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Kinetic evaluation of mechanistic models for O_2 release from ZSM-5-supported $[Cu^{2+}–O–Cu^{2+}]$ ions by thermal reduction or chemical interaction with impinging N_2O molecules

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For a series of oxidized Cu-ZSM-5 catalysts which were characterized in the catalytic amounts of the oxygen-bridged Cu^{2+}-dimers, $[Cu^{2+}–O–Cu^{2+}]$, activation energies required for the reduction of the Cu^{2+}-dimer species by O_2 release were determined using the temperature-programmed experiments of thermal O_2 desorption (TPD) and N_2O decomposition reaction. The activation energy for the thermal reduction of the Cu^{2+}-dimers during the TPD decreased linearly with increasing molar number of the Cu^{2+}-dimers available on the ZSM-5, suggesting that the energy barrier of the O_2 formation via a Langmuir–Hinshelwood (LH) mechanism increased in proportion to the distance between the two Cu^{2+}-dimers in the nearest neighbor. Activation energies of thermal O_2 release were comparable to the literature-reported binding energies of the differently spaced Cu^{2+}-dimers. It was also revealed that the activation energy of O_2 release during the temperature programmed N_2O decomposition reaction over an oxidized catalyst was generally low as compared to that in the TPD, and that the degree of reduction of the Cu^{2+}-dimers was much greater in the N_2O decomposition reaction than in the TPD at the same temperatures. These beneficial effects N_2O decomposition on the reduction of the Cu^{2+}-dimers were discussed in respect of the removal mechanism of the Cu^{2+}-dimer bridged oxygen.

KEY WORDS: Cu-ZSM-5; oxygen-bridged Cu^{2+}-dimers; O_2 desorption; mechanism, activation energy; N_2O decomposition.

1. Introduction

Contributed to a great quantity of extensive studies over more than a couple of decades, the Cu-ion exchanged ZSM-5 catalyst in relation with its efficient catalysis of NO or N_2O decomposition has been mostly uncovered with respect to its physicochemical properties. There are many experimental evidences [1–8] or theoretical analyses [9,10] on literature supporting that oxygen-bridged Cu^{2+}-dimers, $[Cu^{2+}–O–Cu^{2+}]$, are available on the high copper-loaded ZSM-5 catalyst in the oxidized state as responsible species for the well known catalytic activity toward $deNO_x$ reactions. It is also known that the removal of the bridged oxygen from the Cu^{2+}-dimers leads to the reduction of Cu^{2+} to the Cu^+ ion sites, $[Cu^+–O–Cu^+]$, on which NO or N_2O is believed to adsorb initiating the decomposition catalysis. In a recent paper [7], the present author reported experimental results directly demonstrating that the Cu^{2+}-dimers over Cu-ZSM-5 catalysts were involved in the decomposition of NO as active centers, using the catalysts listed in table 1, where the numbers in parentheses following Cu and Z denote the percent Cu exchange level to a ZSM-5 and ratio of Si to Al in framework position (Al_f), respectively. The loaded copper species on the catalysts in oxidized state were found to exist as an isolated Cu^{2+}, $[Cu^{2+}–O–Cu^{2+}]$ and CuO, and the amounts of the species on a catalyst were quantitatively determined, as listed in table 1, by the temperature-programmed reduction using CO and successively using H_2. Details on the preparation of catalysts and experimental method of characterization can be found in the previous paper [7]. It was also revealed that the mol fraction of Cu_d, i.e., copper involved in the Cu^{2+}-dimers of a catalyst, was higher for the catalysts based on the ZSM-5 having the lower ratio of Si to Al_f, and increased at the sacrifice of the isolated Cu^{2+} with increasing level of copper loading to a ZSM-5, ensuring that $[Cu^{2+}–O–Cu^{2+}]$ species could be formed between the two Cu^{2+} in close proximity.

From the TPD in flowing He for the oxidized catalysts, total amounts of oxygen desorbed from the catalysts throughout the TPD were found close to those of oxygen retained by the $[Cu^{2+}–O–Cu^{2+}]$ species available on the catalysts (refer table 1, $O_{desorbed}/Cu_d$). This definitely supported that O_2 release during the TPD resulted from the thermal recombination of the two $[Cu^{2+}–O–Cu^{2+}]$-held oxygen atoms via a LH mechanism as follows:

$$2[Cu^{2+}—O—Cu^{2+}] \rightarrow 2[Cu^{+}—O—Cu^{+}]+O_2 \qquad (1)$$

Then, it may be highly interested for us to determine how and at what level the activation energy of O_2 release from the Cu^{2+}-dimers would be changed upon the variation in the molar amount of the Cu^{2+}-dimers on

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Table 1
Summary of catalysts

	Cu (116)–Z 14.7)	Cu (76)–Z (14.7)	Cu (262)–Z (29)	Cu (156)–Z (29)
Composition, wt%				
Cu	3.31	2.24	3.88	2.25
Si	36.0	37.9	37.5	36.3
Al	2.42	2.50	2.73	2.66
Na	0.08	0.51	0.11	0.64
μmol Cu/g	521	352	611	354
Si/Al_f(atomic ratio)	14.3	14.6	28.7	28.5
Cu/Al_f(atomic ratio)	0.58	0.38	1.31	0.78
Distribution of Cu, mol%				
as Cu^{2+}	48.0	54.0	40.0	54.0
as [Cu^{2+}—O—Cu^{2+}]	38.0	32.0	36.0	30.0
as CuO	14.0	14.0	24.0	16.0
μmol Cu as [Cu^{2+}—O—Cu^{2+}] /g	198	113	220	106
$O^{A}_{desorbed}/Cu^{B}_{d}$ (atomic ratio)	0.53	0.44	0.5	0.43

[A] $O_{desorbed}$ indicates the amount of oxygen desorbed throughout the TPD.

[B] Cu_d indicates Cu species that are involved [Cu^{2+}-O-Cu^{2+}].

the Cu-ZSM-5 catalysts. To the author's knowledge, experimental data on the activation energy associated with the oxygen removal from the [Cu^{2+}–O–Cu^{2+}] species of Cu-ZSM-5 are scarce on literature irrespective of its importance as a key catalysis step in various redox reactions including NO or N_2O decomposition.

The present paper is aimed to report the activation energy of O_2 release from the Cu^{2+}-dimers by thermal reduction and its dependency on the amounts of the Cu^{2+}-dimers on the catalysts, and finally to evaluate the kinetic effect of the N_2O decomposition to N_2 over a Cu-ZSM-5 catalyst on the reduction of the Cu^{2+}-dimers of the catalyst in comparison with the thermal reduction.

2. Activation energy of the thermal reduction of Cu^{2+}-dimers

Arrhenius plots about the turnover frequency of O_2 release (TOF, mol-O_2/mol-Cu_d/s) from the oxidized catalysts listed in table 1 during the TPD in He flow are shown in figure 1. As noted, the TOF of O_2 release was normalized with respect to the catalytic amount of Cu_d. A Cu_d-normalized TPD profile for a catalyst Cu(116)–Z(14.7) is shown in the inset of figure 1. The data collected during the incipient temperature span of O_2 release were used for the Arrhenius plot. At the incipient stage of O_2 release, it is convinced that most of available Cu-dimers over the catalyst are present in oxidized state as [Cu^{2+}–O–Cu^{2+}] species due to the pre-oxidation treatment (for 2 h at 500 °C with 50 cm^3/min of 49% O_2/He). As an instance, the TOF-O_2 data in a range of temperatures 325–366 °C were used for the plot of Cu(116)–Z(14.7). The activation energies of thermal O_2 release with the temperature spans adopted in figure 1 were determined as 35.3 (325–366 °C), 48.4 (343–372 °C), 32.0 (330–370 °C), and 49.9 (345–375 °C) kcal/mol for the catalysts, Cu(116)–Z(14.7), Cu(76)–Z(14.7), I Cu(262)–Z(29), and Cu(156)–Z(29), respectively.

The relationship between the activation energy of thermal O_2 release and the molar amount of Cu_d per a gram catalyst can be well represented by a linear correlation equation: $E_A = 66.0 - 0.1548 \times$ (μmol Cu_d/g), as shown in figure 2. Being linearly dependent on the mol number of Cu_d of a catalyst, it can be assumed that the activation energy of thermal O_2 release varies in proportion to the distance between the two [Cu^{2+}–O–Cu^{2+}] in close neighbor. To verify this proposal, lets imagine a plane of square rectangle with a side length l, as illustrated in figure 3. When each of two

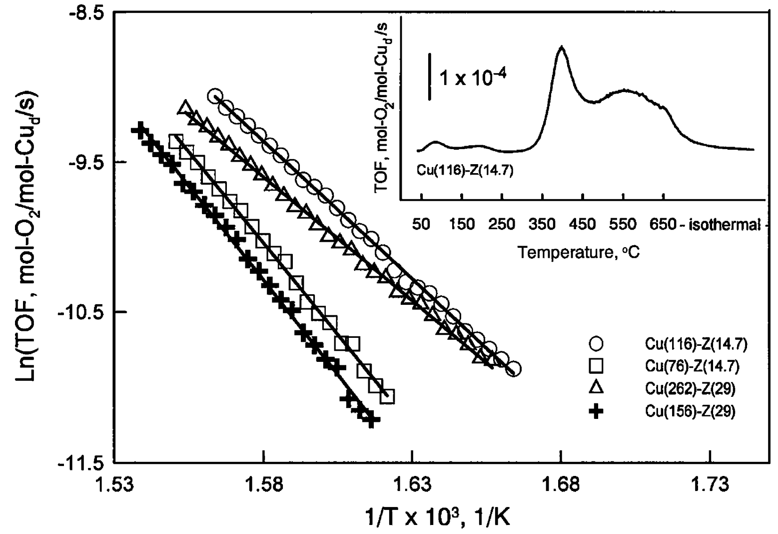

Figure 1. Arrhenius plot for the Cu_d-normalized TOF of O_2 release in the TPD (in He flow 30 cm^3 /min; heating rate, 10 °C/min) for the oxidized catalysts (for 2 h at 500 °C with 50 cm^3/min of 49% O_2/He), where the insert is a Cu_d-normalized TPD profile for a catalyst Cu(116)–Z(14.7).

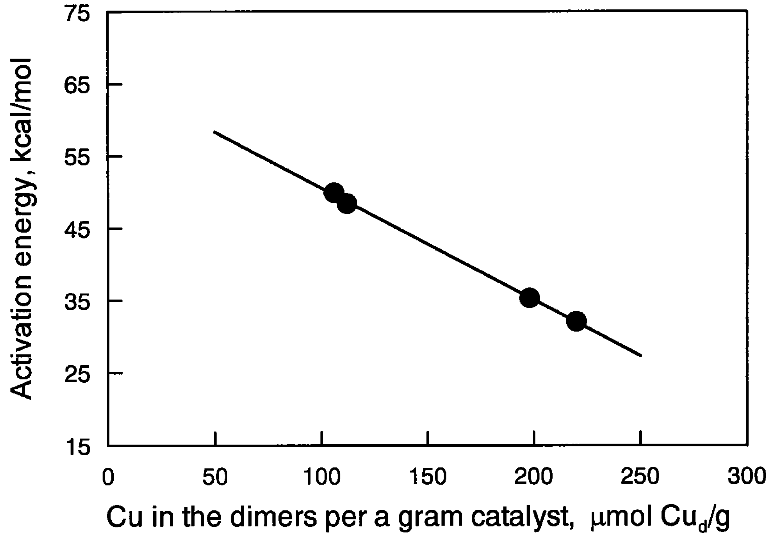

Figure 2. Relationship between the activation energy of O_2 release in the TPD and the molar amount of Cu_d per a gram catalyst.

Cu^{2+}-dimers represented by black circles is located at diagonal corners of the rectangle, the distance between them is $\sqrt{2}$. If the number of the Cu^{2+}-dimers is doubled within the rectangular space, the nearest distance will be decreased to 1. According to the above proposition, the ratio of activation energy of the former to that of the latter should be 1.41:1. Back to figure 1, the obtained correlation equation gives activation energy 50.5 kcal/mol at 100 μmol Cu_d/g, and 35.5 kcal/mol when doubled to 200 μmol Cu_d/g, resulting in a ratio, 1.44:1. This experimental value very close to calculated 1.41:1 verifies that the energy barrier for thermal O_2 desorption decrease as the Cu^{2+}-dimer species are more clustered on the surface.

The binding energy of the $[Cu^{2+}$–O–$Cu^{2+}]$ species relative to two Cu^+ ions and a free O_2 molecule was theoretically obtained as 63 kcal/mol for the species with Cu–Cu separation by 3.45 Å, and 33–38 kcal/mol for species with the spacing by 2.59–2.81 Å, using a single $Al(OH)_4^-$ tetrahedral (T)-site model and multi-T-site model, respectively [9,10]. For the thermal O_2 desorption from the Cu^{2+}-dimers, activation energy at least comparable to the binding energy of the species would be needed. It deserves to be noted that the experimental activation energies, as shown in figure 2, are consistent to the binding energies calculated by Goodman et al. [9,10] in magnitudes. In the case that the Cu^{2+}-dimers are spaced far apart among them, the activation energy of O_2 release from these most refractory species is estimated using the obtained correlation equation to 66.0 kcal/mol, nearly corresponding to the binding energy of 63 kcal/mol for the species with Cu–Cu separation by 3.45 Å. The increase in the number of the Cu^{2+}-dimers on surface should decrease the Cu–Cu spacing, resulting in a decrease in the activation energy of thermal O_2 desorption as well as in the binding energy.

3. Activation energy for O_2 formation during N_2O decomposition

Figure 4 shows the Arrhenius plots for the Cu_d-normalized TOF (mol-O_2/mol-Cu_d/s) of O_2 formation on the oxidized catalyst of Cu(116)–Z(14.7) during the

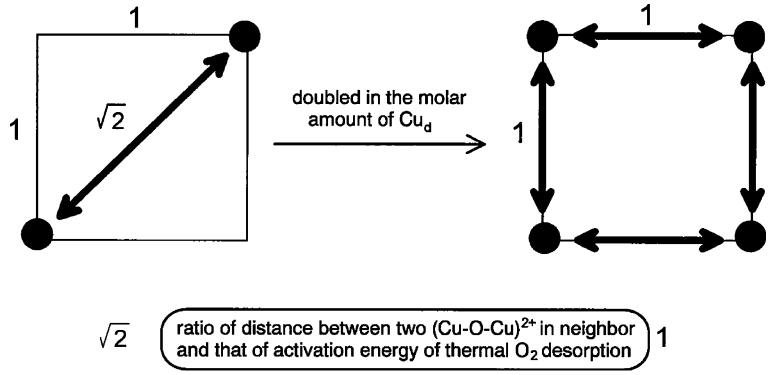

Figure 3. Schematic for illustrating the dependency of the activation energy of thermal O_2 release via LH mechanism between the two $[Cu^{2+}$—O—$Cu^{2+}]$ sites (expressed as a black circle) on their nearest distance apart.

temperature-programmed N_2O decomposition reaction. As shown in the insert in figure 4, the Cu_d-normalized TOFs (mol-gas/mol-Cu_d/s) of N_2 and release appear nearly equivalent to each other at temperature region of 300–360 °C. And, because most of available Cu-dimers over the catalyst exist as $[Cu^{2+}–O–Cu^{2+}]$ at the incipient stage of the temperature programmed N_2O decomposition, the reaction can be thought to proceed via an Eley-Rideal (ER) mechanism as follows:

$$[Cu^{2+}—O—Cu^{2+}] + N_2O \rightarrow [Cu^{+}—\square—Cu^{+}] + O_2 + N_2 \qquad (2)$$

At the very incipient stage (300–343 °C) of the temperature programmed N_2O decomposition, the activation energy of O_2 release from the Cu^{2+}-dimers was estimated as 18.9 kcal/mol, apparently much low as compared to that (35.3 kcal/mol) in the case of the TPD for the same catalyst. It can be understood that the chemical interaction with impinging N_2O molecules on the oxidized Cu-ZSM-5 catalyst makes O_2 release possible via an ER mechanism at the lower temperature region where O_2 formation via a LH mechanism has not yet been fully activated. At the elevated temperatures above 360, N_2O decomposition reaction as follows would be facilitated because of the increased availability of the reduced Cu^+-dimer sites on the catalyst surface:

$$[Cu^{+}—\square—Cu^{+}] + N_2O \rightarrow [Cu^{2+}—O—Cu^{2+}] + N_2 \quad (3)$$

Provided that two of $[Cu^{2+}–O–Cu^{2+}]$ such produced are located each other in nearer neighbor over the surface of Cu(116)–Z(14.7), thermal O_2 release via a LH mechanism (reaction (1)) is also possible with the activation energy of 35.3 kcal/mol. For the N_2O decomposition at the higher temperature region of 360–380 °C, the activation energy of O_2 release was estimated to an increased value, 28.9 kcal/mol, but much less than that (35.3 kcal/mol) in the TPD, meaning that the O_2 release was attributed to both ER and LH mechanisms.

4. N_2O decomposition-facilitated reduction of the oxidized Cu^{2+}-dimers

Figure 5 shows the change in the oxidation state of the Cu^{2+}-dimers and the corresponding percentage of the Cu_d reduction to Cu^+ with temperature increase during the N_2O decomposition in comparison with the TPD in He flow for the catalyst, Cu(116)–Z(14.7). The profile of the oxidation state change in the TPD was obtained by integrating the profile of O_2 release during the TPD, as shown in the inset of figure 1, while that in the N_2O decomposition by integrating the instantaneous net removal rate of oxygen from the $[Cu^{2+}–O–Cu^{2+}]$ species during the N_2O decomposition, as shown in the inset of figure 2. Before the start of the temperature-programmed experiments, the oxidation state of Cu_d is 0.5 O/Cu_d because an oxygen atom is shared by a dimerized couple of Cu^{2+} ions in the initial-oxidized state. There would be little difference in driving force of the Cu^{2+}-dimer bridging oxygen for desorption as O_2 at the same temperature between the two cases because, in both cases, the partial pressures of oxygen were very low, and the same rate of heating (10 °C/min) was employed. From temperatures above 325 °C, it is apparent that the reduction of the Cu_d to Cu^+ by O_2 release is at much higher degree in the N_2O decomposition than in the TPD at the same temperatures. Chemical interaction with impinging N_2O facilitated the

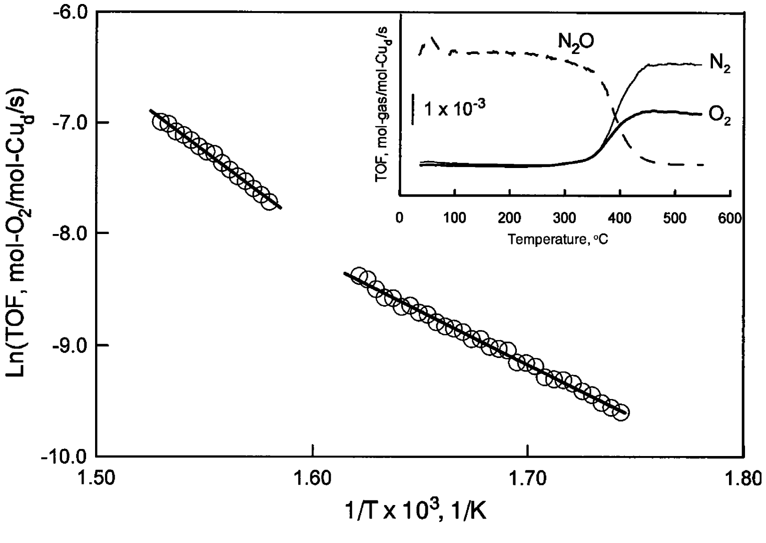

Figure 4. Arrhenius plot for the Cu_d-normalized TOF of O_2 release in the temperature programmed N_2O decomposition (50 cm^3/min of 0.1% N_2O/He; heating rate, 10 °C/min) for the oxidized catalyst (for 2 h at 500 °C with 50 cm^3/min of 49% O_2/He) of Cu(116)–Z(14.7), where the insert is a Cu_d-normalized N_2O decomposition profile for the catalyst.

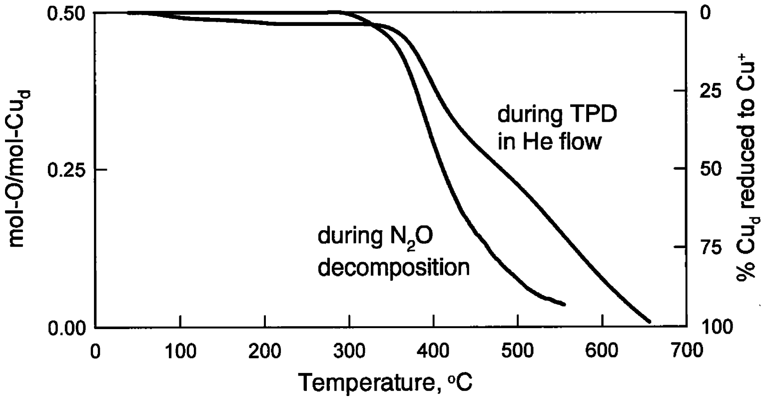

Figure 5. Oxidation state change or the degree of percent reduction of the Cu^{2+}-dimers at initially oxidized state with increasing temperature during the N_2O decomposition in comparison with the TPD in He flow for the catarst Cu(116)–Z(14.7).

removal of oxygen from the $[Cu^{2+}–O–Cu^{2+}]$ species in such a direct way as the O_2 formation via a ER mechanism (reaction (2)). The decomposition reaction of N_2O on a $[Cu^{+}–\square–Cu^{+}]$ (reaction (3)) in the vicinity of an existing $[Cu^{2+}–O–Cu^{2+}]$ with a lack of its nearby homologues can be considered as an indirect way promoting the reduction of Cu^{2+}-dimers, because this makes a favorable condition for the easy formation of O_2 via a LH mechanism between the two resulting adjacent $[Cu^{2+}–O–Cu^{2+}]$ species, as it was proposed in the previous study [7]. A fewer number of the $[Cu^{2+}–O–Cu^{2+}]$ species that survive on the surface throughout the TPD would be more difficult to be reduced because of the lack of the homologues in their nearby surroundings, requiring higher temperature up to 650 °C for the thermal O_2 release.

5. Conclusions

During the incipient period of thermal O_2 desorption, the activation energy of O_2 release (49.9, 48.4, 35.3, and 32.0 kcal/mol) decreased linearly with the increase in the molar amounts of the Cu^{2+}-dimers of the Cu-ZSM-5 catalysts on a gram basis (106, 112, 198, and 220 μmol/g, respectively). The energy barrier of the O_2 release via a LH mechanism increased in proportion to the distance between the two Cu^{2+}-dimers in the nearest neighbor. In the temperature-programmed N_2O decomposition reaction over the catalyst having 198 mol of Cu_d on a gram catalyst, the activation energy of O_2 release at an incipient stage was evaluated as low as 18.9 kcal/mol at temperatures 300–343 °C, where the turnover frequency of O_2 release was nearly the same as that of N_2 release, indicating O_2 formed mainly via an ER mechanism in this temperature region: $[Cu^{2+}—O—Cu^{2+}] + N_2O$ $[Cu^{+}—\square—Cu^{+}] + O_2 + N_2$. At higher temperatures 360–380 °C, the activation energy was increased to 28.9 kcal/mol, but much less than that (35.3 kcal/mol) of the thermal O_2 release. At this higher temperature region where more number of the reduced Cu-dimers were available for facilitating the reaction: $[Cu^{+}—\square—Cu^{+}] + N_2O \rightarrow [Cu^{2+}—O—Cu^{2+}] + N_2$, O_2 release via a LH mechanism would become more significant in parallel with that via an ER mechanism. The reduction of surface surviving $[Cu^{2+}—O—Cu^{2+}]$ species that are hardly reducible due to their surrounds with only $[Cu^{+}—\square—Cu^{+}]$ species could be facilitated through the O_2 release via a LH mechanism, provided that one of the surrounding Cu^{+}-dimers is oxidized to $[Cu^{2+}—O—Cu^{2+}]$ as a result of the N_2O decomposition.

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