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Local Structures of Copper Ion Catalysts Anchored onto Various Oxide Supports and their Photocatalytic Reactivities for the Decomposition of N₂O at 298 K. *In Situ* XAFS, Photoluminescence, EPR Investigations

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Abstract. Cu⁺/(SiO₂/Al₂O₃), Cu⁺/Al₂O₃ and Cu⁺/SiO₂ catalysts were prepared by a combination of the ion-exchange method and thermovacuum treatment. *In-situ* XANES and EXAFS investigations of the catalysts have revealed that Cu⁺ ions are anchored onto Al₂O₃ or SiO₂ as planar 3-coordinate Cu⁺, while being anchored onto SiO₂/Al₂O₃ as linear 2-coordinate Cu⁺. Photoluminescence measurements of the catalysts and their quenching by the addition of N₂O indicated that the Cu⁺ ions interact with N₂O in their photo excited state (3d⁹4s¹). UV irradiation of the catalysts in the presence of N₂O led to the formation of N₂ and O₂ at 298 K, indicating that the photocatalytic decomposition of N₂O proceeds on the Cu⁺ ion catalysts. Reaction proceeds more efficiently on the Cu⁺/(SiO₂/Al₂O₃) catalyst than on the Cu⁺/Al₂O₃ or Cu⁺/SiO₂ catalysts, suggesting that the 2-coordinate Cu⁺ species show the higher activity for the photocatalytic decomposition of N₂O than the 3-coordinate Cu⁺ species.

1. INTRODUCTION

It has been reported that Cu⁺ ion catalysts show high photocatalytic activity for the decomposition of NO_x[1,2]. We have also observed that the coordination geometry and the photoluminescent property of the Cu⁺ ion species were greatly affected by types of supports[3], however, their details have not been fully clarified yet. This study deals with the XAFS and photoluminescence investigations of the Cu⁺ / (SiO₂/Al₂O₃), Cu⁺ / Al₂O₃ and Cu⁺ / SiO₂ catalysts prepared by a combination of the ion exchange method and thermovacuum treatment of Cu²⁺ ion samples in order to clarify the effect of the supports on the local environment of the Cu⁺ ions. The effect of the coordinate geometry of the Cu⁺ ions on the photocatalytic reactivity of the decomposition of N₂O at 298 K has also been investigated.

2. EXPERIMENTAL SECTION

Cu²⁺ / (SiO₂/Al₂O₃) (SiO₂/Al₂O₃ mol ratio =24.6), Cu²⁺ / Al₂O₃ and Cu²⁺ / SiO₂ samples were prepared by the ion exchange with an aqueous Cu(NH₃)₂²⁺ solution. After washing with water and drying in air at 373 K, the copper loadings of the samples were determined by an inductively coupled plasma emission spectrometer; the loading of copper cations as metal was 0.76 wt% for SiO₂/Al₂O₃, 0.55 wt% for Al₂O₃ and 0.33 wt% for SiO₂, respectively. The Cu⁺ ion catalysts were prepared by the evacuation of the Cu²⁺ ion samples at 973 K. EPR spectra of the catalysts were recorded at 298 K. The XAFS spectra (XANES and EXAFS) were obtained at the BL-10B facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. Si(311) channel-cut crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The Cu K-edge absorption spectra were recorded in the transmission mode at 298 K. The Fourier transformation was performed on k³-weighted EXAFS oscillations in the range of 3~12 Å⁻¹. The curve-fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method and the empirical backscattering parameter sets extracted from the shell features of reference copper compounds. Photocatalytic reactions were performed using high pressure Hg lamp and water filter at 298 K. The reaction products were analyzed by gas chromatography.

3. RESULTS AND DISCUSSION

As shown in Fig. 1, the Cu²⁺ / (SiO₂/Al₂O₃) sample degassed at 298 K gives broad and axial EPR signal (g_{||}=2.25, A_{||}=169 G) due to the tetraammine copper(II) complex [4]. Figure 2 (a, a') shows the XANES and FT-EXAFS spectra of the Cu²⁺ / (SiO₂/Al₂O₃) sample degassed at 298 K. The FT-EXAFS spectrum of the sample exhibits an intense peak at around 1.5 Å (without any corrections for phase shift) due to the neighboring N atoms as suggested by the EPR measurement. The curve-fitting of the peak yields a Cu-N bond length of (R) =2.00 Å, a coordination number of (CN) =4.1, and the Debye-Waller factor of (σ²) =0.0020 Å², suggesting that the tetraammine copper(II) complex is formed on the SiO₂/Al₂O₃ surface. The XANES spectrum of the Cu²⁺ / (SiO₂/Al₂O₃) sample exhibits a well-separated weak preedge band (A) due to the 1s-3d transition as well

as an intense band due to the 1s-4p transition (B,C) [3]. The band (B) attributed to the 1s-4p_z transition can be observed as a shoulder of the intense band (C) attributed to the 1s-4p_{x,y} transition accompanied by their weak shake-down bands (B', C') induced by the ligand effect [3]. These peaks are typical for the Cu²⁺ ion having an unoccupied d orbital (3d⁹). These result indicate that the Cu²⁺ / (SiO₂/Al₂O₃) sample contains tetraammine copper(II) complex having slightly distorted symmetry.

As shown in Fig. 3(a), Cu⁺/(SiO₂/Al₂O₃) catalyst which was prepared by the evacuation of the original Cu²⁺/(SiO₂/Al₂O₃) sample at 973 K exhibits a very strong and sharp band (B) due to the 1s-4p_z transition. In the spectrum, this band is clearly separated from the band (C) attributed to the 1s-4p_{x,y} transition. It is known that in a planar or a linear geometry the 1s-4p_z transition is not affected by the ligands, therefore, the copper compounds having these geometries exhibit a strong and sharp band (B) attributed to the 1s-4p_z transition. Band (B) attributed to the 1s-4p_z transition without shake-down bands is intense enough to identify the copper species as the isolated Cu⁺ ions with linear 2 coordinate geometry. As shown in Fig. 3(a'), FT-EXAFS of the Cu⁺/(SiO₂/Al₂O₃) catalyst exhibits a peak at around 1.5 Å due to the neighboring O atoms. A peak due to the neighboring Cu atoms is not observed, indicating that Cu⁺ are anchored onto the SiO₂/Al₂O₃ in an isolated state. The curve-fitting of the Cu-O peak yields Cu-O bond length of (R) = 1.92 Å, a coordination number of (CN) = 1.9, and the Debye-Waller factor of (σ²) = 0.0024 Å², indicating that the 2 coordinate Cu⁺ ion is formed on the SiO₂/Al₂O₃ surface as suggested by the XANES investigation. As shown in Fig. 3(b) and (c), Cu⁺ / Al₂O₃ and Cu⁺ / SiO₂ catalysts which were prepared by the evacuation of the original Cu²⁺/Al₂O₃ and Cu²⁺/SiO₂ samples at 973 K exhibit a sharp band (B) due to the 1s-4p_z transition, however, the intensity of the band is the smaller in compared with that of Cu⁺/(SiO₂/Al₂O₃) catalyst, suggesting that Cu⁺ ions with planar 3 coordinate geometry are formed on these supports. The curve-fitting of the Cu-O peak observed in FT-EXAFS spectra (b', c') of these catalysts yield Cu-O bond length of (R) = 1.90 Å, a coordination number of (CN) = 2.9, and the Debye-Waller factor of (σ²) = 0.0020 Å² for Cu⁺/Al₂O₃, and Cu-O bond length of (R) = 1.86 Å, a coordination number of (CN) = 3.1, and the Debye-Waller factor of (σ²) = 0.0035 Å² for Cu⁺/SiO₂ showing that the 3 coordinate Cu⁺ ions are formed on these catalysts.

The Cu⁺/(SiO₂/Al₂O₃) catalyst exhibited a typical photoluminescence spectrum at around 430 nm upon the excitation at around 300 nm. The absorption band at around 300 nm and photoluminescence band at around 430 nm is attributed to the electronic excitation of the isolated Cu⁺ ion (3d¹⁰ → 3d⁹4s¹) and its reverse radiative deactivation (3d⁹4s¹ → 3d¹⁰), respectively[1]. The addition of N₂O on the Cu⁺/(SiO₂/Al₂O₃) catalyst led to the quenching of the photoluminescence, indicating that N₂O interacts with Cu⁺ ion in a photo excited state. In fact, UV irradiation of the catalyst in the presence of N₂O led to the formation of N₂ and O₂ with a good linearity against the UV irradiation time, indicating that Cu⁺/(SiO₂/Al₂O₃) catalyst acts as an efficient photocatalyst for the decomposition of N₂O. Under the dark condition, the formation of N₂ and O₂ was not observed. Cu⁺ / SiO₂ and Cu⁺ / Al₂O₃ catalysts also acted as a photocatalyst for the decomposition of N₂O, however, their specific activities per one Cu⁺ ion were 1/2 ~ 1/3 of that of the Cu⁺/(SiO₂/Al₂O₃) catalyst, suggesting that linear 2 coordinate Cu⁺ shows the higher activity than planar 3 coordinate Cu⁺. From these results, it was found that by using SiO₂/Al₂O₃ binary oxide as a support linear 2 coordinate Cu⁺ ions are selectively produced which show very high photocatalytic activity for the decomposition of N₂O.

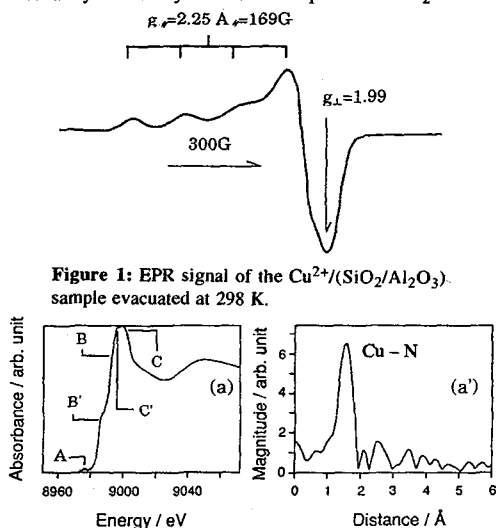


Figure 1: EPR signal of the Cu²⁺/(SiO₂/Al₂O₃) sample evacuated at 298 K.

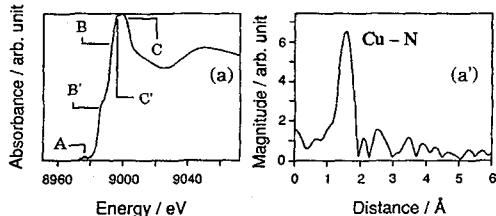


Figure 2: XANES (a) and FT-EXAFS (a') spectra of the Cu²⁺/(SiO₂/Al₂O₃) sample evacuated at 298 K.

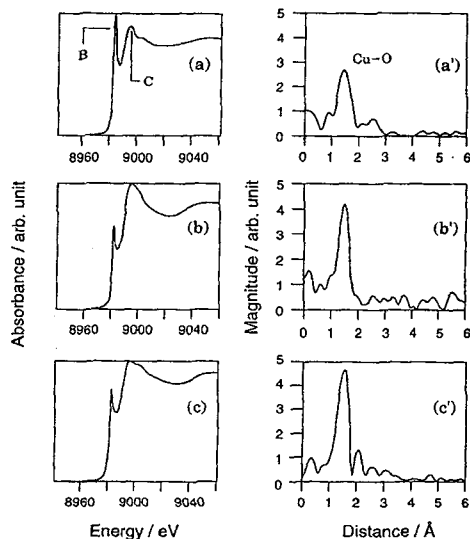


Figure 3: XANES (left) and FT-EXAFS (right) spectra of the (a, a') Cu⁺/(SiO₂/Al₂O₃), (b, b') Cu⁺/Al₂O₃ and (c, c') Cu⁺/SiO₂ catalysts.

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