PHOTOCATALYTIC DECOMPOSITION OF N₂O ON Cu⁺/Y-ZEOLITE CATALYSTS PREPARED BY ION-EXCHANGE

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Abstract—In situ characterization of Cu⁺/Y-zeolite catalysts and their photocatalytic reactivities for the decomposition of N₂O into N₂ and O₂ 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)₆Cu(I)] dimer species as well as the isolated Cu(I) monomer species, their ratio being much dependent on the SiO₂/Al₂O₃ ratio of Y-zeolite. UV irradiation of these Cu⁺/Y-zeolite catalysts in the presence of N₂O led to the photocatalytic decomposition of N₂O into N₂ and O₂ at temperatures as low as 275 K. The electronically excited state of Cu(I) ion (3d⁹4s¹ state) plays a vital role in the photocatalytic decomposition of N₂O into N₂ and O₂. 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 SiO₂/Al₂O₃ ratio of Y-zeolite. The isolated linear 2 co-ordinated Cu(I) monomer species formed on Y-zeolite having a moderate SiO₂/Al₂O₃ ratio exhibited a high photocatalytic reactivity for the direct decomposition of N₂O into N₂ and O₂, clearly showing the importance of the coordinative unsaturation of the active sites.

Key words: Photocatalyst, Photocatalytic Decomposition of N₂O, 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 into N₂ and O₂ 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 NO₂ 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 N₂ and O₂ 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 Cu(I) ion species and their photocatalytic reactivities for the decomposition of N₂O into N₂ and O₂ at 275 K has been investigated by changing the ratio of SiO₂/Al₂O₃ of Y-zeolites using in situ photoluminescence, X-ray absorption fine structure (XAFS), and ESR techniques.

EXPERIMENTAL SECTION

Two types of Y-zeolite (SiO₂/Al₂O₃=5.6, 13.9) were used. Cu⁺/Y-zeolite samples were prepared by ion-exchange with an aqueous Cu(NH₃)₄Cl 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⁺/Y-zeolite samples at 77-1,073 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 (λ > 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⁺/Y-zeolite samples exhibited a typical ESR spectrum due to the hydrated Cu(I) 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...
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(0.8 0.6 0.4 0.2 0.0)

\(273 \quad 473 \quad 673 \quad 873 \quad 1073\)

Degassing temperature / K

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 Cu²⁺/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, \((3d^{10}\rightarrow 3d^44s)\) and its reverse radiative deactivation \((3d^44s\rightarrow 3d^9)\), respectively [Anpo et al., 1994; Barrie et al., 1989; 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, \(3d^9\rightarrow 4s\sigma^*\) and its reverse radiative deactivation \(4s\sigma^*\rightarrow 3d^9\), 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.

The shape and peak position of the photoluminescence were found to strongly depend on the \(\text{SiO}_2/\text{Al}_2\text{O}_3\) 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 Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) catalyst exhibits a photoluminescence band at around 430 nm, while the Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=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 (SiO₂/Al₂O₃=13.9) most of the copper ions exist as isolated Cu(I) monomer species, while in the Y-zeolite (SiO₂/Al₂O₃=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 Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) sample (a, a') and the spectra of the Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) (b, b') and Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=5.6) catalysts (c, c') prepared by the evacuation of the corresponding original Cu²⁺/Y-zeolite samples at 1,073 K for 2 h. The XANES spectra of these sam-

![Fig. 1. Effects of the evacuation temperature of the Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) sample on (a) the relative intensity of the ESR spectra due to Cu²⁺ and (b) the relative yields of the photoluminescence due to Cu⁺.](image1)

![Fig. 2. Photoluminescence spectra measured at 77 K with the Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) (a) and Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=5.6) (b) catalysts.](image2)

![Fig. 3. XANES (a-c) and FT-EXAFS (a’-c’) spectra of the Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) sample (a, a’) and the Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=13.9) (b, b’) and Cu²⁺/Y-zeolite (SiO₂/Al₂O₃=5.6) (c, c’) catalysts. Coordination numbers (CN) and atomic distances (R) obtained from curve-fitting analysis of EXAFS spectra are shown in Fig.](image3)