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XAFS Studies on the Metal Ion (Cu, Ag) Photocatalysts Prepared Within Zeolite Cavities Using an Ion-Exchange Method

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Abstract. Using a combination of in-situ XAFS, photoluminescence and diffuse reflectance measurements, the characterization of the coordination geometry of metal (Cu, Ag) ion photocatalysts prepared within zeolites by an ion-exchange method and thermovacuum treatment has been carried out. The metal ions within zeolites were found to exist as isolated monomers, dimers and clusters, their relative concentration strongly depending of types of zeolites used. Within ZSM-5 and mordenite zeolites, most of the metal ions (Cu^+ , Ag^+) were found to exist as isolated monomers with low coordinate numbers (planar 3 or linear 2 coordinate geometry), in contrast to the case of the Y-zeolite having dimers and/or clusters.

1. INTRODUCTION

It is of special interest to design the ion and/or cluster size photocatalysts within the zeolites having unique nanopore structure and ion-exchange capacities. Recently, we have found that the Cu^+ and Ag^+ ion photocatalysts included within zeolite cavities exhibit the high photocatalytic reactivity for NO decomposition and their reactivities much depend on the types of zeolites used [1-3]. In the present study, a combination of in-situ XAFS, photoluminescence and diffuse reflectance measurements has been applied to characterize the local environment of metal (Cu, Ag) ion photocatalysts prepared within various types of zeolites using ion-exchange method and thermovacuum treatment.

2. EXPERIMENTAL

Three types of zeolites and SiO_2 (300 m^2/g) were used as supports; ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=23.3$), Y-zeolite (5.5) and mordenite (14.9). $\text{Cu}^{2+}/\text{zeolite}$ and $\text{Ag}^+/\text{support}$ samples were prepared by ion-exchange with aqueous $(\text{Cu}(\text{NH}_3)_4)_2^{2+}$ and $\text{Ag}(\text{NH}_3)_2^+$ solutions, respectively; the loadings as metal were 3.0 (ZSM-5), 2.6 (Y-zeolite) and 1.9 wt% (mordenite) for $\text{Cu}^{2+}/\text{zeolite}$, 6.7 (ZSM-5), 6.5 (Y-zeolite) and 2.8 wt% (SiO_2) for $\text{Ag}^+/\text{support}$ samples. The Cu K-edge and Ag K-edge XAFS spectra were recorded in the transmission mode at 295 K at the BL-10B facility of the Photon Factory in Tsukuba.

3. RESULTS AND DISCUSSION

Figure 1 shows the XANES spectra of the $\text{Cu}^{2+}/\text{ZSM-5}$ sample (a) and $\text{Cu}^+/\text{zeolite}$ catalysts (b-d) prepared by the evacuation at 973 K. The spectra of these samples exhibit four kinds of bands due to 1s-3d transition (A), 1s-4pz ($1s-4p\pi^*$) transition (B), 1s-4px,y ($1s-4p\sigma^*$) transition (C) and multiple scattering (D). $\text{Cu}^{2+}/\text{ZSM-5}$ sample dried at 373 K shows a well-separated weak preedge band due to 1s-3d transition (A) and an intense band due to 1s-4p (B,C), accompanied by their shake-down bands (B',C') indicating that the $\text{Cu}^{2+}/\text{zeolite}$ samples contain predominantly Cu^{2+} ions having slightly distorted symmetries. The band due to 1s-4pz (B) observed with $\text{Cu}^+/\text{ZSM-5}$ and $\text{Cu}^+/\text{mordenite}$ catalysts is intense enough to identify the copper species as isolated Cu^+ ions with a planar 3 or a linear 2 coordinate geometry. Figure 1 also shows the corresponding FT-EXAFS spectra. $\text{Cu}^+/\text{ZSM-5}$ and $\text{Cu}^+/\text{mordenite}$ catalysts exhibit only a small peak which can be assigned to the neighboring O atoms (Cu-O), indicating that the isolated Cu^+ ions are present with 2 or 3-coordinate geometry. On the other hand, $\text{Cu}^+/\text{Y-zeolite}$ exhibits an intense peak due to neighboring copper atoms (Cu-Cu) as well as Cu-O peak, indicating the aggregation of Cu^+ ions. These $\text{Cu}^+/\text{zeolite}$ catalysts show a typical photoluminescence spectrum at around 400-600 nm at 77 K upon excitation at around 300 nm. The excitation band at around 300 nm and the photoluminescence bands at around 400-500 nm are attributed to the electronic excitation of the Cu^+ ion ($3d^{10} \rightarrow 3d^9 4s^1$) and its reverse radiative deactivation ($3d^9 4s^1 \rightarrow 3d^{10}$),

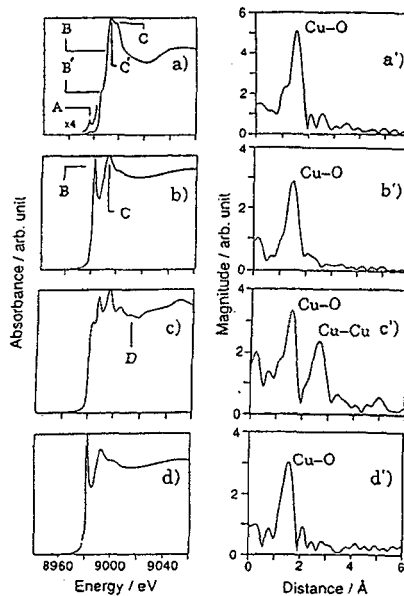


Figure 1. XANES (left) and FT-EXAFS (right) spectra of the (a,a') $\text{Cu}^{2+}/\text{ZSM-5}$ sample and (b,b') $\text{Cu}^+/\text{ZSM-5}$, (c,c') $\text{Cu}^+/\text{Y-zeolite}$ and (d,d') $\text{Cu}^+/\text{mordenite}$ catalysts. (The catalysts were prepared by evacuation of the original $\text{Cu}^{2+}/\text{zeolite}$ samples at 973 K).

respectively. On the other hand, the photoluminescence band at around 500-600 nm is attributed to the presence of the $(\text{Cu}^{+}-\text{Cu}^{+})$ dimer or high (more than 4) coordinated Cu^{+} species. The results in Fig. 2 show that the photoluminescence band at around 430-460 nm is the major component for the $\text{Cu}^{+}/\text{ZSM-5}$ and $\text{Cu}^{+}/\text{mordenite}$ catalysts, while the $\text{Cu}^{+}/\text{Y-zeolite}$ catalyst exhibits two different photoluminescence bands at around 450 and 525 nm. These results clearly indicate that in the ZSM-5 and mordenite zeolites most of the copper ions exist as isolated Cu^{+} monomer species, but in the Y-zeolite both isolated Cu^{+} and aggregated $(\text{Cu}^{+}-\text{Cu}^{+})$ dimer species are present, in good agreement with the results obtained by the XAFS measurements.

Figure 3 shows the XAFS spectra of the $\text{Ag}^{+}/\text{zeolite}$ and $\text{Ag}^{+}/\text{SiO}_2$ catalysts. In the FT-EXAFS spectra, $\text{Ag}^{+}/\text{ZSM-5}$ exhibits only a peak due to the neighboring O atoms (Ag-O) indicating the presence of the isolated Ag^{+} ions. By the curve-fitting analyses of this Ag-O peak, atomic distance and coordination numbers were obtained to be 2.15 Å and 1.9, respectively. On the other hand, the $\text{Ag}^{+}/\text{Y-zeolite}$ and $\text{Ag}^{+}/\text{SiO}_2$ catalysts exhibit a peak due to the neighboring Ag atoms (Ag-Ag) in addition to the Ag-O peak, indicating that some parts of silver ions are reduced and aggregated to form Ag ion clusters or Ag metal particles. Figure 4 shows the diffuse reflectance spectra of these catalysts. The $\text{Ag}^{+}/\text{ZSM-5}$ exhibits an intense absorption band at around 220 nm which is attributed to the $4d^{10} \rightarrow 4d^9 5s^1$ electronic transition on the Ag^{+} ions. On the other hand, $\text{Ag}^{+}/\text{Y-zeolite}$ and $\text{Ag}^{+}/\text{SiO}_2$ exhibit the broad absorption band in wavelength regions longer than 250 nm which can be assigned to the Ag_n^0 and Ag_m^{n+} clusters. These results clearly indicate that in the ZSM-5 most of the silver ions exist as isolated Ag^{+} monomers, but in the Y-zeolite as well as on SiO_2 the Ag_n^0 and Ag_m^{n+} clusters are formed, in good agreement with the results obtained by the XAFS measurements.

It can be expected that the metal ions (Cu^{+} , Ag^{+}) in the Y-zeolite with large supercages may diffuse more easily to form the metal ions dimers or clusters, while in the narrow channels of ZSM-5 and mordenite, the metal ions are less mobile and form isolated Cu^{+} or Ag^{+} monomer species. In addition to these differences, the Y-zeolite has a much higher density of ion-exchangeable sites than ZSM-5 and mordenite. This allows the metal ions to exist so close to each other that they aggregate easily during heating treatments.

In conclusions, the present in-situ XAFS investigations indicated that Cu^{+} ions in the ZSM-5 and mordenite zeolites exist as isolated Cu^{+} monomers with planar 3 or linear 2 coordinate geometry while in the Y-zeolite they exist as the $(\text{Cu}^{+}-\text{Cu}^{+})$ dimer species as well as the isolated Cu^{+} monomer species. The Ag^{+} ions prepared within ZSM-5 zeolites were also found to exist as isolated Ag^{+} monomers with 2 coordinate geometry. These results indicate that the application of the ion-exchange method and the use of ZSM-5 zeolites as supports are suitable and significant in the preparation of isolated metal ion photocatalysts with low coordinate numbers which exhibit high photocatalytic reactivity for NO decomposition [1-3].

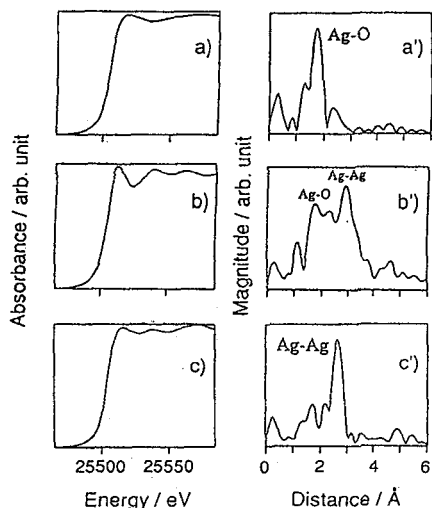


Figure 3. XANES (left) and FT-EXAFS (right) spectra of the (a,a') $\text{Ag}^{+}/\text{ZSM-5}$, (b,b') $\text{Ag}^{+}/\text{Y-zeolite}$ and (c,c') $\text{Ag}^{+}/\text{SiO}_2$ catalysts. (The catalysts were prepared by calcination of the original $\text{Ag}^{+}/\text{support}$ samples at 673 K and evacuation at 473 K.)

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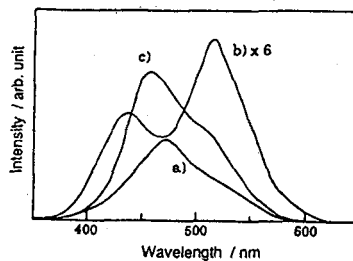


Figure 2. The photoluminescence spectra of the (a) $\text{Cu}^{+}/\text{ZSM-5}$, (b) $\text{Cu}^{+}/\text{Y-zeolite}$ and (c) $\text{Cu}^{+}/\text{mordenite}$ catalysts measured at 77 K.

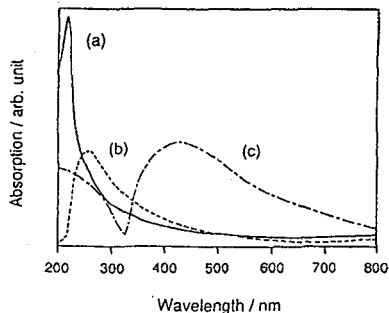


Figure 4. Diffuse reflectance spectra of the (a,a') $\text{Ag}^{+}/\text{ZSM-5}$, (b,b') $\text{Ag}^{+}/\text{Y-zeolite}$ and (c,c') $\text{Ag}^{+}/\text{SiO}_2$ catalysts.