Korean J. Chem. Eng., **14**(6), 498-501 (1997)

PHOTOCATALYTIC DECOMPOSITION OF N_2O ON Cu^+/Y-ZEOLITE CATALYSTS PREPARED BY ION-EXCHANGE

Masakazu Anpo[†], **Masaya Matsuoka, Kanami Hano, Hirotsugu Mishima, Takehiko Ono and Hiromi Yamashita**

Department of Applied Chemistry, College of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Sakai, Osaka 599, Japan

(Received 18 September 1997 • accepted 14 October 1997)

Abstract – *In situ* characterization of Cu^+/Y-zeolite catalysts and their photocatalytic reactivities for the decomposition of N_2O into N_2 and O_2 have been investigated by means of *in situ* photoluminescence, XAFS, and ESR techniques along with an analysis of the reaction products. It was found that Cu(I) ions included within the nanopores of Y-zeolite exist as the [Cu(I)--Cu(I)] dimer species as well as the isolated Cu(I) monomer species, their ratio being much dependent on the SiO_2/Al_2O_3 ratio of Y-zeolite. UV irradiation of these Cu^+/Y-zeolite catalysts in the presence of N_2O led to the photocatalytic decomposition of N_2O into N_2 and O_2 at temperatures as low as 275 K. The electronically excited state of Cu(I) ion ($3d^94s^1$ state) plays a vital role in the photocatalytic decomposition of N_2O into N_2 and O_2. 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 SiO_2/Al_2O_3 ratio of Y-zeolite. The isolated linear 2 coordinated Cu(I) monomer species formed on Y-zeolite having a moderate SiO_2/Al_2O_3 ratio exhibited a high photocatalytic reactivity for the direct decomposition of N_2O into N_2 and O_2, clearly showing the importance of the coordinative unsaturation of the active sites.

Key words: Photocatalyst, Photocatalytic Decomposition of N_2O, Copper Ion, Y-Zeolite, Photoluminescence, EXAFS

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, since zeolites have fascinating physical and chemical properties, unusual internal surface topology, and ion-exchange capacities, just to name a few [Anpo and Yamashita, 1996; Anpo et al., 1996, 1997a,b]. After the pioneering works by Iwamoto and Kagawa, 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 [Iwamoto et al., 1992; Li and Hall, 1990]. On the other hand, Anpo et al. 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 [Anpo et al., 1994; Giamello et al., 1992; Yamashita et al., 1996].

In the present study, a comprehensive characterization of the relationship between the local structure of the Cu(I) ion species and their photocatalytic reactivities for the decomposition of N_2O into N_2 and O_2 at 275 K has been investigated by changing the ratio of SiO_2/Al_2O_3 of Y-zeolites using *in situ* photoluminescence, X-ray absorption fine structure (XAFS), and ESR techniques.

EXPERIMENTAL SECTION

Two types of Y-zeolite (SiO_2/Al_2O_3=5.6, 13.9) were used. Cu^{2+}/Y-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 wt% as metal. The standard Cu^+/Y-zeolite catalysts were prepared by evacuation of the Cu^{2+}/Y-zeolite samples at 973-1,073 K. The photoluminescence spectra of the catalysts and their lifetimes were recorded at 77 K. The ESR spectra were recorded at 77 K. The XAFS spectra (XANES and FT-EXAFS) were obtained at the Photon Factory in Tsukuba. 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 [Anpo et al., 1994; Giamello et al., 1992, Yamashita et al., 1996].

RESULTS AND DISCUSSION

Cu^{2+}/Y-zeolite samples exhibited a typical ESR spectrum due to the hydrated Cu(II) ion anchored within zeolite cavities [Giamello et al., 1994]. The increased evacuation temperature led to a drastic decrease in the intensity of the ESR signals with

---

[†] To whom all correspondence should be addressed.
E-mail: anpo@chem.osakafu-u.ac.jp

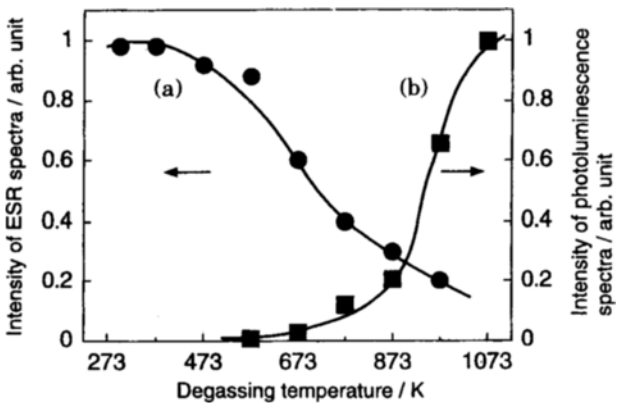

Fig. 1. Effects of the evacuation temperature of the Cu^{2+}/Y-zeolite (SiO_2/Al_2O_3=13.9) sample on (a) the relative intensity of the ESR spectra due to Cu^{2+} and (b) the relative yields of the photoluminescence due to Cu^+.

very minor changes in their spectrum parameters and line-shapes and also to the color changes of the samples from blue to white. With the catalysts prepared in this way a photoluminescence was observed at around 400-500 nm upon excitation at around 270-300 nm. As shown in Fig. 1, with increasing evacuation temperature, the intensity of the ESR signals due to the Cu(II) ions decreases and the intensity of the photoluminescence due to the Cu(I) ions increases at the same time, indicating that the chemical reduction of Cu(II) to Cu (I) had occurred under the evacuation at the higher temperatures.

Fig. 2 shows the typical photoluminescence spectra of the Cu^+/Y-zeolite catalysts at 77 K which were prepared by evacuation at 1,073 K for 2 h. The absorption band at around 270-300 nm and the photoluminescence spectrum at around 400-500 nm are attributed to the electronical 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 [Anpo et al., 1994; Barrie et al., 1989; Dedecek and Wichterlova, 1994; Strome and Klier, 1980; Yamashita et al., 1996]. 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 [Anpo et al., 1994; Barrie et al., 1989; Strome and Klier, 1980; Yamashita et al., 1996]. 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.

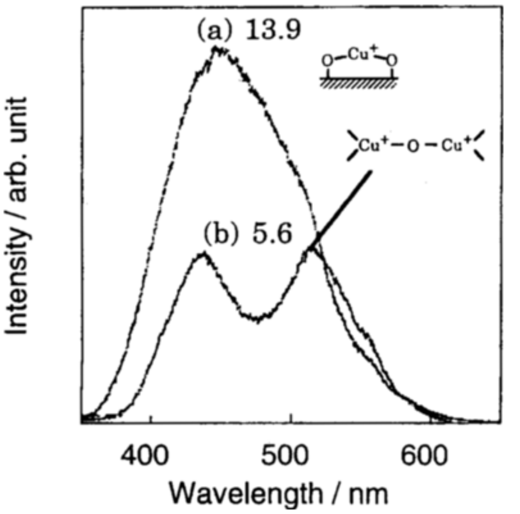

Fig. 2. Photoluminescence spectra measured at 77 K with the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) (a) and Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) (b) catalysts.

The shape and peak position of the photoluminescence were found to strongly depend on the SiO_2/Al_2O_3 ratio of Y-zeolites, indicating that local structure of Cu(I) ion is significantly modified by changing the ratio of Y-zeolites. As shown in Fig. 2, the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) catalyst exhibits a photoluminescence band at around 430 nm, while the Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) catalyst exhibits a photoluminescence band at around 510 nm as well as the band at around 430 nm. These results clearly show that in the Y-zeolite (SiO_2/Al_2O_3=13.9) most of the copper ions exist as isolated Cu(I) monomer species, while in the Y-zeolite (SiO_2/Al_2O_3=5.6) both isolated Cu(I) and an aggregated [Cu(I)--Cu(I)] dimer species are present.

The local structure of Cu(I) ion was investigated by means of Cu K-edge XAFS (XANES and FT-EXAFS) measurements. Fig. 3 shows the XANES and FT-EXAFS spectra of the original Cu^{2+}/Y-zeolite (SiO_2/Al_2O_3=13.9) sample (a, a') and the spectra of the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) (b, b') and Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) catalysts (c, c') prepared by the evacuation of the corresponding original Cu^{2+}/Y-zeolite samples at 1,073 K for 2 h. The XANES spectra of these sam-

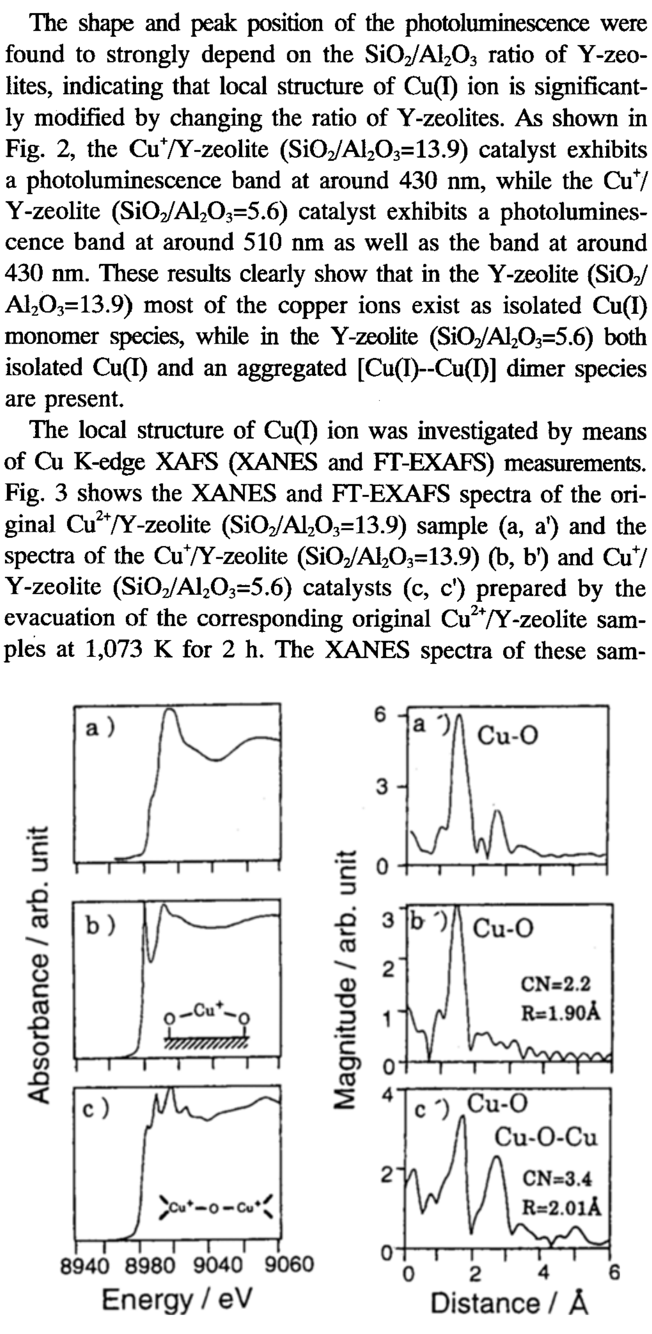

Fig. 3. XANES (a-c) and FT-EXAFS (a'-c') spectra of the Cu^{2+}/Y-zeolite (SiO_2/Al_2O_3=13.9) sample (a, a') and the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) (b, b') and Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) (c, c') catalysts. Coordination numbers (CN) and atomic distances (R) obtained from curve-fitting analysis of EXAFS spectra are shown in Fig.

ples exhibit several kinds of bands due to 1s-3d transition, 1s-4pz (1s-4pπ*) transition, 1s-4px, y (1s-4pσ*) transition and multiple scattering [Kau et al., 1989; Yamashita et al., 1996]. Cu^{2+}/Y-zeolite sample dried at 373 K (Fig. 3-a) shows a very weak preedge band due to 1s-3d transition and an intense band due to 1s-4p, accompanied by their shake-down bands indicating that the Cu^{2+}/zeolite samples contain predominantly Cu(II) ions having slightly distorted symmetries.

The XANES spectrum of Cu^+/Y (SiO_2/Al_2O_3=13.9) exhibits a very sharp preedge peak due to the 1s-4pz transition with strong intensity which is separated clearly from a main band due to 1s-4px, y transition, indicating that a linear 2-coordinate Cu(I) ion is formed. As shown in Fig. 3-b', the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) exhibits a Cu-O peak only at around 1.5 Å, also indicating the presence of isolated Cu(I) ions on the catalyst. These results indicate that the photoluminescence at around 430 nm can be attributed to the existence of linear 2-coordinate Cu(I) monomer. In the case of Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) catalyst (Fig. 3-c'), the peak due to the Cu-O-Cu bond is observed in the FT-EXAFS spectrum at around 2.6 Å in addition to a peak at around 1.5 Å due to the Cu-O bonds, suggesting that some aggregated copper species is also formed except for linear 2-coordinate Cu(I) in the Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) catalyst. Thus, the photoluminescence at around 510 nm can be attributed to the existence of Cu(I) dimer. These results obtained by XAFS measurements are in good agreement with those obtained by the photoluminescence measurements.

These results obtained by ESR, XAFS, and photoluminescence measurements with the Cu^{2+}/Y-zeolite samples as well as Cu^+/Y-zeolite catalysts clearly indicate that in the Y-zeolite both isolated Cu(I) ions and an aggregated Cu(I)--O--Cu(I) dimer species are present, their ratio being much dependent on the SiO_2/Al_2O_3 ratio of Y-zeolite.

As can be seen in Fig. 4, the addition of N_2O molecules onto the Cu^+/Y-zeolite catalyst (SiO_2/Al_2O_3=13.9) was found to lead to the efficient quenching of the photoluminescence in its intensity and lifetime, its extent depending on the pressure of the N_2O molecules added. Such an efficient quenching can be attributed to the dynamic interaction between N_2O and the Cu(I) ion species, not only in the ground state but also in its excited state ($3d^94s^1$ state). The quenching of the photoluminescence by the addition of N_2O was also observed with Cu^+/Y-zeolite catalyst (SiO_2/Al_2O_3=5.6). In this case, the band observed at around 430 nm was quenched more efficiently than the band at around 510 nm, indicating monomer Cu(I) ion can interact with N_2O more strongly than the dimer species.

Fig. 5 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 and 13.9. As shown in Fig. 5, UV irradiation of the Cu^+/Y-zeolite catalysts even at temperatures as low as 275 K in the presence of N_2O 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 N_2O molecules into N_2 and O_2. Thus, UV irradiation of the Cu^+/Y-zeolite catalysts at 275 K in the presence of N_2O molecules brought about the photocatalytic decomposition of N_2O into N_2 and O_2. Although it is difficult to determine the actual quantum yields in such very small powdered systems, the results in Fig. 5 show that the Cu^+/Y-zeolite catalyst exhibits high photocatalytic reactivity for the direct decomposition of N_2O into N_2 and O_2 at 275 K. It is also clear that the photocatalytic reactivity of the Cu^+/Y-zeolite strongly depends on the SiO_2/Al_2O_3 ratio of the zeolite supports.

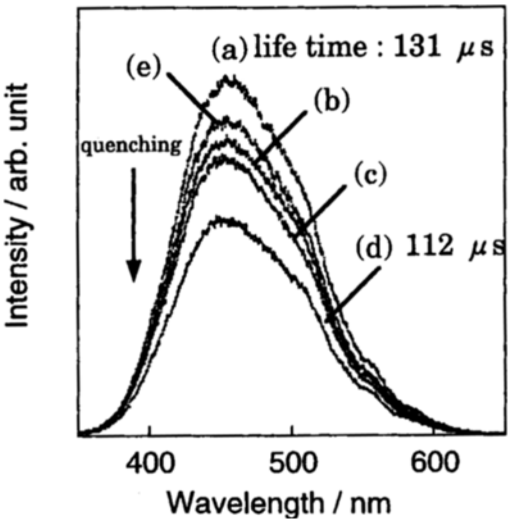

Fig. 4. Effects of the addition of N_2O on the photoluminescence spectrum of the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) catalyst. N_2O pressure (in Torr); (a) 0, (b) 0.01, (c) 1, (d) 10, (e) evacuation at 298 K after (d).

We have thus demonstrated that the local structure of the Cu(I) ion species changes dramatically when the SiO_2/Al_2O_3 ratio of the zeolites is varied. The results obtained by XAFS, photoluminescence and ESR measurements clearly indicate that the Cu(I) ion species on the Y-zeolite with a SiO_2/Al_2O_3 ratio of 13.9 exists as the isolated linear 2 coordinate Cu(I) monomer species in a similar manner to the species on the ZSM-5 and mordenite zeolites [Anpo et al., 1994; Yamashita et al.,

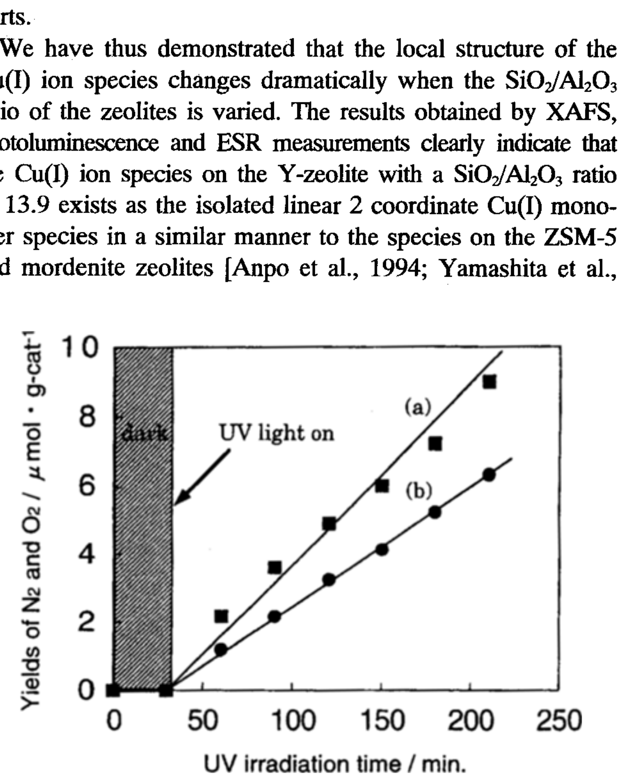

Fig. 5. Reaction profiles of the photocatalytic decomposition of N_2O into N_2 and O_2 at 275 K on the Cu^+/Y-zeolite (SiO_2/Al_2O_3=13.9) (a) and Cu^+/Y-zeolite (SiO_2/Al_2O_3=5.6) (b) catalysts.

1996] while on the Y-zeolite with a SiO_2/Al_2O_3 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 2 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 N_2O into N_2 and O_2 even at 275 K.

Although the detailed mechanism for the photocatalytic decomposition reaction of N_2O into N_2 and O_2 on the Cu^+/zeolite catalyst will be the subject of our future work, these results clearly suggest that 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 N_2O molecule initiates the decomposition of N_2O. A similar reaction mechanism has already been proposed for the photocatalytic decomposition of NO into N_2 and O_2 on highly dispersed Cu(I) ions prepared on SiO_2 or zeolites [Anpo et al., 1996; Yamashita et al., 1996b].

CONCLUSIONS

The local structures of the Cu(I) ion species on the Cu^+/Y-zeolite catalysts were clarified by means of *in situ* photoluminescence, XAFS and ESR measurements of the catalysts. UV irradiation of the Cu^+/Y-zeolite catalysts in the presence of N_2O molecules led to the direct decomposition of N_2O 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 N_2O molecule initiates the photocatalytic decomposition of N_2O 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 2 coordinated Cu(I) monomer species exhibits the highest photocatalytic reactivity for the direct decomposition of N_2O into N_2 and O_2, clearly showing the importance of the coordinative unsaturation of the active sites.

ACKNOWLEDGMENT

This work was supported in part by the Grant-in-Aid on Priority-Area-Research on "Catalytic Chemistry of Unique Reaction Fields" (09218250) and "Electrochemistry of Ordered Interfaces" (09237258) of the Ministry of Education, Science, Sports, and Culture of Japan. M. Anpo is much indebted to the Tosoh Corporation for kindly providing the Y-zeolite samples.

REFERENCES

Anpo, M. and Yamashita, H., "Photochemistry of Surface Species Anchored on Solid Surfaces", in M. Anpo (editor), Surface Photochemistry, Wiley, West Sussex, 117 (1996).

Anpo, M., Yamashita, H. and Zhang, S., "Photoinduced Surface Chemistry", *Current Opinion in Solid State & Materials Science,* **1**, 219 (1996).

Anpo, M., Matsuoka, M., Mishima, H. and Yamashita, H., "The Design of Photocatalysts for the Removal of NO_x at Normal Temperatures --Copper (I) and Silver (I) Ion Catalysts Anchored within Zeolite Cavities", *Res. Chem. Intermed.,* **23**, 197 (1997a).

Anpo, M., Yamashita, H., Ichihashi, Y., Fujii, Y. and Honda, M.,"Photocatalytic Reduction of CO_2 with H_2O on Titanium Oxides Anchored within Micropores of Zeolites: Effects of the Structure of the Active Sites and the Addition of Pt", *J. Phys. Chem. B,* **101**, 2632 (1997b).

Anpo, M., Matsuoka, M., Shioya, Y., Yamashita, H., Giamello, E., Morterra, C., Che, M., Patterson, H. H., Webber, S., Ouellette, S. and Fox, M. A., "The Preparation of the Cu^+/ZSM-5 Catalyst and Its Interaction with NO, and Photocatalytic Decomposition of NO into N_2 and O_2 on the Catalyst at 275 K-*In Situ* Photoluminescence, ESR and FT-IR Investigation-", *J. Phys. Chem.,* **98**, 5744 (1994).

Barrie, J. D., Dunn, B., Hollingsworth, G. and Zink, J. I., "Optical Spectroscopy of Copper(I)-Doped Na^+-β''-Alumina", *J. Phys. Chem.,* **93**, 3958 (1989).

Dedecek, J. and Wichterlova, B, "Siting and Redox Behavior of Cu Ions in CuH-ZSM-5 Zeolites", *J. Phys. Chem.,* **98**, 5721 (1994).

Giamello, E., Murphy, D., Magnacca, G., Morterra, C., Shioya, Y., Nomura T. and Anpo, M., "The Interaction of NO with Copper Ions in ZSM5: An EPR and IR Investigation", *J. Catal.,* **136**, 510 (1992).

Iwamoto, M., Yahiro, H., Mizuno, N., Zhang, W. X., Mine, Y., Furukawa, H. and Kagawa, S., "Removal of Nitrogen Monooxide through a Novel Catalytic Process", *J. Phys. Chem.,* **96**, 9360 (1992).

Kau, L. S., Hodgson, K. O. and Solomon, E. I., "X-ray Absorption Edge and EXAFS Study of the Copper Sites in ZnO Methanol Synthesis Catalysts", *J. Am. Chem. Soc.,* **111**, 103 (1989).

Li, Y. and Hall, W. K., "Stoichiometric Catalytic Decomposition of Nitric Oxide over Cu-ZSM-5 Catalysts", *J. Phys. Chem.,* **94**, 6145 (1990).

Strome, D. H. and Klier, K., "The Effect of Oxygen on Photoluminescence and Resonance Energy Transfer in Cu(I) Y Zeolite", *J. Phys. Chem.,* **84**, 981 (1980).

Yamashita, H., Ichihashi, Y., Anpo, M., Hashimoto, M., Louis, C. and Che, M., "Photocatalytic Decomposition of NO at 275 K on Titanium Oxides Included within Y-Zeolites Cavities: The Structure and Role of the Active Sites", *J. Phys. Chem.,* **100**, 16041 (1996a).

Yamashita, H., Matsuoka, M., Tsuji, K., Shioya, Y. and Anpo, M., "*In Situ* XAFS, Photoluminescence, and IR Investigations of Copper Ions Included within Various Kinds of Zeolites-The Structure of Cu(I) Ions and Their Interaction with CO Molecules-", *J. Phys. Chem.,* **100**, 397 (1996b).