

Quantification and Redox Property of the Oxygen-Bridged Cu^{2+} Dimers as the Active Sites for the NO Decomposition over Cu-ZSM-5 Catalysts

Deuk Ki Lee[†]

Division of Civil and Environmental Engineering, Gwangju University, Gwangju 503-703, Korea

(Received 12 December 2003 • accepted 17 March 2004)

Abstract—For a range of Cu-ZSM-5 catalysts with different Cu-exchange levels on the two kinds of ZSM-5 with different Si/Al ratios, temperature programmed reduction using CO (CO-TPR) followed by H_2 (H_2 -TPR), and temperature programmed desorption of oxygen (O_2 -TPD) were conducted using an online mass spectrometer to characterize and quantify the copper species on the catalysts in the calcined state. Copper species on the ZSM-5 were quantitatively characterized as Cu^{2+} , $(\text{Cu-O-Cu})^{2+}$ and CuO after calcination in oxygen environment. The N_2 formation activities of the catalysts in the decomposition of NO were well correlated with the quantified catalytic amounts of the Cu^{2+} ions involved in the Cu-dimers, $(\text{Cu-O-Cu})^{2+}$. The mol fraction of the Cu ions present as the Cu-dimers increased at the sacrifice of the isolated Cu^{2+} with increasing Cu ion exchange level, suggesting that the species could be formed between the two Cu^{2+} in close proximity. Oxygen that could be thermally desorbed from the oxidized catalysts in the O_2 -TPD was responsible for the reduction of the Cu-dimers. It was concluded that the decomposition of NO over Cu-ZSM-5 catalyst proceeded by the redox of $(\text{Cu-O-Cu})^{2+}$, as active centers. With the temperature programmed surface reaction using N_2O or NO over an oxidized catalyst sample as well as the O_2 -TPD, it was possible to estimate the change of the oxidation state of the Cu ions engaged in the Cu-dimers.

Key words: NO Decomposition, Cu-ZSM-5, Characterization, Oxygen-bridged Cu-dimers, Active Sites, Redox Mechanism, Oxidation State

INTRODUCTION

Direct decomposition of NO to N_2 and O_2 has been receiving considerable attention as the most desirable way to remove nitrogen oxides because the reaction is thermodynamically favored at working temperatures and does not need any kind of reductants. Since the Cu-ion exchanged ZSM-5 catalyst was found highly active for this reaction at early 1980s, there has been much debate on the catalytic active species, and the NO decomposition process leading to N-N bond and O-O bond formation over this catalyst. Concerning the nature of active site of Cu-ZSM-5 for the reaction, Li and Hall [1991] reported that the reduction of the oxidized Cu species by the desorption of oxygen was a key requirement for the NO decomposition reaction. Jang et al. [1996] showed by using FTIR that the concentration of the Cu^+ sites changed reversibly upon switching the pretreatment gas from He to O_2 . Grunert et al. [1994] confirmed, using X-ray photoelectron spectroscopy and X-ray absorption spectroscopy, for the active catalysts a ready conversion between Cu^+ and Cu^{2+} depending on the atmosphere present. Throughout the study, using X-ray absorption near-edge structure, Liu and Robota [1993, 1994] obtained a linear correlation between the concentration of Cu^+ in Cu-ZSM-5 and the NO decomposition rate. All these results support the proposal that the reduced Cu^+ species are responsible for the NO decomposition reaction over Cu-ZSM-5 as active sites. In contrast, Shelef [1992] proposed a mechanism involving Cu^{2+} sites as active centers without any redox process. Teraoka et al. [2000] suggested that both Cu^{2+} and Cu^+ are involved in the NO decom-

position catalysis over Cu-MFI.

As to the mechanism of the NO decomposition on the Cu^+ as active species, two major conflicting opinions were suggested about the formation of N_2 molecules. One is that two NO molecules adsorb onto a single Cu^+ sites to form dinitrosyl complex $\text{Cu}^+(\text{NO})_2$, which decomposes, forming N_2O and leaving an oxygen atom behind as Cu^{2+}O^- [Li and Hall, 1991; Aylor et al., 1995; Spoto et al., 1994; Hall and Valyon, 1993; Hwang and Woo, 1997]. Aylor et al. [1995] proposed the sequence of the reaction that N_2 was formed via the reaction of N_2O with Cu^+ sites. O_2 formation was assumed to proceed via the release of O atoms from Cu^{2+}O^- and the subsequent reaction of O atoms with another Cu^{2+}O^- to produce Cu^{2+}O_2 . This mechanism was confronted with the problem of charge balance in the case that the oxygen left behind the decomposition of the dinitrosyl remains as O^{2-} because Cu^+ can only undergo a single electron oxidation [Valyon and Hall, 1993]. There was a report [Konduru and Chuang, 1999] that no correlation was found between the formation of N_2 and the $\text{Cu}^+(\text{NO})_2$ species at 35 °C. Alternatively to this mechanism, the mechanism that one NO molecule is adsorbed on one reduced copper site and another molecule on the other reduced Cu site located in close proximity to each other has been proposed, assuming the active sites in oxidized state as the oxygen bridged Cu-dimers, $(\text{Cu}^{2+}\text{-O}^{2-}\text{-Cu}^{2+})$ [Sakany et al., 1992; Moretti, 1994; Lei et al., 1995; Beutel et al., 1996; Kuroda et al., 1999; Campa et al., 1994; Yan et al., 1996; Goodman et al., 1998; Moden et al., 2002a]. This mechanism based on the oxygen bridged Cu-dimers not only solves the issue of charge unbalance, but makes it possible to explain much higher rates of N_2 formation that are usually observed for the excessively ion-exchanged Cu-ZSM-5 catalyst as compared with the under-exchanged [Moretti, 1994; Campa et al., 1994]. How-

[†]To whom correspondence should be addressed.

E-mail: dklee@gwangju.ac.kr

Table 1. Catalysts prepared

	Cu(116)-Z(14.7)	Cu(76)-Z(14.7)	Cu(262)-Z(29)	Cu(156)-Z(29)	Cu(51)-Z(29)
Composition, wt% Cu	3.31	2.24	3.88	2.25	0.76
Si	36.0	37.9	37.5	36.3	38.2
Al	2.42	2.50	2.73	2.66	2.76
Na	<0.08	0.51	<0.11	0.64	1.69
$\mu\text{mol Cu/g}$	521	352	611	354	120
Si/Al _f (atomic ratio)	14.3	14.6	28.7	28.5	28.9
Cu/Al _f (atomic ratio)	0.58	0.38	1.31	0.78	0.25
% Cu exchange level	116	76	262	156	51

ever, it has not been quantitatively determined how much proportion of the Cu loaded into ZSM-5 can participate in the oxygen bridged Cu-dimers, depending on the Cu ion exchange level and the Si/Al ratio of ZSM5, and their specific activity in the NO decomposition reaction.

In order to elucidate the NO decomposition reaction mechanism on the Cu-ZSM-5, copper species of the catalyst should be prior characterized quantitatively so that the catalytic activity of a catalyst could be evaluated on the basis of the number of working active sites. In relation to this, the researchers at Iglesia's group reported mechanistic evidence for the involvement of Cu-dimers during NO decomposition by analyzing the transient catalytic behavior [Moden et al., 2002b], and the spectroscopic and chemical characterization [Da Costa et al., 2002] of Cu-ZSM-5. However, the data in those papers were analyzed excluding the possible existence of CuO in the oxidized Cu-ZSM-5 catalysts. A number of authors [Sakany et al., 1992; Moretti, 1994; Lei et al., 1995; Beutel et al., 1996; Kuroda et al., 1999; Campa et al., 1994; Yan et al., 1996; Goodman et al., 1998] suggest that copper species on the Cu-ZSM-5 catalyst in oxidized state consist of $(\text{Cu-O-Cu})^{2+}$, CuO and Cu^{2+} . The present article is aimed at characterizing and quantifying the Cu species of Cu-ZSM-5 considering the possible existence of bulk CuO in the catalysts, and to evaluate the NO decomposition activity on the basis of the quantified number of actual active sites and its redox behavior during NO decomposition catalysis. Here, Cu-ZSM-5 catalysts with different Cu-exchange levels using two kinds of ZSM-5 of different Si/Al ratios were prepared and their NO decomposition activity to N_2 was measured. For characterization, CO-TPR followed by H_2 -TPR as well as O_2 -TPD with an online mass spectrometer (MS) was conducted. TPSR using NO or N_2O over an oxidized catalyst sample was conducted to investigate the NO decomposition catalysis in relation with the change of the oxidation state of the active Cu species of the catalyst with increasing temperature.

EXPERIMENTAL

1. Catalyst Preparation

Cu-ZSM-5 catalysts with different Cu loadings were prepared by ion exchange of Cu^{2+} ions (1,000 mL of deionized water solutions of 0.01–0.1 M copper acetate (Sigma Aldrich)) into about 10 g of Na-ZSM-5 (Zeochem). Two kinds of Na-ZSM-5 with different ratio of Si to Al in framework positions (Al_f) (Si/Al_f=14.7, or 29) were used. One (Si/Al_f=14.7) is free from extraframework Al, but the other (Si/Al_f=29) consists of 46% of total Al in extraframework

positions. Ion exchange was carried out at room temperature followed by rinsing with 1,000 ml of doubly de-ionized water three times. The exchange procedure was repeated for some samples to increase the Cu-content. The exchanged samples were dried at 110 °C for 24 h, and made to 60–120 mesh (125–250 μm) particles. ICP analysis results of the catalysts for Si, Al, Na and Cu content are found in Table 1. For the notation of a catalyst, the number in parentheses following Cu and Z indicates the %Cu exchange level (%Cu EL) and the Si/Al_f, respectively. The %Cu EL is defined as two hundred times the atomic ratio of total copper to Al_f of ZSM-5, i.e., 100% corresponds to one Cu^{2+} exchanged per two Al atoms.

2. Measurement of Catalytic Activity

Catalytic activities of the prepared samples were measured with a multitube reactor designed for conducting the activity test of catalysts for up to eight samples simultaneously. The reactor consisted of eight stainless steel tubes (inner diameter 2.5 mm) in parallel, which were inserted within a stainless steel block in order to ensure uniform temperatures. For each reactor, thermocouples (type K) were placed in small side holes in the steel block, ending at the wall of each reactor in which the mid-point of the catalyst bed was located, and the measured temperature difference between them during the run was within 2 °C. The steel block was placed in a tube furnace. About 0.05 g of each fresh catalyst samples was loaded to the reactors. The catalysts in the reactors were pretreated with 30 cm^3/min of He (UHP grade) for 2 h at 550 °C before their exposure to the reactant gas. The reactant gas was the mixture of 1.0% NO/9.98% Ar/89.02% He (1% NO gas). The 1% NO gas flow through each reactor was controlled to 60 cm^3/min (0.05 $\text{g}/(\text{cm}^3/\text{min})$). Exit streams at steady state were routed to an online MS (MKS Instruments) one by one using an eight-port switching valve (Valco) for analysis. The monitored species by the MS were as follows: He (4 amu), O (16), H_2O (18), NO (30), N_2 (28), O_2 (32), Ar (40), N_2O (44) and NO_2 (46). In order to calibrate the MS, a calibration gas mixture containing 0.05% N_2 , 0.05% O_2 , 0.05% N_2O , 10% Ar (used as internal standard) and 89.85% He was used. For the calibration of NO_2 MS signal, a mixed gas of 0.05% NO_2 /9.94% Ar/90.01% He was used.

3. Temperature Programmed Experiments

CO-TPR for the oxidized samples followed by subsequent H_2 -TPR as well as the O_2 -TPD was conducted for all the catalysts. NO-TPSR was conducted for the catalyst Cu(116)-Z(14.7) in oxidized state. All these experiments were carried out in a quartz reactor loaded with 200–300 mg of catalyst sample, using the on-line MS. The pretreatment procedure for the fresh catalyst samples was as fol-

lows: For the catalyst oxidation, the loaded sample was pretreated with a gas mixture of 49% O₂/He (O₂ gas) flowing at 50 cm³/min. During this pretreatment, the reactor was heated at a rate 10 °C/min up to 500 °C, and maintained at this temperature for 2 h. The reactor was then cooled to room temperature. At room temperature, pure He (100 cm³/min) was introduced instead of the O₂ gas in order to remove physisorbed oxygen on the catalyst. If the MS signal of O₂ decreased enough to be insignificant in the flow of He, the catalyst sample was ready for each of the experiments. For the CO-TPR, He was replaced with 1% CO/He flowing at 30 cm³/min. After the stabilization of all the MS signals, reactor temperature was raised by 10 °C/min up to 550 °C. For the subsequent H₂-TPR following the CO-TPR, the CO gas was replaced with He (100 cm³/min), and the temperature was kept at 500 °C for the removal of CO from the catalyst sample. The reactor, then, was allowed to cool to room temperature, at which He gas was replaced with 5% H₂/Ar at 25 cm³/min. After all the MS signals had been stabilized, temperature was raised by 10 °C/min up to 650 °C. For the O₂-TPD, the flow rate of He was 30 cm³/min, and the reactor was heated to 650 °C at 10 °C/min and kept at the same temperature for 20 min. During these experiments, the MS signals of H₂ (2 amu), He (4), H₂O (18), CO (28), O₂ (32), Ar (40), and CO₂ (44) were monitored. CO₂ produced from the CO-TPR was calibrated by using a known amount of CuO (Aldrich). In the experiment of NO-TPSR, 0.464% NO gas was used as reactant by mixing the 1% NO gas with He (UHP grade). This diluted NO gas was introduced at a rate of 100 cm³/min to the catalyst sample after pretreatment procedure. Reactor temperature was raised by 10 °C/min from room temperature to 650 °C after all the MS signals had been stabilized. In the N₂O-TPSR for the oxidized catalyst, 0.1% N₂O in He was used as reactant by mixing the two streams of 1% N₂O/He and He. Total flow rate of the mixture was 100 cm³/min. During the TPSR, the same compounds as described in the measurement of catalytic activity were monitored by using the MS.

RESULTS AND DISCUSSION

1. NO Decomposition Activity

Activities of the catalysts in the decomposition reaction of NO at various temperatures are shown in Fig. 1. The turnover frequency (TOF) of NO to N₂ is defined as twice the number of N₂ molecules formed per Cu atom per second. Except the catalyst Cu(51)-Z(29) showing very low catalytic activity, the dependence of activities of the catalysts on temperature shows the usual behavior observed in the NO decomposition reaction over Cu-ZSM-5 catalysts [Li and Hall, 1991; Goodman et al., 1998]. The catalytic activity increases up to 500 °C and decreases with further increase in temperature. As long as the catalysts based on the same parent ZSM-5 are concerned, the catalyst with higher %Cu EL shows higher NO decomposition activity.

2. CO-TPR Followed by H₂-TPR

CO-TPR was conducted to characterize the Cu species in association with oxygen as a result of oxidative pretreatment. During the course of CO-TPR, pure copper ions on Cu-ZSM-5 samples are not reduced, but copper oxides and oxo-cations are reduced to Cu metals and cations, respectively, with simultaneous production of CO₂. Copper species present in the catalyst after the CO-TPR

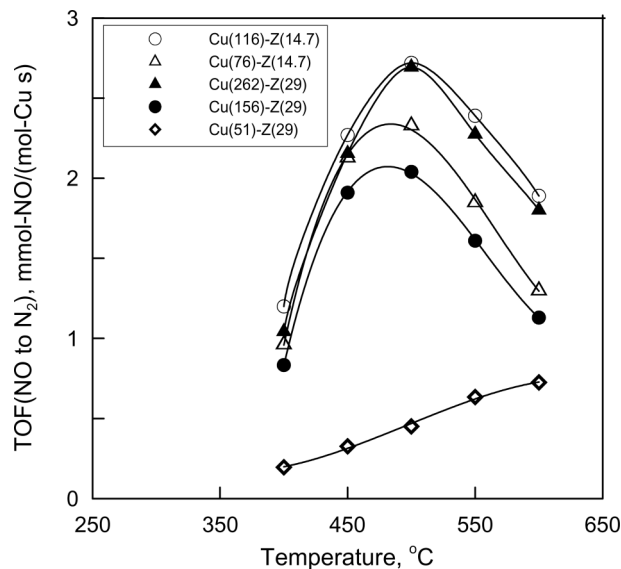


Fig. 1. NO decomposition activities of the catalysts with temperature (modified from the paper of Da Costa et al., 2002).

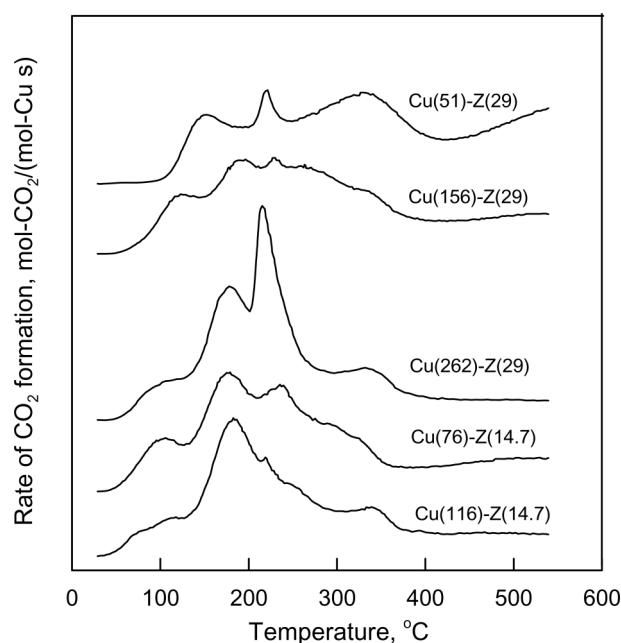


Fig. 2. CO-TPR profiles of the oxidized catalysts.

consist of copper metal and ions such as Cu⁺ and Cu²⁺. In the H₂-TPR following the CO-TPR, such copper ions can be reduced to Cu metals by consuming H₂. So, the combined method of CO-TPR for an oxidized catalyst and a subsequent H₂-TPR enables us to determine the amounts of each copper species present in the sample of oxidized state.

Fig. 2 shows the CO-TPR profiles of all the catalysts, represented by the molar rate of CO₂ formation per Cu atom per second. Except the catalyst Cu(51)-Z(29) having the lowest %Cu EL, it is a common feature that a main peak with the largest reduction area appears at temperatures between 180-190 °C. A sharp reduction peak appears at temperatures between 220-240 °C for all the catalysts, and par-

ticularly for the Cu(262)-Z(29) catalyst having the highest %Cu EL, it appears with a strong intensity. Shoulder-like peaks with relatively small and broad intensities are present at lower temperatures (100–121 °C) and at higher temperatures (330–350 °C). For the catalysts of oxidized state, these suggest that the copper species in association with oxygen exist as at least two major different kinds. As reported [Sakany et al., 1992; Moretti, 1994; Lei et al., 1995; Beutel et al., 1996; Kuroda et al., 1999; Campa et al., 1994; Yan et al., 1996; Goodman et al., 1998], copper species on the Cu-ZSM-5 catalyst in oxidized state consist of $(\text{Cu-O-Cu})^{2+}$, CuO and Cu^{2+} , as the first two reducible with CO. However, not so many data in literature are available for the CO-TPR of Cu-ZSM-5. From the CO-TPR for an oxidized Cu-ZSM-5 with 150% Cu EL, Sarkany et al. [1992] obtained only two completely separated reduction peaks centered at about 190 and 260 °C, which were assigned to $(\text{Cu-O-Cu})^{2+}$ and CuO, respectively. In view of the Sarkany et al.'s assignments, the major peaks between 180–190 °C can be assigned to the reduction of $(\text{Cu-O-Cu})^{2+}$ species, while the sharp peaks between 220–240 °C to that of CuO. The total amounts of CO_2 formation in the CO_2/Cu molar ratio during CO-TPR for the catalysts are shown in Table 2. If the CO-reducible copper species in the oxidized catalysts consist only of both $(\text{Cu-O-Cu})^{2+}$ and CuO, then the stoichiometry of CO reduction for each species is as follows [Sakany et al., 1992]:



Fig. 3 shows the H_2 -TPR profiles of the CO-reduced samples, expressed as the molar rate of H_2 consumption per Cu atom per second. In general, two reduction peaks appear for all the catalysts. After the CO reduction, copper species which can further be reduced in the H_2 -TPR are only the copper cations such as Cu^+ and Cu^{2+} , where Cu^+ has been generated by the CO-reduction of $(\text{Cu-O-Cu})^{2+}$ by the reaction (1) whereas Cu^{2+} has survived from the catalyst of oxidized state. In reference to the H_2 -TPR results of Sarkany et al. [1992], Beutel et al. [1996], and Kim et al. [2001], the peak at about 150 °C can be assigned to the reduction of Cu^{2+} to Cu^+ , while the peak at higher temperature to that of Cu^+ to Cu^0 by the reduction reaction as follows:

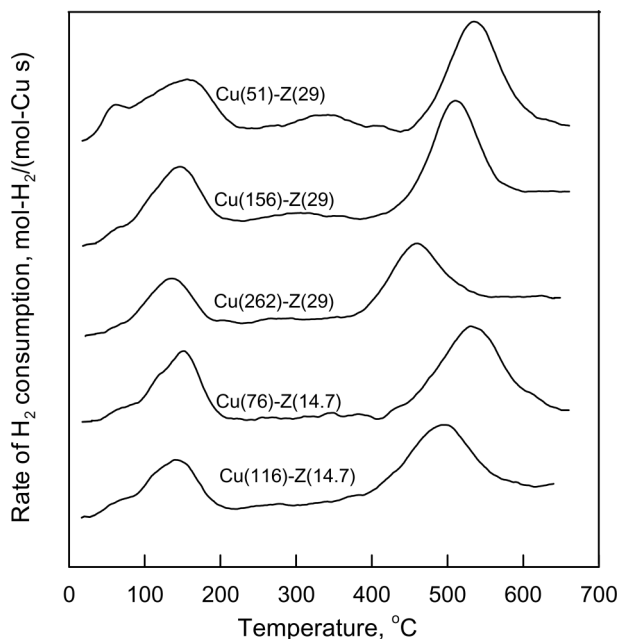
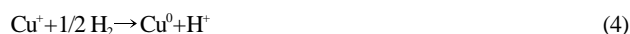


Fig. 3. H_2 -TPR profiles of the catalysts after CO-TPR.



The amounts of H_2 consumption in the molar ratio of H_2/Cu are shown in Table 2. It is possible to calculate the quantity of Cu^{2+} present on a catalyst by using the amount of H_2 consumed in the first reduction peak. By the stoichiometry in the reaction (3), the mol fraction of Cu in the form of Cu^{2+} for a catalyst is twice the molar ratio of H_2/Cu obtained from the first reduction peak of H_2 -TPR. In order to estimate the mol fraction of Cu involved in the $(\text{Cu-O-Cu})^{2+}$ species, the H_2 consumption attributable to the reduction of the Cu^+ species, generated by reaction (3) in the first reduction peak, needs to be subtracted from the second H_2 consumption peak area. This net consumption of H_2 is responsible for the reduction of Cu^+ generated by the reaction (1); therefore, the mol fraction of Cu present as the Cu-dimers can be calculated as follows:

Table 2. Characterization results

	Cu(116)-Z(14.7)	Cu(76)-Z(14.7)	Cu(262)-Z(29)	Cu(156)-Z(29)	Cu(51)-Z(29)
CO-TPR, CO_2 produced/ Cu^a	0.31	0.30	0.38	0.31	0.23
H_2 -TPR, H_2 consumed/ Cu^a					
total	0.67	0.70	0.58	0.69	0.73
1 st peak	0.24	0.27	0.20	0.27	0.33
2 nd peak	0.43	0.43	0.38	0.42	0.40
Distribution of Cu, mol%					
as Cu^{2+}	48.0	54.0	40.0	54.0	66.0
as $(\text{Cu-O-Cu})^{2+}$	38.0	32.0	36.0	30.0	14.0
as CuO	14.0	14.0	24.0	16.0	20.0
Calculated O/ Cu^a based on the mol% Cu distribution	0.33	0.30	0.42	0.31	0.27
O_2 -TPD, $\text{O}_{\text{desorbed}}/\text{Cu}^a$	0.20	0.14	0.18	0.13	0.07

^ain molar ratio.

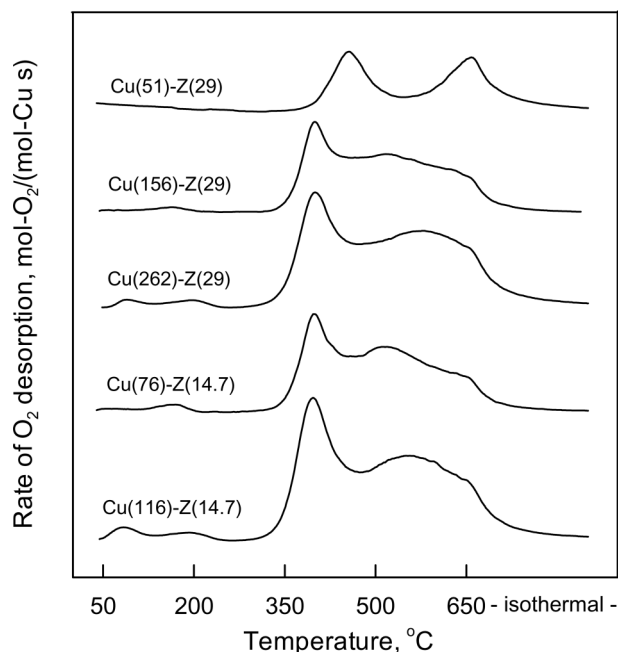


Fig. 4. O₂-TPD profiles of the oxidized catalysts (partly published in the paper of Da Costa et al., 2002).

$$\text{Mol fraction of Cu in } (\text{Cu-O-Cu})^{2+} = 2 \times [(\text{H}_2/\text{Cu})_{2\text{nd peak}} - (\text{H}_2/\text{Cu})_{1\text{st peak}}] \quad (5)$$

The mol fraction of Cu as CuO can be obtained with a balance. The mol percents of Cu involving in each species on oxidized samples are summarized in Table 2. Based on these mol% values, the average molar ratio of O to Cu for the catalysts has been calculated as shown in Table 2. The calculated molar ratios O/Cu are in a reasonable agreement with the ratios, CO₂/Cu obtained from CO-TPR.

3. O₂-TPD

Fig. 4 shows the O₂-TPD profiles represented by the molar rate of O₂ desorption per Cu atom per second. These O₂ desorption profiles were obtained in He flow by raising the temperature up to 650 °C and maintaining it isothermally for additional 20 min. For the catalysts with %Cu EL higher than 51%, a narrow desorption peak appears at around 400 °C, accompanied by a broad peak at higher temperature. Only for the catalyst Cu(51)-Z(29), in contrast to the other catalysts, this first narrow desorption peak appears at higher temperature, 462 °C. As far as these high Cu% EL catalysts, except the Cu(51)-Z(29), are concerned, the obtained O₂-TPD profiles are consistent with the results reported previously [Teraoka et al., 2000; Konduru and Chuang, 1999; Eranen et al., 1994]. The weak peaks at temperatures less than 300 °C can be interpreted as possibly due to the desorption of molecularly adsorbed oxygen, whereas the oxygen desorbed at higher temperatures to the oxygen in atomic form [Teraoka et al., 2000; Eranen, 1994; Wang et al., 1997]. The total amounts of oxygen desorbed from the catalysts throughout the O₂-TPD are listed in Table 2. In the case of the catalyst, Cu(116)-Z(14.7), the amount oxygen desorption, 0.2 O/Cu is the same as that obtained by Valyon and Hall [1993] for the Cu-ZSM-5 catalyst with %Cu EL 114%.

4. N₂O- or NO-TPSR for an Oxidized Catalyst Sample

In order to investigate the redox behavior of Cu-ZSM-5 in the NO decomposition, N₂O- or NO-TPSR has been conducted for the

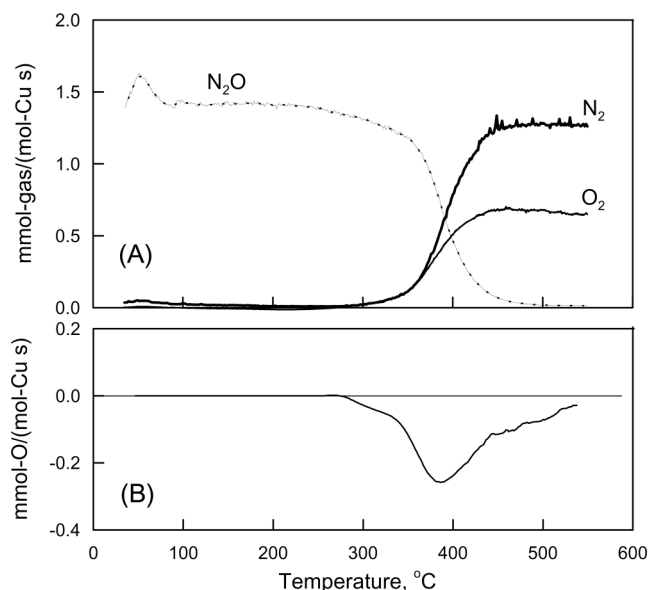


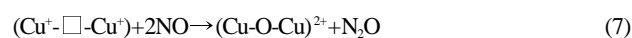
Fig. 5. (A) N₂O-TPSR profiles over the oxidized catalyst of Cu(116)-Z(14.7). (B) Instantaneous rate of surface atomic oxygen in-out per Cu atom.

oxidized catalyst, Cu(116)-Z(14.7), which has been determined as the most active and having the highest mol% of Cu as the Cu-dimers. Fig. 5(A) shows the N₂O-TPSR profiles for the oxidized Cu(116)-Z(14.7). At temperatures below 100 °C, the amount of N₂O desorbed is negligibly small, indicating that N₂O hardly stays on the catalyst as adsorbed. At about 280 °C, N₂O starts to decompose into N₂ and O₂, and above 450 °C, it decomposes completely with N₂/O₂ stoichiometric ratio, 2. Up to about 373 °C, stoichiometric ratio of N₂ to O₂ is 1, suggesting that surface oxygen is removed from the catalyst. Using the stoichiometry of N₂O decomposition, instantaneous surface oxygen balance of the catalyst throughout N₂O-TPSR can be set up as follows:

$$\text{O/Cu}(1/\text{s}) = \text{TOF}(\text{N}_2) - 2 \times \text{TOF}(\text{O}_2) \quad (6)$$

Fig. 5(B) shows the incoming and outgoing rate of surface oxygen calculated by Eq. (6). The maximum rate of surface oxygen removal is observed at 392 °C. Total amount of oxygen removed from the catalyst up to 550 °C is 0.175 O/Cu.

NO-TPSR profiles of the oxidized catalyst of Cu(116)-Z(14.7) are shown in Fig. 6(A). In this figure, the original MS intensity of NO can be obtained by four times the plotted intensity. As a result of the surface reaction of NO, various kinds of products appear with increasing temperature. In a range of relatively low temperatures, it can be observed that N₂O is formed in a dynamic relation with reactant NO. In the redox mechanism [Lei et al., 1995; Beutel, 1996], the formation of N₂O needs the adsorption of two NO on the reduced Cu-dimer:



Up to 230 °C, any oxygen-containing products besides N₂O are not evolved in significant amounts. That means a gradual increase on the catalyst surface oxygen, and a gradual change in the structure of the surface-adsorbed species. An instantaneous surface oxygen

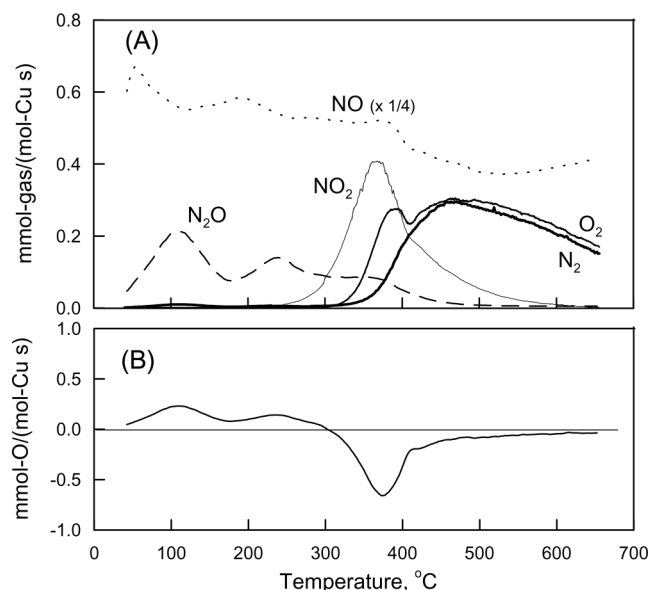
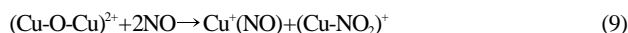


Fig. 6. (A) NO-TPSR profiles over the oxidized catalyst of Cu(116)-Z(14.7) (partly published in the paper of Modén et al., 2002b). (B) Instantaneous rate of surface atomic oxygen in-out per Cu atom (partly published in the paper of Modén et al., 2002b).

balance of the catalyst throughout the NO-TPSR can be made as follows:

$$\text{O/Cu}(1/\text{s}) = 2 \times \text{TOF}(\text{N}_2\text{O}) + \text{TOF}(\text{N}_2\text{O}) - 2 \times \text{TOF}(\text{O}_2) - \text{TOF}(\text{NO}_2) \quad (8)$$

As shown in Fig. 6(B), oxygen on the catalyst surface continues to be increased up to 311 °C as a result of N₂O evolution without accompanying any other products. The appearance of NO₂ starting from 230 °C is thought to result from the desorption rather than the instant reaction of NO, because there is no corresponding decrease in the intensity of reactant NO. As shown in Fig. 6(B), it should be noted that the desorption of a large amount of NO₂ contributes to the removal of oxygen from the catalyst. It is therefore understood that the oxygen left behind on the surface due to the evolution of N₂O has been stored mainly in the form of NO₂, consistently with Wang et al. [1997] and as evidenced in the IR study [Aylor et al., 1995; Hwang et al., 1998]. According to Beutel et al. [1996], an oxidized Cu-dimer can be reduced by the adsorption of two NO, yielding Cu⁺-NO and NO₂, possibly adsorbed on Cu⁺ forming a (Cu-NO₂)⁺ complex:



They stated that this reaction takes place swiftly even at room temperature. As suggested in reaction (7), N₂O evolution is possible between two Cu⁺(NO) species generated by reaction (9) if closely located, leaving (Cu-O-Cu)²⁺ again. As a result of this process, the surface concentration of the adsorbed NO₂ species will be increased. The adsorbed NO₂ begins to desorb at 230 °C, with a peak at 370 °C. The occurrence of NO₂ continues up to 600 °C. Total amount of NO₂ evolved throughout the TPSR for the oxidized catalyst is 0.27 NO₂/Cu.

Following the NO₂ desorption, the removal of surface oxygen begins to occur in the form of molecular oxygen at about 300 °C,

with a peak at 395 °C. It is thought that the molecular oxygen evolved in this range of temperatures originates from the same source as observed in the O₂-TPD, as shown in Fig. 4. Following this oxygen removal, N₂ starts to evolve. Most of oxygen evolved at temperatures above 412 °C can be regarded as resulting from the NO decomposition reaction because TOF(N₂) and TOF(O₂) are nearly equivalent each other. However, as can be seen in Fig. 6(B), oxygen removal from the catalyst still continues up to 650 °C. During the course of NO-TPSR for the oxidized Cu(116)-Z(14.7), total amount of oxygen added to the surface is 0.2 O/Cu, and that removed from the surface is 0.35 O/Cu.

5. (Cu-O-Cu)²⁺ Species as Active Sites for NO Decomposition Reaction

Throughout the combined TPR using CO and H₂ in series, not only the total amount of oxygen retained by the oxidized Cu-ZSM-5 catalyst, but also the mol fractions of Cu engaged in each three species Cu²⁺, (Cu-O-Cu)²⁺ and CuO, have been determined, as listed in Table 2. When comparing the amount of oxygen desorbed throughout the O₂-TPD with that determined by the CO-TPR, it is apparent that not all the oxygen retained by the oxidized catalyst can desorb in the O₂-TPD. The species responsible for the oxygen desorbed throughout the O₂-TPD (Fig. 4) is the oxidized Cu-dimer, (Cu-O-Cu)²⁺. This is confirmed by a parity plot about the amount of O desorbed in the O₂-TPD against that of O retained in the Cu-dimers present on a gram of catalyst. As shown in Fig. 7, quite a good correspondence exists between the two, suggesting that the oxidized Cu-dimers are reduced to the Cu⁺ cations by getting rid of the bridged oxygen throughout the O₂-TPD. It is also proved that most of the oxygen desorbed throughout the O₂-TPD shown in Fig. 4 result from the oxygen in the oxidized Cu-dimers irrespective of their peak locations of desorption. In order to ascertain the involvement of Cu-dimers as the active sites for NO decomposition reaction to N₂, the catalytic activities in a gram weight base were plotted against the amounts of the Cu-dimers contained per gram of catalysts. As shown in Fig. 8, excellent correlations at various temperatures exist between

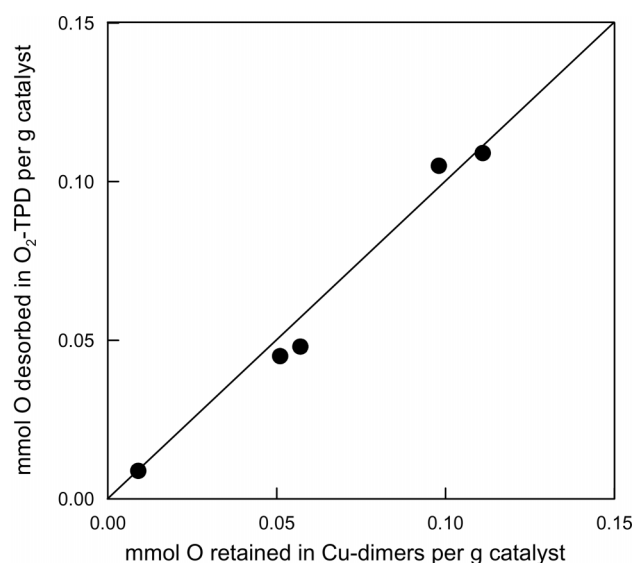


Fig. 7. Parity plot for the amount of atomic oxygen desorbed throughout O₂-TPD against that retained in the Cu-dimers per a gram of the oxidized catalyst, Cu(116)-Z(14.7).

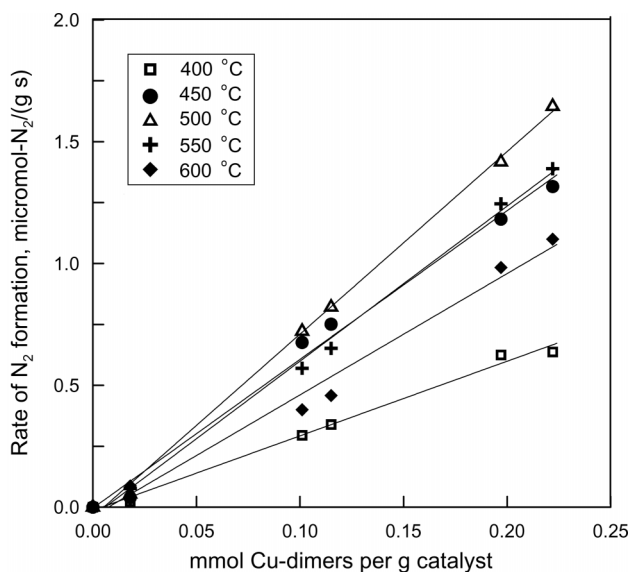


Fig. 8. Changes of the rate of N_2 formation with the amount of Cu-dimers based on a gram of catalysts.

the two. It is therefore assuredly concluded that the copper cations consisting of the Cu-dimers are directly responsible for the catalysis of the NO decomposition reaction.

It is therefore of prime importance for an active Cu-ZSM-5 catalyst to get the loaded copper in the form of Cu-dimers as much as possible. The effects of the %Cu EL and the Si/ Al_T of parent ZSM-5 upon the mol% of Cu formed as the Cu-dimers and the isolated Cu^{2+} ions need to be investigated. As shown in Fig. 9, the trend is the same as generally evidenced by previous experiments [Moretti, 1994; Campa et al., 1994]. At low %Cu EL, most of the exchanged Cu ions remain in the isolated Cu^{2+} . With increasing %Cu EL, the fraction of exchanged Cu ions in the Cu-dimers increases at the sac-

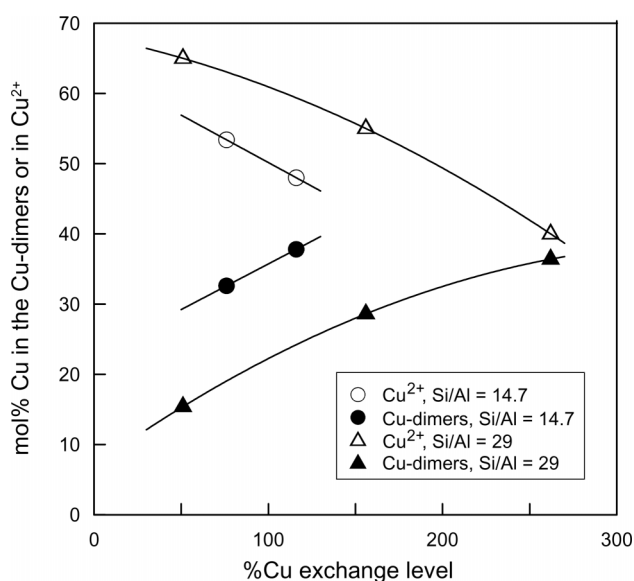


Fig. 9. Effects of the %Cu exchange level and the Si/ Al_T ratio of parent ZSM-5 upon the mol-percents of the exchanged Cu in the Cu-dimers or in Cu^{2+} .

rifice of the isolated Cu^{2+} . This is a clear evidence for the hypothesis that the Cu-dimers can be formed between the two Cu^{2+} in close proximity. As a matter of course, catalysts based on the ZSM-5 with Si/ Al_T ratio 14.7 show higher fractions of Cu in the Cu-dimers than those on the ZSM-5 with the ratio 29 because the former has twice more ion-exchangeable framework Al sites than the latter. In contrast, the formation of CuO is mostly not thought to be dependent on the %Cu EL. However, as can be seen in Table 2, the presence of the extraframework Al in the parent ZSM-5 possibly results in greater amount of CuO formation. As clearly observed by a sharp CO-TPR peak at 220 °C in Fig. 2, the catalyst Cu(262)-Z(29) based on the ZSM-5 containing extra-framework Al (54%) has the largest fraction of Cu as CuO.

6. Redox Behavior of the $(\text{Cu-O-Cu})^{2+}$ Species in NO Decomposition

It is important to understand how the Cu-dimers work as active centers in the actual NO decomposition reaction. This could be answered by investigating the redox behavior of the Cu-dimers in the reaction. Throughout the N_2O - or NO-TPSR (Fig. 5, Fig. 6) as well as the O_2 -TPD (Fig. 4), it has been confirmed that the catalyst surface oxygen increases or decreases depending on temperature and gas phase environment. This behavior is certainly related to the redox of the Cu-dimers. The molar ratio of O to the Cu (O/Cu_d) involved in the dimer as oxidized $(\text{Cu-O-Cu})^{2+}$ is given by $0.5 \text{ O}/\text{Cu}_d$. When the dimer is fully reduced to two Cu^+ , O/Cu_d is 0. Under this concept, it is possible to evaluate the change of oxidation state occurring in the Cu-dimers with temperature and the environment of gas phase, as shown in Fig. 10. This plot was obtained by integrating the instantaneous rate of surface incoming-outgoing atomic oxygen obtained from the O_2 -TPD, and N_2O - and NO-TPSR for the catalyst Cu(116)-Z(14.7) in oxidized state, as shown in Fig. 4, Fig. 5(B), and Fig. 6(B), respectively. At room temperature before heating, the oxidation state of the catalyst in all the cases shown in Fig. 10 is $0.5 \text{ O}/\text{Cu}_d$ because the Cu-dimers are present as $(\text{Cu-O-Cu})^{2+}$ by pre-oxidation. The value of oxidation state given in Fig. 10 can be regarded as indicating an average oxidation state of all Cu-dimers on the catalyst.

During the course of O_2 -TPD in He, the oxidation state decreases just a little by 340 °C, and above that temperature, begins to decrease

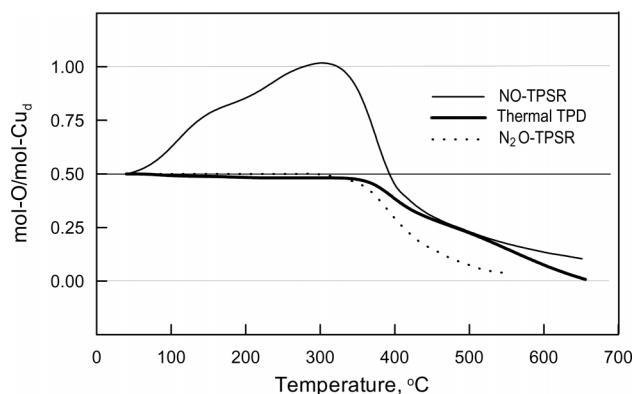


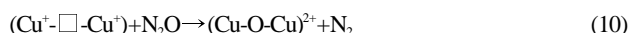
Fig. 10. Changes of the oxidation state of the Cu ion engaged in the Cu-dimers during the various temperature programmed experiments for the initially oxidized catalyst of Cu(116)-Z(14.7).

with increasing temperature, and comes to 0 O/Cu_d (fully reduced state) at 650 °C. The total amount of oxygen desorbed throughout the O₂-TPD has been measured as 0.53 O/Cu_d (=0.2 O/Cu), close to the difference (0.5 O/Cu_d) between the oxidized and the reduced state. For N₂O-TPSR, similar to the O₂-TPD in He, there is no net oxidation effect of N₂O on the catalyst before it decomposes on the catalyst. Therefore, oxidation state does not change at low temperature region, but above about 300 °C, it decreases at a faster rate than that in the O₂-TPD. Oxidation state is lowered to 0.04 O/Cu_d at 550 °C, indicating that about 92% of the total Cu-dimers contained in the catalyst are reduced and available for the reaction.

During the course of NO-TPSR with increasing temperature, the oxidation state of initial 0.5 O/Cu_d increases to the value 1.02 O/Cu_d by 320 °C, and above that temperature, it decreases rapidly to 0.4 O/Cu_d, and slowly to 0.1 O/Cu_d at 650 °C. At 650 °C, the oxidation state 0.1 O/Cu_d indicates that about 80% of the Cu-dimers are in the reduced state. The fact that the difference (0.92 O/Cu_d) between the highest and the lowest O/Cu_d is given by the value close to 1.0 O/Cu_d, clearly demonstrates that the catalysis of NO decomposition reaction over Cu-ZSM-5 is accomplished by the redox cycle of the Cu-dimers. The oxidation state 1.02 O/Cu_d observed between 300 and 320 °C is possible for the case that each of the Cu ions in the Cu-dimers has adsorbed NO₂ on it, i.e., possibly (Cu-NO₂)⁺ as suggested by Beutel et al. [1996]. The oxidation state of (Cu-NO₂)⁺ species is calculated as 1.0 O/Cu_d because the oxygen in one NO needs to be excluded from the calculation, considering that the adsorption/desorption of NO without decomposition has no effect on the net oxidation state, as designated by Eq. (8). The existence of the adsorbed NO₂ species has been supported by the desorption of a large amount of NO₂ above 300 °C, as shown in Fig. 6(A). Along with molecular oxygen desorption starting from 320 °C, this large amount of NO₂ desorbed from the oxidized catalyst significantly contributes to the rapid decrease of the oxidation state from 1.02 to 0.4 O/Cu_d at 410 °C. Above 350 °C, the catalysis of NO decomposition to N₂ proceeds rapidly, as evidenced by the concurrent decrease in NO intensity.

7. N₂ Formation and the Oxygen Removal on Oxidized Cu-Dimers as O₂

In the direct NO decomposition reaction over Cu-ZSM-5, the rate of N₂ formation was reported to suffer from oxygen inhibition, particularly at low temperature. Li and Hall [1991] reported that the oxygen inhibition effect decreases with increasing temperature but some active sites might remain occupied by oxygen also at higher temperatures. Efficient removal of the oxygen from the active sites in working conditions is crucial to the catalysis of NO decomposition. Based on the redox mechanism of the Cu-dimers as active sites, the process of N₂ formation is described by the reaction of N₂O over the reduced Cu-dimer, resulting in the oxidation of the Cu-dimer with simultaneous production of N₂:



The major route of N₂O formation is via the adsorption of two NO on the reduced Cu-dimer, as described in reaction (7). Kapteijn et al. [1997] reported for the N₂O decomposition reaction over the Cu-ZSM-5 catalyst that the N₂ formation rate was inhibited by the presence of O₂ in gas phase. This suggests that the N₂O decomposition reaction mainly takes place on the reduced Cu-dimers as represented

by reaction (10). The result of N₂O-TPSR (Fig. 5) also supports that the removal of oxygen from the Cu-dimers of oxidation state 0.5 O/Cu_d is prerequisite for the formation of N₂.

In view of the above consideration about the O₂-TPD and the N₂O-TPSR experiments, the thermal recombined desorption of the bridged atomic oxygen as molecular oxygen can be considered as a working way of oxygen removal for the oxidized Cu-dimers. This can be regarded as highly effective for NO decomposition catalysis because two reduced Cu-dimers, i.e., four Cu⁺ sites in close proximity, can be generated once a molecule of oxygen is released. The reduced Cu-dimers created by this way are immediately ready for the next catalysis of NO decomposition reaction as soon as they are generated. The evolution of O₂ on the oxidized Cu-ZSM-5 will be easy at first because many of (Cu-O-Cu)²⁺ species are initially available all around the surface of Cu-ZSM-5, as shown in Fig. 4, and as illustrated in Fig. 11(A). As the oxidized Cu-dimers are reduced to the (Cu⁺-□-Cu⁺) species, the reduction of those remaining in oxidized state becomes more difficult and slow due to less availability for an oxidized Cu-dimer with another in its vicinity (refer Fig. 11(B)). This difficulty in the O₂ formation can be observed in Fig. 4, requiring more activation energy, i.e., higher temperature at the later stage of the O₂ desorption. For the Cu(51)-Z(29) catalyst of which the Cu-dimers are expected to be distant among them, such a difficulty in the O₂ formation is significant as compared to other catalysts with higher %Cu EL.

As shown in Fig. 10, the oxygen removal is more facilitated in the N₂O-TPSR than in the O₂-TPD in He. Actually, there would be little difference in the driving force of the dimer-bridged oxygen for desorption as O₂ at the same temperature between the N₂O-TPSR

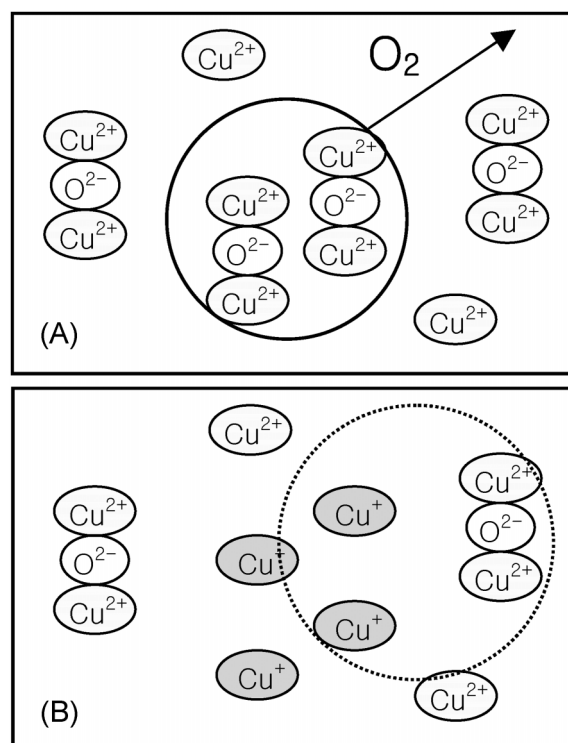


Fig. 11. Schematic for the thermal recombined oxygen removal as O₂ from the oxidized Cu-dimers, (A): easy removal, and (B): difficult to be removed.

and the O₂-TPD in He because the partial pressures of oxygen in both cases were very low. It can be consequently considered that the facilitated oxygen removal via O₂ formation during the N₂O-TPSR as compared to the O₂-TPD is possibly due to the reaction of N₂O on a reduced (Cu-□-Cu)²⁺ (reaction (10)) in the vicinity of an existing (Cu-O-Cu)²⁺ with a lack of its nearby homologues, making a favorable condition for the easy formation of O₂ between the two resulting adjacent (Cu-O-Cu)²⁺ species. In other words, if the reduced Cu-dimer inside the dotted circle, as shown in Fig. 10(B), is re-oxidized as a result of the reaction with N₂O, the thermal recombined desorption of O₂ occurs easily therein. Considering that N₂O is an intermediate for the N₂ formation in the redox mechanism of NO decomposition catalysis, such a reaction of N₂O on the reduced (Cu-□-Cu)²⁺, as observed in the N₂O-TPSR, can be an aid to facilitate the thermal recombined oxygen removal process of the Cu-ZSM-5 catalyst in the actual NO decomposition reaction.

CONCLUSIONS

Throughout this study, it was clearly demonstrated that the decomposition of NO over Cu-ZSM-5 catalyst proceeded by the redox of Cu-dimer species, (Cu-O-Cu)²⁺, as active centers. The exchanged copper species present on the calcined catalysts were isolated Cu²⁺, (Cu-O-Cu)²⁺ and CuO, and their compositions were quantitatively determined. The amount of thermally desorbed oxygen throughout the O₂-TPD was closely correspondent to that retained by the (Cu-O-Cu)²⁺ species for each catalyst. The mol fraction of exchanged Cu ions involving in the Cu-dimers increased at the sacrifice of the isolated Cu²⁺ with increasing %Cu EL, suggesting that the Cu-dimers could be formed between the two Cu²⁺ in close proximity. The activities of catalysts in terms of the rate of N₂ formation were well correlated with the amounts of the (Cu-O-Cu)²⁺ species determined. The redox mechanism as the working way of NO decomposition catalysis over Cu-ZSM5 was supported by the N₂O- or NO-TPSR experiment demonstrating that the oxidation state of the Cu ions involved in the Cu-dimers varied from maximum 1.0 (with the adsorbed NO₂) to 0.04 or 0.1 O/Cu₄ in the reduced state. N₂O-TPSR showed that the removal of oxygen from the Cu-dimers of initial oxidation state 0.5 O/Cu₄ was prerequisite for the formation of N₂. Thermal recombined desorption as O₂ between the two adjacent (Cu-O-Cu)²⁺ species could be thought as a major route of oxygen removal from the oxidized Cu-dimers in the NO decomposition catalysis. This process of oxygen removal would be facilitated by the reaction of N₂O on the reduced (Cu-□-Cu)²⁺ in the vicinity of an existing (Cu-O-Cu)²⁺ with a lack of nearby homologues, making a favorable condition for easy formation of O₂ between the two resulting adjacent (Cu-O-Cu)²⁺ species.

ACKNOWLEDGMENT

The author is deeply grateful to Professor Enrique Iglesia and Mr. Björn Modén in the Department of Chemical Engineering, University of California at Berkeley, USA, for their help and academic discussion during author's stay in UC Berkeley. A part of the financial support for the author from the Korea Science and Engineering Foundation (KOSEF) through the Overseas Post-Doctoral Support Program is acknowledged.

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