 pulse followed by O_2 pulse: (■) C_3H_6, (●) NO, (▲) O_2, (▼) CO_2 and (◆) N_2.

species are converted to vacant Cu ions by the oxidation of propene adsorbed on Cu ions with O_2. Fig. 5 shows the results of sequential pulse reaction using the pulse of the mixture gas of NO and propene, and O_2. This experiment was repeated two times. One was for the detection of CO_2. The other was for N_2. On the pulse of NO and propene, N_2 was produced. The consumption of propene was almost constant, while the production of N_2 decreased exponentially. In the pulse of O_2 following propene and NO pulse, CO_2 was produced, but N_2 was not detected. This is in agreement with in situ IR study discussed later. This procedure was repeated one more time. The amount of reactant consumption and the product yield was similar to that of the reactant consumption and the product yield in the first pulse cycle.

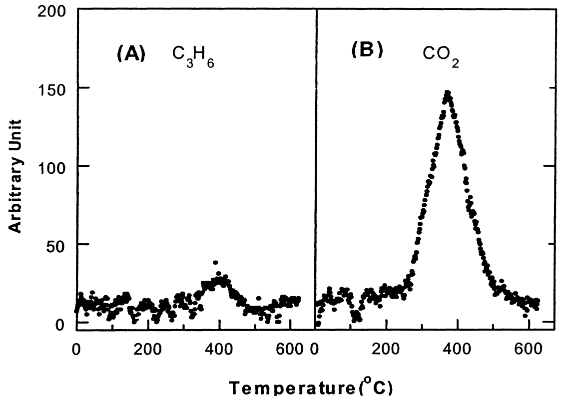

Fig. 6. TPD spectrum (A) and TPO spectrum (B) over Cu/ZSM-5 after treatment of propene at 623 K.

TPD of propene followed by TPO was performed to study the species on Cu/ZSM-5 after propene reaction at 623 K. A significant desorption of propene was not observed, indicating that C_3H_6 was not chemisorbed on Cu ions at 623 K. However, the evolution of CO_2 was observed around 673 K during the TPO as shown in Fig. 6.

TPO spectra for Cu/ZSM-5 and H-ZSM-5 after propene reaction at 623 K are shown in Fig. 7. In H–ZSM-5, the significant evolution of CO_2 was not observed below 623 K and the small evolution of CO_2 was observed above 673 K. However, CO_2 production peak appeared at 623 K for Cu/ZSM-5. These results suggest that carbonaceous species are present on Cu sites after propene reaction at 623 K on Cu/ZSM-5. Fig. 8 shows TPO spectra measured by CO_2 evolution after the reaction with NO/C_3H_6, C_3H_6/O_2 and $NO/C_3H_6/O_2$ at 623 K. As shown in Fig. 8(A), after reaction with NO and C_3H_6, CO_2 evolution was detected at 623 K in the same manner as in the case of reaction with propene (Fig. 7). After propene oxidation and SCR of NO in the presence of O_2, the evolution of CO_2 at 623 K disappeared and the large amount of CO_2 evolution was observed between 673 and 873 K. d'Itri

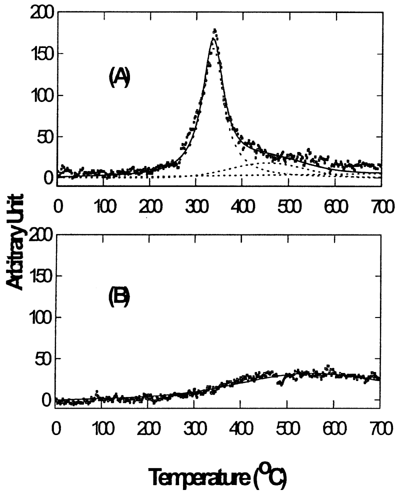

Fig. 7. TPO spectrum of: (A) Cu/ZSM-5 and (B) H–ZSM-5 after reaction with propene at 623 K.

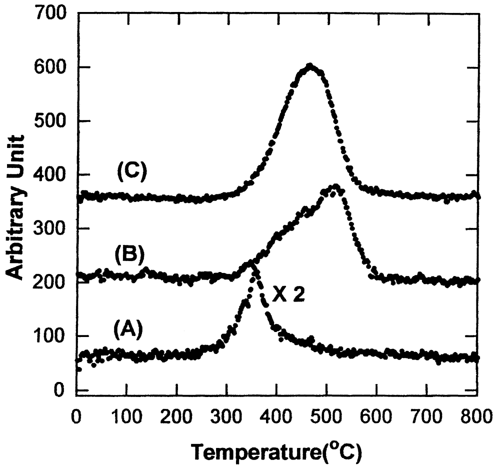

Fig. 8. TPO spectrum of Cu/ZSM-5 after reaction of: (A) NO/ C_3H_6, (B) C_3H_6/O_2 and (C) $NO/C_3H_6/O_2$.

and Sachtler [10] reported similar results after the SCR reaction using propene as a reductant. CO_2 evolution was due to the carbonaceous material deposited on the catalysts. The amount of carbonaceous deposits on the catalysts depended crucially on the reaction temperature and the composition of the reactant. During the reaction with C_3H_6/O_2, and with NO/ C_3H_6/O_2, new carbonaceous deposits, which are oxidized above 673 K, were produced.

The TPD spectra of NO adsorbed on Cu/ZSM-5 after various reactions are shown in Fig. 9. Cu/ZSM-5

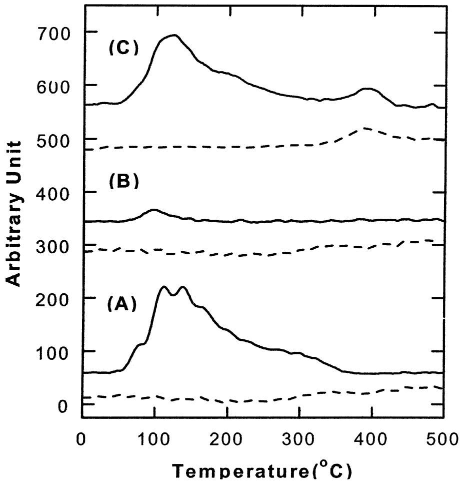

Fig. 9. TPD spectrum of NO following the adsorption of NO on Cu/ZSM-5 at RT: (A) after evacuation of fresh catalyst at 773 K, (B) after reaction with propene at 623 K and (C) after reaction with C_3H_6 and O_2 at 623 K. (———) NO and (- - -) O_2.

was pretreated in He flow at 773 K for 1 h. NO(5%)/He was adsorbed for 20 min at RT. NO desorption peaks appeared between 363 and 473 K. Several researchers [11–14] reported that these peaks were due to desorption of NO on Cu (+1). After the reaction with propene on Cu/ZSM-5, NO was adsorbed at RT. During the TPD of this sample, the only small peak appeared at 373 K. It is suggested that the sites on which NO can be adsorbed are covered with the carbonaceous species. After reaction with C_3H_6 and O_2 at 623 K, the catalyst was cooled down to RT in He and then NO was adsorbed. The desorption of NO was detected between 363 and 473 K and O_2 desorption peak appeared with NO desorption peak at 643 K. Armor and Li [11] reported that NO and O_2 peak at high temperature is due to the decomposition of NO_2 on the Cu ions and these desorption peaks are found to be due to the adsorption of NO on the oxidized Cu ions. It was indicated that after the reaction with C_3H_6 and O_2, Cu ions were cleaned and oxidized by O_2.

The intermediates formed during the SCR of NO by propene over Cu–ZSM-5 were identified and their reactivities were measured using FTIR. As shown in Fig. 10, the band at 1624 cm^{-1} assigned to NO_2 species adsorbed on Cu(II) was observed after exposing Cu/ZSM-5 to NO or NO/O_2 at 623 K. Also, the band at 2250 cm^{-1} assigned to –NCO species was

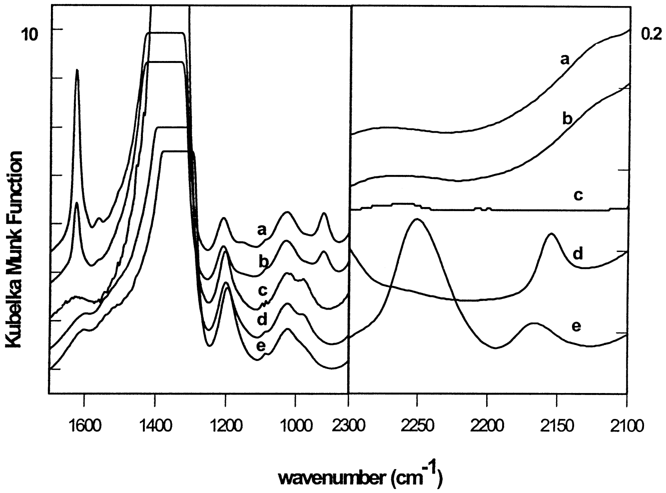

Fig. 10. In situ DRIFT spectra during the reaction with (a) NO/O_2, (b) NO, (c) NO/C_3H_6, (d) C_3H_6/O_2 and (e) $NO/C_3H_6/O_2$.

observed during the SCR at 623 K. The NO_2 species adsorbed on Cu ions was reduced to produce N_2 by propene without the formation of –NCO.

After Cu/ZSM-5 was treated in $NO/C_3H_6/O_2$ (3300 ppm/3300 ppm/7%) at 623 K, the catalyst was exposed to either 20% O_2 or NO/O_2 (5000 ppm/10%) at various temperatures. The IR band of the –NCO species did not decrease after exposure to O_2 at 350°C for 53 min (Fig. 11(A)). This band was significantly weakened as the O_2 exposure temperature increased above 723 K (Fig. 11(B)). However, when exposed to NO/O_2 at 623 K, the intensity of the band of the –NCO species decreased markedly as shown in Fig. 12.

Fig. 13 shows Cu $2p_{3/2}$ XPS spectra of Cu/ZSM-5 as a function of temperature in the SCR reaction. SCR reaction condition is in the strongly oxidizing condition ($NO/C_3H_6/O_2$=3300 ppm/3300 ppm/7%). The oxidation of Cu(I) to Cu(II) was achieved at 623 K in the SCR reaction. However, the peak at 937 eV significantly decreased in the SCR reaction at 773 K as shown Fig. 13(C). This indicates that the Cu(II)–O species decomposed at high temperature even in oxidizing conditions.

4. Discussion

It has been known that oxygen plays a very important role in SCR reaction over Cu/ZSM-5 because the SCR activity is drastically enhanced when oxygen is added to NO and hydrocarbon [15]. One of the roles of oxygen is the removal of carbonaceous species deposited on Cu ions as shown in the pulse experiment. At 623 K, propene was continued to make a carbonaceous deposit on the Cu site (Fig. 1). Since these species were maintained on Cu ions without desorption, Cu ions were occupied with these species after reaction with a small amount of propene. In the pulse reaction of C_3H_6 and NO, the exponential decrease in N_2 production indicates that when Cu sites are covered by carbonaceous species, the reaction does not proceed. Hence, NO should be adsorbed on Cu ions before propene is adsorbed on Cu ions to form a catalytic cycle. In the presence of oxygen, the carbonaceous species on Cu sites is oxidized. In the TPO spectrum the carbonaceous species on the Cu ions were found to be completely removed at about 623 K. Hence, NO can be reduced continuously by propene as shown in the sequential pulse reaction. Cho [16] reported that the maximum conversion of NO is closely related to the complete conversion of hydrocarbon reductants. It can be explained by the fact that at the temperature of complete conversion of hydrocarbon, all of the copper ions will be free of carbonaceous species which can inhibit the adsorption of NO. These results also indicate that the activation of NO on Cu ions is the first step for SCR.

Another role of oxygen is the oxidation of Cu ions. TPD results show that Cu/ZSM-5 contains oxygen

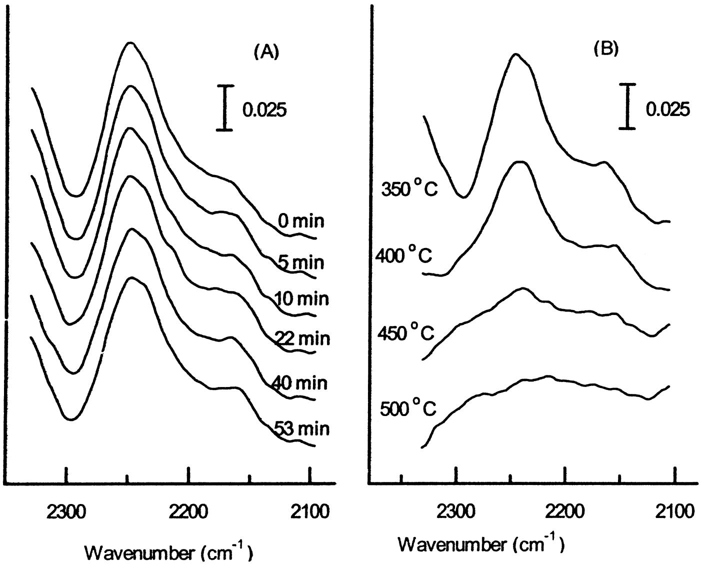

Fig. 11. (A) IR spectra of Cu/ZSM-5 as a function of time after O_2 is introduced at 623 K. (B) IR spectra of Cu/ZSM-5 for 40 min after O_2 (20%) is introduced at various temperatures to Cu/ZSM-5 pretreated with $NO/C_3H_6/O_2$ (3300 ppm/3300 ppm/7%) at 623 K. (All spectra were acquired by the subtraction of the background spectrum of Cu/ZSM-5 from the original spectrum.)

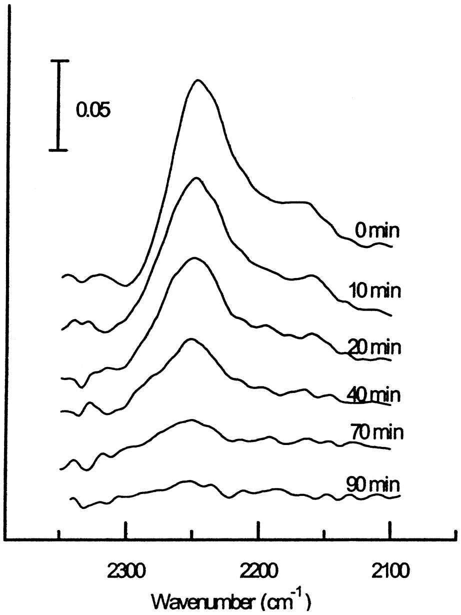

Fig. 12. IR spectra of Cu/ZSM-5 as a function of time after NO/O_2 (5000 ppm/10%) is introduced at 623 K to Cu/ZSM-5 pretreated with $NO/C_3H_6/O_2$ (3300 ppm/3300 ppm/7%) at 623 K. (All spectra were acquired by the subtraction of the background spectrum of Cu/ZSM-5 from the original spectrum.)

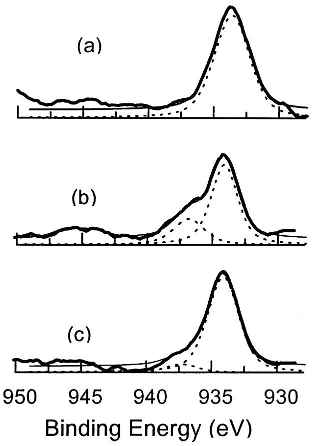

Fig. 13. Cu $2p_{3/2}$ core level spectra after the SCR reaction at: (A) 523, (B) 623 and (C) 773 K on Cu/ZSM-5, which was pretreated by the heating in He at 773 K.

species on the surface after reaction with C_3H_6/O_2 at 623 K. In pulse reaction of C_3H_6/O_2, part of the oxygen was adsorbed on the catalysts. Moreover, XPS spectra after reaction at various temperatures confirm that Cu–oxygen species are formed and correlated with the catalytic activity of the SCR reaction.

Jacobs and Beyer [17] reported that in Cu–Y zeolite, oxygen is adsorbed in a nondissociated form below 523 K, but at 523 K reoxidation occurs on Cu(I) ions that are able to dissociate oxygen. Valyon and Hall [18] supposed that Cu(II)–O–Cu(II) species are formed by extra lattice oxygen (ELO) carried into the catalysts during the preparation, and ELO is desorbed as O_2 at 623 K. Shpiro et al. [19–21] suggested the structure of Cu–oxygen species by XPS, ESR and X-ray absorption. Cu ions on ZSM-5 zeolite consists of both the isolated atom and a small aggregate containing ELO. ELO on Cu ion formed during the propene oxidation in excess oxygen can produce NO_2 with NO gas easily. It is considered that strong NO_2 peak at 1627 and 1507 cm^{-1} is due to the facile NO_2 formation by oxygen on Cu ion. Valyon and Hall [22] also found the NO_2 species stabilized on Cu/ZSM-5. They explained that high activity of Cu/ZSM-5 for NO decomposition can be due to these species.

DRIFT spectra illustrate the reactivities of –NCO with O_2 and NO/O_2 at 673 K, respectively. The decrease of IR 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 673 K. From these results it is thought that the SCR of NO can proceed via the reaction of surface nitro species with propene without the formation of –NCO, and after –NCO is produced on Cu/ZSM-5, it also can react with NO/O_2 to produce N_2 at 673 K. Hence, the dual site mechanism is proposed based on intermediates such as –NCO and $–NO_2$ in DRIFT spectra.

Pulse reaction shows that NO can be reduced by propene even without oxygen at the beginning of the reaction. NO is adsorbed on Cu ions containing oxygen which was formed through NO decomposition. Cu(II)–NO_2 species remained. This was evidenced by IR spectrum obtained during the reaction of NO on Cu/ZSM-5 as shown in Fig. 10. These NO_2 species are reacted with propene to produce N_2.

Li et al. [23] have proposed that adsorbed NO_2 is involved in the rate determining step and crucial in activating CH_4. Cowan et al. [24] observed that a first-order isotope effect in the rate of SCR over Co/ZSM-5 and H/ZSM-5 when CD_4 was substituted for CH_4, indicating that breaking a C–H bond is a rate limiting step in the formation of N_2. They suggested that CH_4 was activated by adsorbed NO_2 and the formed methyl species reacted further with NO_2 to produce N_2 and CO_2 over Co/ZSM-5. Lukyanov et al. [25] also suggested that NO_2 appears to be involved in initiating radical formation and intermediates are formed on the catalyst surface which can couple with NO or NO_2 to form the N–N bond. These results show that SCR reaction proceeds through the activation of hydrocarbon by NO_2.

The remaining problem is how NO_2 reacts with hydrocarbon to be reduced to N_2. Yokoyama and Misono [5] suggested the organic nitro-compounds like R–NO_2 and/or R–ONO as the possible intermediates during the SCR over Ce/ZSM-5. They observed that the IR bands assignable to organic nitro- and nitrite-compounds were developed on the surfaces of Ce/ZSM-5, SiO_2 and Pt–SiO_2 upon the exposure to a $NO_2/C_3H_6/O_2$ between RT and 473 K. These species can be a possible intermediate for the formation of N–N bond. Several FTIR studies have shown that HCN or –NCO are formed during the reaction between propene and NO over Cu/ZSM-5. The low reactivity of these species with NO and O_2 is in contrast with rapid reaction between NO_2 and propene [26]. Our result in TPO study showed that the carbonaceous compounds are formed during the reaction of propene over Cu/ZSM-5. It was shown in the pulse reaction between NO and propene that NO was constantly consumed even when CO_2 was not produced. This consumption of NO is considered to be due to the coupling of NO with the carbonaceous radicals. Kucherov et al. [27] showed that the presence of NO in the gas strongly inhibits the narrow ESR line associated with the carbonaceous deposits at 773 K. They explained that this could be due to the coupling of unpaired electron in the NO with the carbonaceous radicals. These results indicate that the compounds with carbon–nitrogen bonds can be present on the catalysts during the reaction between propene and NO over Cu/ZSM-5. However, this species is different from the intermediate formed by the reaction between propene and Cu–NO_2.

5. Conclusions

The role of oxygen during SCR reaction of NO can be summarized as follows:

1. Above 623 K propene is oxidized by O_2 and carbonaceous species are removed from Cu ions.

2. Cu ions are oxidized to Cu(II) adsorbed by oxygen, which enhances the formation of Cu(II)–NO_2 species.
3. The considerable reactivity of –NCO species with NO and O_2 is lower than that of NO_2 with propene.
4. Oxygen can partially oxidize the hydrocarbon species adsorbed on Cu.
5. Cu(II)–O species characterized by XPS are well correlated with the activity of NO SCR.

References

[1] M. Iwamoto, Symposium on Catalytic Technology for the Removal of Nitrogen Oxides, Catalysis Society of Japan, 1990, p. 17.
[2] W. Held, A. Konig, T. Richter, L. Puppe, SAE Paper 900469 (1990).
[3] M. Sasaki, H. Hamada, Y. Kintaichi, T. Ito, Catal. Lett. 15 (1992) 297.
[4] J.O. Pentunchi, W.K. Hall, Appl. Catal. B 2 (1993) L17.
[5] C. Yokoyama, M. Misono, J. Catal. 150 (1994) 9.
[6] M. Shelef, C.N. Montreuil, H.W. Jen, Catal. Lett. 26 (1994) 277.
[7] H. Yahiro, Y. Yu-u, H. Takeda, N. Mizuno, M. Iwamoto, Shokubai 35 (1993) 126.
[8] R.J. Argauuer, G.R. Landolt, US Patent 702 886 (1972).
[9] H.W. Jen, K. Otto, Catal. Lett. 26 (1994) 217.
[10] J.L. d'Itri, W.M.H. Sachtler, Appl. Catal. B 2 (1993) L7.
[11] J.N. Armor, Y. Li, Appl. Catal. 76 (1991) L1.
[12] W.X. Zang, H. Yahiro, N. Mizuno, J. Izumi, M. Iwamoto, Langmuir 9 (1993) 2337.
[13] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. Rajaran, T.J. Truex, A.P. Walker, Appl. Catal. B 2 (1993) 81.
[14] I.C. Hwang, M. Xin, S.I. Woo, Appl. Surf. Sci. 121/122 (1997) 310.
[15] M. Iwamoto, H. Yahiro, Y. Yu-u, N. Mizuno, Shokubai 32 (1990) 430.
[16] B.K. Cho, J. Catal. 142 (1993) 418.
[17] P.A. Jacobs, H.K. Beyer, J. Phys. Chem. 83 (1979) 174.
[18] J. Valyon, W.K. Hall, J. Phys. Chem. 97 (1993) 3054.
[19] E.S. Shpiro, W. Grunert, R.W. Joyner, G.N. Baeva, Catal. Lett. 24 (1994) 159.
[20] E.S. Shpiro, R.W. Joyner, W. Grunert, N.W. Hayes, M.R.H. Siddiqui, G.N. Baeva, Stud. Surf. Sci. Catal. 84 (1994) 1483.
[21] W. Grunert, N.W. Hayes, R.W. Joyner, E.S. Shpiro, M.R.H. Siddiqui, G.N. Baeva, J. Phys. Chem. 98 (1994) 10832.
[22] J. Valyon, W.K. Hall, J. Phys. Chem. 97 (1993) 1204.
[23] Y. Li, T.L. Slager, J.N. Armor, J. Catal. 150 (1994) 388.
[24] A.D. Cowan, R. Dumpelmann, N.W. Cant, J. Catal. 151 (1995) 356.
[25] D.B. Lukyanov, G. Sill, J.L. d'Itri, W.K. Hall, J. Catal. 153 (1995) 265.
[26] D.H. Kim, I.C. Hwang, S.I. Woo, Stud. Surf. Sci. Catal. 105 (1997) 1557.
[27] A.V. Kucherov, J.L. Gerlock, H. Jen, M. Shelef, J. Catal. 152 (1995) 63.