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The relationship between the local structure of copper(I) ions on Cu^+/zeolite catalysts and their photocatalytic reactivities for the decomposition of NO_x into N_2 and O_2 at 275 K

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Contents

Abstract

Cu^+/zeolite catalysts were prepared by a combination of ion-exchange and thermovacuum treatments. In situ characterization of these catalysts and their photocatalytic reactivities for the decomposition of NO_x (NO and N_2O) have been investigated by means of in situ photoluminescence, XAFS, ESR, UV, and FT-IR techniques along with an analysis of the reaction products. It was found that Cu(I) ions included within the nanopores of ZSM-5 and mordenite zeolites exist as isolated Cu(I) monomers with planar three-coordinate or two-coordinate geometry, while in the Y-zeolite cavities they exist as the [Cu(I)–Cu(I)] dimer species as well as the isolated Cu(I) monomer species. UV irradiation of these Cu^+/zeolite catalysts in the presence of NO_x led to the photocatalytic decomposition of NO_x into N_2 and O_2 at temperatures as low as 275 K. A local charge separation involving an electron transfer from the electronically excited state of a Cu(I) ion ($3d^94s^1$ state) to the anti-π-bonding orbital of an NO molecule was found to play a vital role in initiating the photocatalytic decomposition

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of NO_x. Furthermore, the photocatalytic reactivity of these Cu^+/zeolite catalysts was found to be strongly affected by the local structure of the Cu(I) ions which could easily be modified by changing the type of zeolites and loading of the copper ion. Special attention has, therefore, been focused on the relationship between the local structure of copper ions on the catalysts and their photocatalytic reactivities.

Keywords: NO_x decomposition; Photocatalysis; Cu^+ ion; Zeolite

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1. Introduction

The design of well-defined molecular and/or cluster size photofunctional materials as well as catalysts within the micropores or frameworks of zeolites is of special interest because of their fascinating physical and chemical properties, unusual internal surface topology, and ion-exchange capacities, just to name a few [1–4]. Recently, the ion-exchanged copper/ZSM-5 catalyst has attracted a great deal of attention as a potential thermal catalyst for the direct decomposition of NO_x into N_2 and O_2 at around 600–700 K [5,6]. On the other hand, we have found that only the Cu^+/ZSM-5 catalyst which showed catalytic activity for the decomposition of NO_x exhibits a characteristic photoluminescence spectrum at around 400–500 nm which can be attributed to the radiative decay process from the excited state of the Cu(I) ion species and also found that UV irradiation of Cu^+/ZSM-5 catalysts in the presence of NO leads to the direct decomposition of NO into N_2 and O_2 with a good linearity and stoichiometry even at 275 K [7–9]. These results clearly suggest that the electronic excited state of the partially reduced Cu(I) ion species ($3d^94s^1$ state) plays a significant role as active sites in the photocatalytic decomposition of NO_x into N_2 and O_2.

In the present study, a comprehensive characterization of the relationship between the local structure of the copper ion species and their photocatalytic reactivities for the decomposition of NO_x (NO and N_2O) into N_2 and O_2 at 275 K has been investigated by changing the type of zeolites and loading amounts of copper ions using in situ photoluminescence, X-ray absorption fine structure (XAFS), ESR, UV, and FT-IR techniques. Special attention has been focused on the relationship between the local structure of copper ions included within zeolite cavities and their photocatalytic reactivities for the direct decomposition of NO_x into N_2 and O_2 at 275 K.

2. Experimental section

Three types of zeolites (supplied by the TOSOH Co.) were used: ZSM-5 (Si/Al = 23.3), mordenite (Si/Al = 14.9), and the Y-zeolite (Si/Al = 5.6, 13.9, 390). Cu^{2+}/zeolite samples were prepared by ion-exchange with an aqueous $Cu(NH_3)_4^{2+}$ solution. After washing with water and drying in air at 373 K, the copper loadings were determined to be 1.5–3.0 wt% as metal. Prior to spectral measurements and subsequent reactions, the samples were degassed at 673 K, heated at 673 K in O_2, and then finally evacuated at the desired temperature. The standard Cu^+/zeolite catalysts were prepared by evacuation of the Cu^{2+}/zeolite samples at 973–1073 K. The photoluminescence spectra of the catalysts and their lifetimes were recorded at 77 K. The FT-IR and UV absorption spectra were measured at 295 K. The ESR spectra were recorded at 77 K. The XAFS spectra (XANES and FT-EXAFS) were obtained at the Photon Factory in Tsukuba. An Si(311) channel-cut crystal was used to monochromatize the X-ray from the 2.5 GeV electron storage ring. UV irradiation was carried out using a 100 W high pressure mercury lamp through water and color filters at 275 K ($\lambda > 280$ nm). The photoreaction products were analyzed by gas chromatography and mass spectrometry. Further experimental details can be found in previous papers [7–9].

3. Results and discussion

Cu^{2+}/zeolite samples exhibited a typical ESR spectrum due to the hydrated Cu^{2+} ion anchored within zeolite cavities. The increased evacuation temperature led to a drastic decrease in the intensity of the ESR signals with very minor changes in their spectra parameters and line-shapes and also to the color changes of the samples from blue to white, indicating that the chemical reduction of Cu^{2+} to Cu^+ had occurred. With the Cu^+/zeolite catalysts prepared in this way, a photoluminescence was observed at around 400–500 nm upon excitation at around 270–300 nm. Fig. 1 shows the typical photoluminescence spectra of the Cu^+/ZSM-5 (a), Cu^+/Y-zeolite (Si/Al = 5.6) (b), and Cu^+/mordenite (c) at 77 K, respectively. The absorption band at around 270–300 nm and the photoluminescence spectrum at around 400–500 nm are attributed to the electronic excitation of the Cu(I) ion ($3d^{10} \rightarrow 3d^9 4s^1$) and its reverse radiative deactivation ($3d^9 4s^1 \rightarrow 3d^{10}$), respectively.

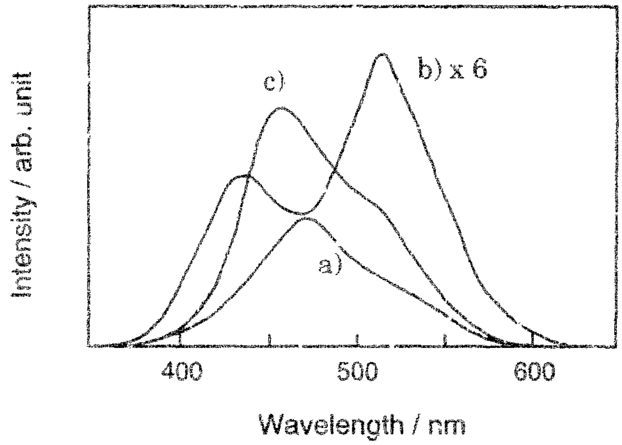


Fig. 1. Photoluminescence spectra of the (a) Cu^+/ZSM-5, (b) Cu^+/Y-zeolite, and (c) Cu^+/mordenite catalysts; measured at 77 K.

On the other hand, the absorption band at around 300–320 nm and the photoluminescence spectrum at around 480–580 nm can be attributed to the presence of a dimer ($3d\sigma^* \rightarrow 4s\sigma$) and its reverse radiative deactivation ($4s\sigma \rightarrow 3d\sigma^*$), respectively [7,10,11]. This assignment is supported by the fact that the intensity of the peak at around 480–580 nm increases when the copper content of the catalyst is increased, whereas the intensity of the peak at around 400–500 nm remains almost constant.

Fig. 2 shows the XANES and FT-EXAFS spectra of the Cu^+/ZSM-5 (b, b'), Cu^+/Y-zeolite (Si/Al = 5.6) (c, c'), and Cu^+/mordenite (d, d') at 77 K, respectively, together with the spectra of the original Cu^{2+}/ZSM-5 sample (a, a'). As shown in Fig. 2(b) and (d), the Cu^+/ZSM-5 and Cu^+/mordenite catalysts exhibit a very strong and sharp band (B) due to the 1s-$4p_z$ transition without any shake-down bands, and these were sufficient in identifying the copper ion species as isolated Cu(I) ions having a planar three-coordinate or linear two-coordinate geometry [9,12]. As shown in Fig. 2(b') and (d'), these catalysts exhibit a Cu–O peak only at

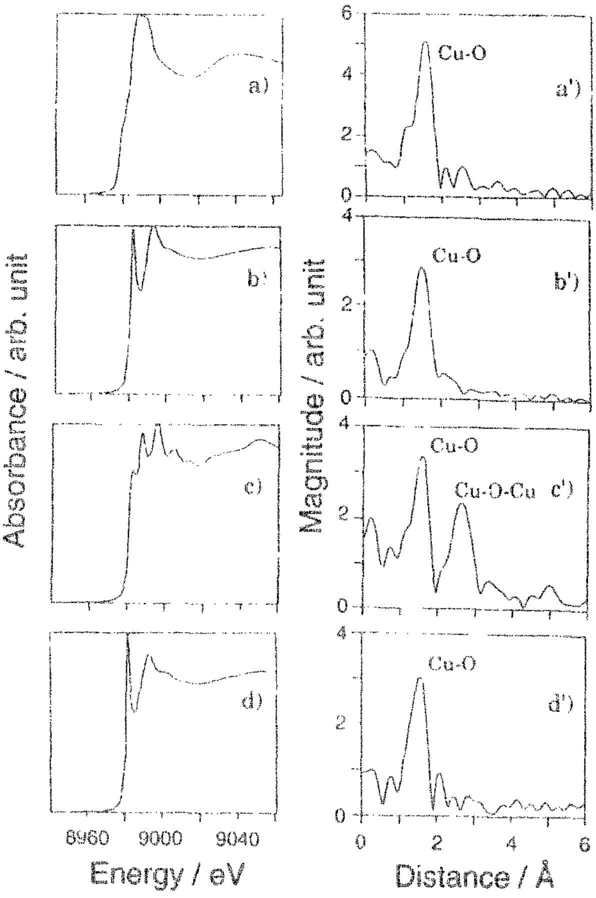


Fig. 2. XANES (a–d) and FT-EXAFS (a'–d') spectra of the (a, a') Cu^{2+}/ZSM-5 sample, and the (b, b') Cu^+/ZSM-5, (c, c') Cu^+/Y-zeolite, and (d, d') Cu^+/mordenite catalysts.

around 1.5 Å (uncorrected value), also indicating the presence of isolated Cu(I) ions on these catalysts. On the other hand, as shown in Fig. 2(c) and (c′), the Cu^+/Y-zeolite exhibits an intense peak at 2.6 Å in addition to a peak at 1.5 Å due to the Cu–O bonds. The peak at 2.6 A can be attributed to the neighboring copper atoms (Cu–O–Cu), indicating the presence of aggregated Cu(I) ions.

These results obtained by ESR, XAFS, UV, and photoluminescence measurements of the Cu^{2+}/zeolite samples as well as Cu^+/zeolite catalysts clearly indicate that in the ZSM-5 and mordenite zeolites almost all of the copper cations exist as an isolated Cu(I) monomer species with planar three-coordinate or linear two-coordinate geometry, while in the Y-zeolite both isolated Cu(I) ions and an aggregated Cu(I)–O–Cu(I) dimer species are present.

As shown in Fig. 3, UV irradiation of the Cu^+/zeolite catalysts even at temperatures as low as 275 K in the presence of NO_x molecules leads to the formation of N_2 and O_2 with a good linear relationship between the UV irradiation time and the conversion of NO_x molecules into N_2 and O_2. Thus, UV irradiation of the Cu^+/zeolite catalysts at 275 K in the presence of NO_x molecules brought about the photocatalytic decomposition of NO_x into N_2 and O_2 with a good stoichiometry (N_2:O_2 = 1:1). Although it is difficult to determine the actual quantum yields in such very small powdered systems, the results in Fig. 3 show that the Cu^+/ZSM-5 catalyst exhibits the highest photocatalytic activity for the direct decomposition of NO into N_2 and O_2 at 275 K. We can estimate about 1–2% as the apparent quantum yield of this system by comparing the results with the quantum yields determined for other supported catalysts such as vanadium oxide and silver(I) ion photocatalysts.

As shown in Fig. 4, the photocatalytic activity of the Cu^+/ZSM-5 catalyst increases with the evacuation temperature of the Cu^{2+}/ZSM-5 sample, passing through a maximum at 1173 K and then decreasing at much higher degassing temperatures. It

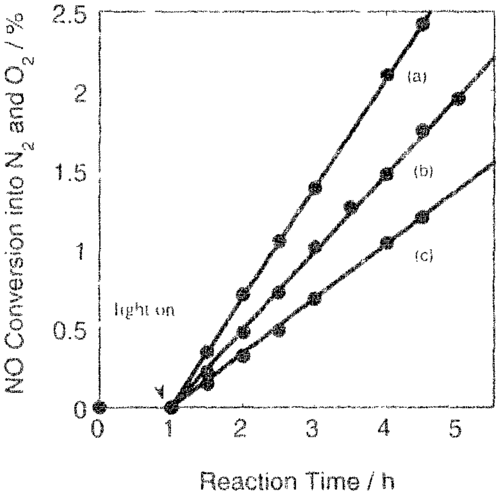


Fig. 3. Reaction profiles of the photocatalytic decomposition of NO into N_2 and O_2 at 275 K on the (a) Cu^+/ZSM-5, (b) Cu^+/Y-zeolite, and (c) Cu^+/SiO_2 catalysts.

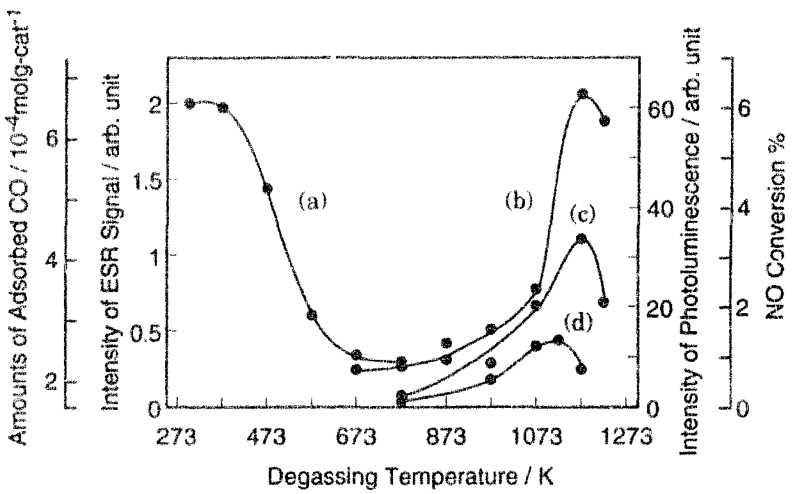


Fig. 4. Effects of the evacuation temperature of the Cu^{2+}/ZSM-5 sample on (a) the relative intensity of the ESR signal due to Cu^{2+}, (b) the relative yields of the photoluminescence due to Cu^{+}, (c) the relative conversions (yields) of the photocatalytic decomposition of NO at 275 K, and (d) the amount of CO molecules selectively adsorbed on the Cu^{+} ions on the catalyst at 295 K.

can also be seen that the photoluminescence yields attributed to the isolated Cu(I) ion species change dramatically in a similar way. Furthermore, the number of isolated Cu(I) ion sites which could be determined by the selective adsorption of CO molecules onto the isolated Cu(I) ions was also found to change in the same way, the curves of which are shown in Fig. 4. It was thus found that the yield of the photocatalytic decomposition of NO parallels the yield of the photoluminescence due to the number of isolated Cu(I) ions. These results clearly indicate that the presence of the isolated Cu(I) ion species plays a vital role in the photocatalytic decomposition reaction of NO_x on the Cu^{+}/zeolite catalysts.

As can be seen in Fig. 5, the addition of NO molecules onto the Cu^{+}/zeolite catalyst was found to lead to the efficient quenching of the photoluminescence in its intensity and lifetime, its extent depending on the pressure of the NO molecules added. Such an efficient quenching can be attributed to the dynamic interaction between NO and the Cu(I) ion species, not only in the ground state but also in its excited state ($3d^9 4s^1$ state).

It was found that the ESR signals and FT-IR spectra of the Cu^{+}/ZSM-5 catalyst in the presence of NO molecules show the formation of mononitrosylic adducts, i.e. a Cu^{+}–NO$^{\delta-}$ species and UV irradiation of systems having mononitrosylic adducts led to a decrease in the intensities of the ESR and FT-IR spectra attributed to the Cu^{+}–NO$^{\delta-}$ species, without the appearance of any new ESR signals and IR peaks [7,8]. After UV irradiation was discontinued, the intensities of these spectra returned to their original levels. Such reverse changes in these spectra suggest not only that Cu^{+}–NO$^{\delta-}$ species act as reaction precursors, but also that the photoinduced decomposition of NO_x proceeds catalytically at 275 K.

From these results, the mechanism of the photocatalytic decomposition reaction

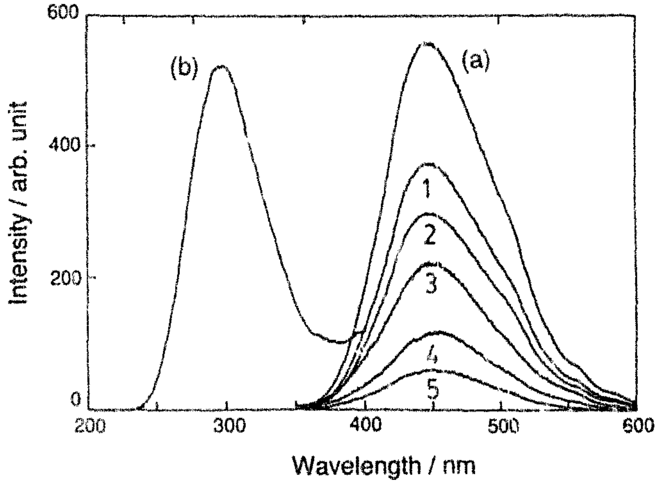


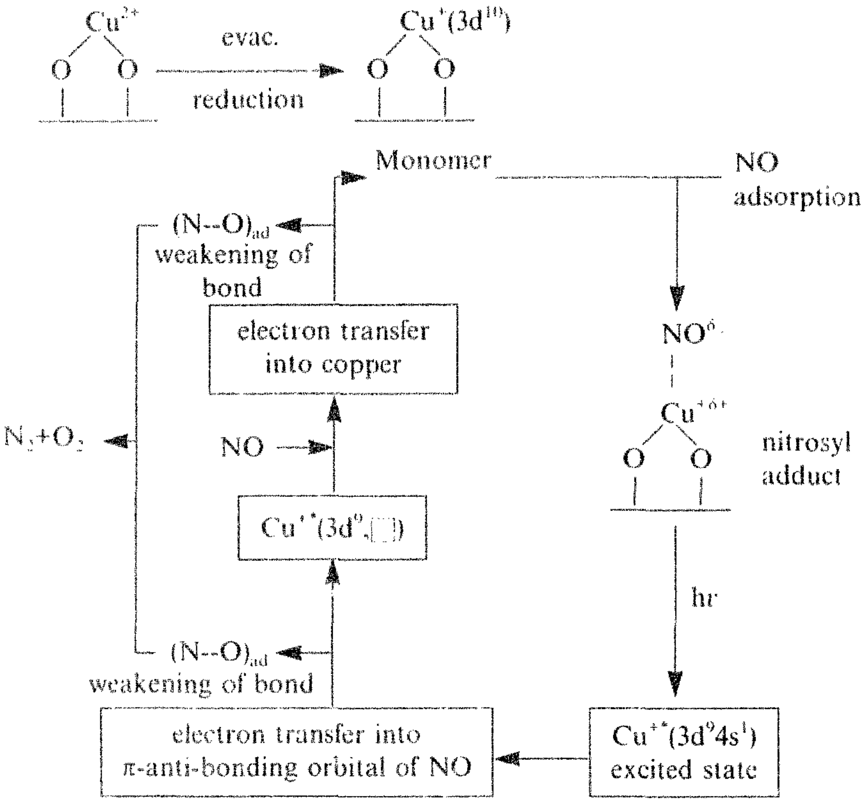
Fig. 5. Effects of the addition of NO on the photoluminescence spectrum of the Cu^+/ZSM-5 catalyst. (a) Photoluminescence and (b) excitation spectra. NO pressure (Torr): 1:0.1, 2:0.3, 3:0.5, 4:1, 5:20.

of NO_x into N_2 and O_2 on the Cu^+/zeolite catalyst can be proposed as follows (Scheme 1): an electron transfer from the electronically excited state of the Cu(I) ion ($3d^94s^1$ state) to an anti-π-bonding orbital of an NO molecule and a simultaneous electron transfer from the π-bonding orbital of another NO molecule to the vacant electron state of the Cu(I) ion ($3d^94s^0$ state) which causes a local charge separation and initiates the decomposition of NO. Two different NO molecules are simultaneously activated at a Cu(I) ion site in the local electron transfer within the lifetime of the excited state of the Cu(I) ion, resulting in the selective formation of N_2 and O_2 without any formation of N_2O and/or NO_2. Only this mechanism can explain the selective formation of N_2 and O_2 in the decomposition of NO. A similar mechanism has also been proposed for the selective formation of N_2 and O_2 in the decomposition of NO on highly dispersed tetrahedrally coordinated titanium oxide photocatalysts prepared within the zeolite cavities [13].

Fig. 6 shows the reaction time profiles of the photocatalytic decomposition of N_2O into N_2 and O_2 on the Cu^+/Y-zeolite catalysts with differing Si/Al ratios of Si/Al = 5.6, 13.9, and 390. It is clear that the photocatalytic reactivity of the Cu^+/Y-zeolite strongly depends on the Si/Al ratio of the zeolite supports. In connection with this phenomenon, the local structure of the Cu(I) ion species as an active site has also been investigated.

Fig. 7 shows the XANES and FT-EXAFS spectra of the Cu^+/Y-zeolite catalysts with different Si/Al ratios of Si/Al = 5.6, 13.9, and 390. The Cu^+/Y-zeolite catalyst with a Si/Al ratio of 13.9 exhibits quite similar XANES and FT-EXAFS spectra with those obtained from the Cu^+/ZSM-5 catalyst shown in Fig. 2(b) and (b′). It was also found that the photoluminescence spectrum of the Cu^+/Y-zeolite catalyst with Si/Al ratio of 13.9 is in good agreement with that of the Cu^+/ZSM-5 catalyst as shown in Fig. 1(a).

We have thus demonstrated that the local structure of the Cu(I) ion species was



Scheme 1. Reaction scheme of the photocatalytic decomposition of NO into N_2 and O_2 on the Cu^+/zeolite catalyst at 275 K.

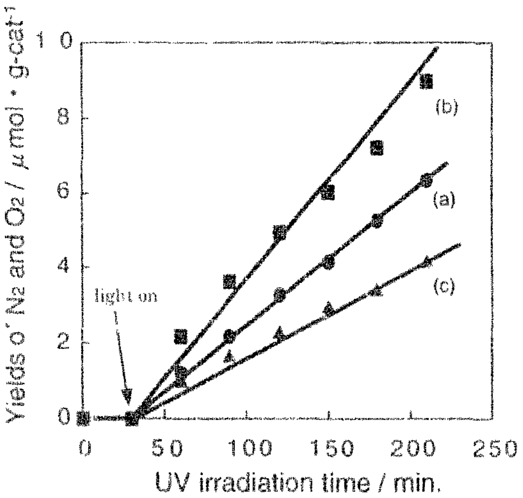


Fig. 6. Reaction profiles of the photocatalytic decomposition of N_2O into N_2 and O_2 at 275 K on the Cu^+/Y-zeolite catalysts with different Si/Al ratios: (a) 5.6, (b) 13.9, (c) 390.

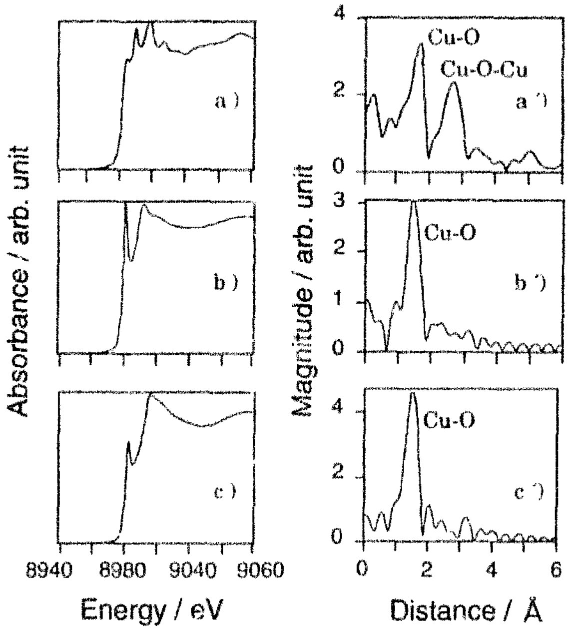


Fig. 7. XANES (a–c) and FT-EXAFS (a′–c′) spectra of the Cu^+/Y-zeolite catalysts with different Si/Al ratios: (a, a′) 5.6, (b, b′) 13.9, (c, c′) 390.

found to change dramatically when the amounts of copper ions loaded onto the zeolites were varied and the results obtained by XAFS, photoluminescence and ESR measurements clearly indicate that the Cu(I) ion species on the Y-zeolite with Si/Al ratio of 13.9 exist as the isolated linear two-coordinate Cu(I) monomer species in a similar manner to the species on the ZSM-5 and mordenite zeolites, while on the Y-zeolite with Si/Al ratio of 5.6, the Cu(I) ion species exists both as an isolated Cu(I) monomer species and a Cu(I)–Cu(I) dimer species. Therefore, it can be concluded that the isolated linear two-coordinate Cu(I) monomer species, which has the highest extent of coordinative unsaturation, exhibits the highest and most unique photocatalytic reactivity for the direct decomposition of NO_x into N_2 and O_2 even at 275 K.

4. Conclusions

The local structures of the Cu(I) ion species on the Cu^+/zeolite catalysts were clarified by means of in situ photoluminescence, XAFS, ESR, UV, and FT-IR measurements of the catalysts. UV irradiation of the Cu^+/zeolite catalysts in the presence of NO_x molecules led to the direct decomposition of NO_x into N_2 and O_2 even at 275 K. An electron transfer from the electronically excited state of Cu(I) ion to the anti-π-bonding orbital of an NO molecule initiates the photocatalytic decomposition of NO_x into N_2 and O_2. Comprehensive investigations into the relationship between the local structures and the photocatalytic reactivities of the Cu^+/zeolite catalysts showed that the isolated linear two-coordinated Cu(I) monomer species exhibits the highest photocatalytic reactivity for the direct decomposition of NO_x into N_2 and O_2, clearly showing the importance of the coordinative unsaturation of the active sites.

References

[1] M. Anpo, H. Yamashita, in: M. Anpo (Ed.), Surface Photochemistry, Wiley, West Sussex, 1996, p. 117.
[2] M. Anpo, H. Yamashita, S. Zhang, Curr. Opinion Solid State Mater. Sci. 1 (1996) 219.
[3] M. Anpo, M. Matsuoka, H. Mishima, H. Yamashita, Res. Chem. Intermed. 23 (1997) 197.
[4] M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, M. Honda, J. Phys. Chem. B 101 (1997) 2632.
[5] Y. Li, W.K. Hall, J. Phys. Chem. 94 (1990) 6145.
[6] M. Iwamoto, H. Yahiro, N. Mizuno, W.X. Zhang, Y. Mine, H. Furukawa, S. Kagawa, J. Phys. Chem. 96 (1992) 9360.
[7] M. Anpo, M. Matsuoka, Y. Shioya, H. Yamashita, E. Giamello, C. Morterra, M. Che, H.H. Patterson, S. Webber, S. Ouellette, M.A. Fox, J. Phys. Chem. 98 (1994) 5744.
[8] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura, M. Anpo, J. Catal. 136 (1992) 510.
[9] H. Yamashita, M. Matsuoka, K. Tsuji, Y. Shioya, M. Anpo, J. Phys. Chem. 100 (1996) 397
[10] D.H. Strome, K. Klier, J. Phys. Chem. 84 (1980) 981.
[11] J.D. Barrie, B. Dunn, G. Hollingsworth, J.I. Zink, J. Phys. Chem. 93 (1989) 3958.
[12] L.S. Kau, K.O. Hodgson, E.I. Solomon, J. Am. Chem. Soc. 111 (1989) 103.
[13] H. Yamashita, Y. Ichihashi, M. Anpo, M. Hashimoto, C. Louis, M. Che, J. Phys. Chem. 100 (1996) 16041.