

Time-resolved energy-dispersive XAFS study on the reduction process of Cu-ZSM-5 catalysts

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The time-resolved reduction process of copper cations in ZSM-5 during temperature-programmed reduction (300–700 K) was studied by energy dispersive X-ray absorption fine structure (DXAFS). The Cu K-edge DXAFS spectra for isolated Cu²⁺ species in the channels of ZSM-5 were recorded at an interval of 1 s during the reduction. The curve fitting analysis of the EXAFS data and the XANES analysis revealed that the isolated Cu²⁺ species in the channels were reduced stepwise. They were reduced to isolated Cu⁺ species at 400–450 K and the Cu⁺ species to Cu⁰ metallic clusters at 550–650 K. Small clusters like Cu₄ were initially formed, followed by particle growth. A small part of them went out to the outer surfaces of ZSM-5 during the reduction.

Keywords: time-resolved XAFS, energy-dispersive XAFS, Cu-ZSM-5, reduction process

1. Introduction

It is important to know the time-resolved structural change of supported metal ions in zeolites and on oxide surfaces during the reduction in order to develop highly dispersed metal catalysts. The time-resolved information on the reduction behavior of metal sites will provide a clue to find the reduction mechanism and preferable reduction conditions as well as to understand surface chemistry of dispersed metal ions.

XAFS is a powerful tool to elucidate the local structure of non-crystalline materials, such as supported metal catalysts (Koningsberger & Prins, 1988, Iwasawa, 1996). However, the difficulty of a conventional XAFS is in that it takes several ten minutes to acquire a spectrum. Time resolution of several seconds is required to study the structural change of metal sites during the reduction with H₂. New techniques called dispersive XAFS (DXAFS) (Matsushita & Phizackerley, 1981, Flank *et al.*, 1983, Dartyge *et al.*, 1986, Allison *et al.*, 1988, Hagelstein *et al.*, 1989) and quick EXAFS (QEXAFS) (Frahm, 1988, Cattaneo *et al.*, 2000) capable of data acquisition in several seconds have been developed. QEXAFS is a technique to speed up a conventional X-ray monochromator and can reduce the data collection time to a few seconds, while DXAFS is a technique to measure the whole energy range of spectra simultaneously by using a bent crystal as a polychromator and a position sensitive detector. DXAFS can reduce the acquisition time to second or sub-second.

We have studied the reduction process of Cu-ZSM-5 during temperature-programmed reduction (TPR) by DXAFS in this study, because Cu-ZSM-5 has a unique catalytic property for NO decomposition (Iwamoto *et al.*, 1986, Iwamoto *et al.*, 1991, Shelef, 1995, Parvulescu *et al.*, 1998). The reduction of Cu-ZSM-5 has been investigated by TPR, EXAFS, and so on (Sarkany *et al.*, 1992, Beutel *et al.*, 1996). However, the structure change of the copper species that occurs during the reduction with H₂ is still unknown. Time-resolved structure analysis of dispersed metal sites is crucial to understand the chemistry of catalyst pretreatment and reduction.

2. Experimental

The Cu-ZSM-5 samples were prepared by ion exchange using copper nitrate solution. An aqueous Cu(NO₃)₂ solution was used to ion exchange the proton of HZSM-5. The pH during ion exchange was 5.5. After continuous stirring for 24 h at room temperature, the samples were filtered and washed by distilled water several times, and then dried at 393 K for 6 h. These samples were calcined in a flow of O₂(20 %)/He(80 %) (50 cm³ min⁻¹) at 773 K for 2 h before reduction. The degree of the ion exchange of the sample was 84 %. Energy-dispersive XAFS measurements were carried out using synchrotron radiation at BL-9C at KEK-PF in Institute of Materials Structure Science. The ring energy and current were 2.5 GeV and 200–350 mA, respectively. A triangle-shaped Si(111) bent crystal was used to focus polychromatic X-ray beam. The sample was placed at the focus. A Pt-coated mirror after the sample was used to reject higher harmonics. The diverging X-rays were detected by a position sensitive X-ray detector. The detector was a photodiode array consisted of 1024 sensing elements (0.025 mm wide, 2.5 mm high) and a fluorescence material coated fiber-plate in front of the sensing elements. The energy resolution was 3–5 eV. Energy calibration was carried out by using a spectrum for Cu foil. The channels of the photodiode array were correlated to the x-ray energy with a second-order polynomial. The energy range was 8800–9800 eV. Absorption spectra were calculated by $\ln(I_0(E)/I(E))$, where $I(E)$ and $I_0(E)$ are X-ray intensity with and without sample as a function of X-ray energy (E). The measuring conditions for I and I_0 were controlled to be as equal as possible except the sample mounting to avoid making artifacts.

The spectra were acquired at an interval of 1 s under the temperature-programmed reduction condition and analyzed by the UWXAFS package. After background subtraction using AUTOBK (Newville *et al.*, 1993), k³ weighted EXAFS functions were Fourier transformed into a R-space and fitted in the R-space. The k range of the Fourier transformation and the fitting R range were 30–90 nm⁻¹ and 0.08–0.3 nm, respectively. The calculated Debye-Waller factors were used to fit the DXAFS spectra. They were calculated from Debye temperatures and the coefficients of the statistical disorder obtained from CuO and Cu metal particles, the conventional EXAFS spectra of which were measured at different temperatures. Different ΔE_0 's were used for metallic Cu and Cu cations (Cu⁺ and Cu²⁺). They were fixed at certain values and the same values were used in the same series of DXAFS spectra. The values were determined so that the average residual factor was minimized.

3. Results and discussion

Figure 1 shows a series of the raw DXAFS data for Cu-ZSM-5 at Cu K-edge during TPR in H₂ (5.3 kPa) at a heating rate of 5 K min⁻¹ in the range from 300 K to 700 K. The data acquisition time for each spectrum was 1 s. The quality of the spectra was reasonably good enough for EXAFS analysis. After the background subtraction, k³-weighted EXAFS functions were Fourier transformed into a R-space

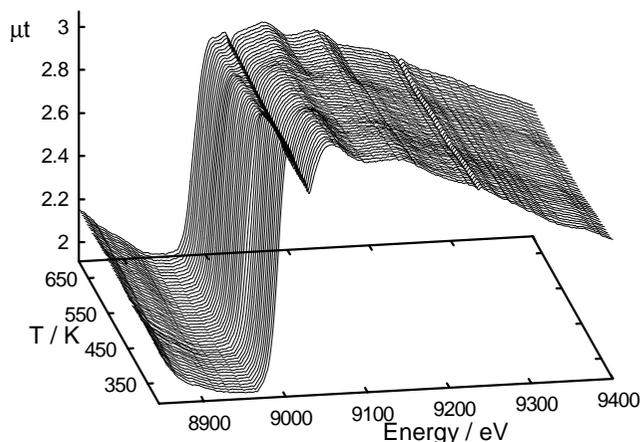


Figure 1 DXAFS spectra at Cu K-edge during the TPR of Cu-ZSM-5(84 %) under 5.3 kPa of H₂ from 300 K to 700 K. The acquisition time of each spectrum is 1 s.

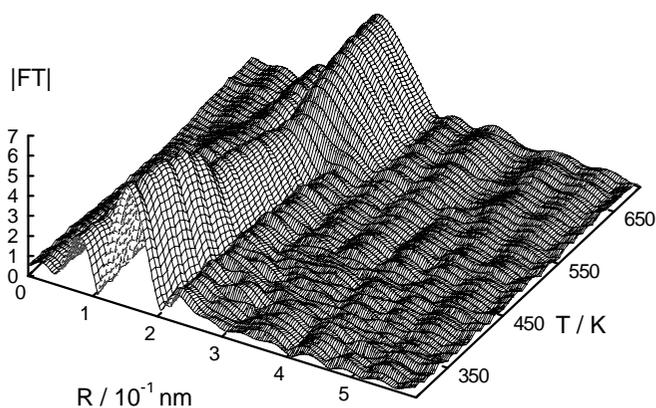


Figure 2 Fourier transformed k^3 -weighted DXAFS functions obtained by background subtraction from the spectra shown in Figure 1.

as shown in figure 2. Phase shift correction was not carried out in these spectra. A Cu-O peak was observed at 0.15 nm (phase shift uncorrected) for the calcined Cu-ZSM-5. Under the TPR condition, the intensity of the peak decreased at 430 K, and further a Cu-Cu peak at 0.20 nm emerged at 560 K. The spectra below 550 K were well fitted only by Cu-O and the contribution of metallic Cu-Cu bonding was included above 550 K.

Figure 3 shows the temperature dependence of the coordination numbers (CN) and distances (R) of Cu-O and Cu-Cu determined by the curve fitting analysis. The residual factor for the curve fitting was less than 10 % in all temperatures. The bond distances of Cu-O and Cu-Cu did not change during TPR. On the other hand, the CN of Cu-O changed stepwise. It was 2.8 at the initial Cu state and did not change till 410 K. It began to decrease after this temperature and became 1.5 (nearly half of the initial value) decrease above 550 K and became 0.1 at 700 K. The second change was accompanied by appearance of a metallic Cu-Cu peak at a distance of 0.25 nm, which is similar to the Cu-Cu distance of Cu metal. It indicates that all the Cu species were reduced to form Cu metallic particles at 700 K. We assume that the two-stage change in the CN of Cu-O corresponds to the reduction steps, $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$. The CN's of Cu^{2+} -O and Cu^+ -O bonds were calculated to be 2.8 ± 0.8 and 1.5 ± 0.5 , respectively. The bond distances of Cu-O were not affected by the oxidation state of copper and they were 0.195 ± 0.002 nm during the

TPR experiment. These parameters agree with the structural parameters for the isolated Cu^{2+} and Cu^+ cations derived by EXAFS analysis in the literature (Yamashita *et al.*, 1996). Thus, the stepwise change in figure 3 is attributable to the stepwise reduction of isolated Cu^{2+} ions to isolated Cu^+ ions and then to Cu^0 particles (Sarkany *et al.*, 1992, Beutel *et al.*, 1996).

To estimate the population of Cu^{2+} , Cu^+ and Cu^0 species, the observed XANES spectra (8950-9050 eV) were deconvoluted using the three independent XANES spectra for Cu^{2+} , Cu^+ and Cu^0 . We assumed that the observed XANES spectrum was a linear combination of the XANES spectra for Cu^{2+} , Cu^+ and Cu^0 to analyze the data as presented in the following formula.

$$X_{\text{obs}} = c_2 X_2 + c_1 X_1 + c_0 X_0,$$

where X_{obs} , X_2 , X_1 , X_0 , c_2 , c_1 and c_0 represent observed XANES, XANES of Cu^{2+} , Cu^+ and Cu^0 , and the proportion of Cu^{2+} , Cu^+ and Cu^0 , respectively. As the XANES spectra are affected by the local structure as well as the valence state, XANES spectra of bulk CuO , Cu_2O or Cu foil cannot be used as references of Cu^{2+} , Cu^+ or Cu^0 . The XANES spectra at 300 K and 700 K are reasonably regarded as references of Cu^{2+} and Cu^0 . The XANES spectrum at 500 K was not able to be reproduced by a linear combination of X_2 and X_0 , which means that the species at 500 K is an "independent" species. Thus, the XANES spectrum can be used as reference of Cu^+ . The coefficients c_0 , c_1 , and c_2 were evaluated by a linear least square fitting. Figure 4 depicts the three coefficients (c_0 , c_1 , and c_2) derived by the fitting, sum of the coefficients ($c_0 + c_1 + c_2$) and the residual factor (R_f) as a function of reduction temperature. The result implies that the observed XANES spectra can be reproduced basically by a linear combination of the three references, because the sum of c_0 , c_1 , and c_2 are close to unity and because the residual factor is as very small as less than 0.5 % for the samples at all TPR temperatures. The results in figure 4 agree with the results of the curve fitting analysis in figure 3. The Cu^{2+} species are converted into Cu^+ species in the temperature range of 400-450 K and the Cu^+ species to Cu^0 in the range 550-650 K, which consistent with the temperature ranges in which the CN values of Cu-O change stepwise in figure 3. The

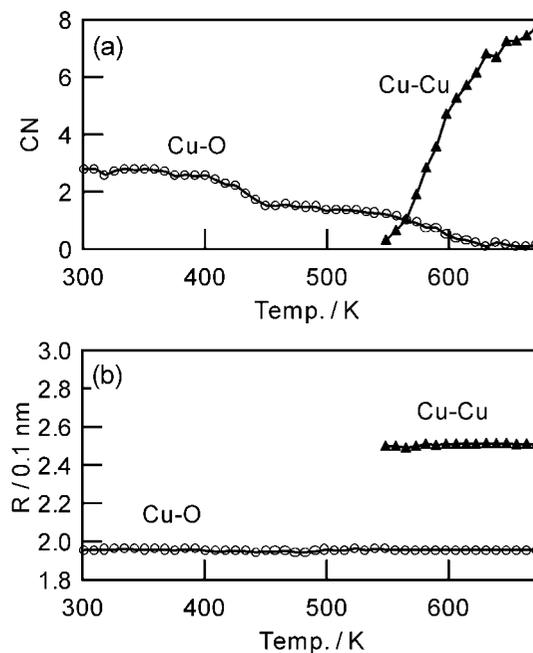


Figure 3 The coordination numbers (CN) (a) and bond distances (R) (b) as a function of reduction temperature.

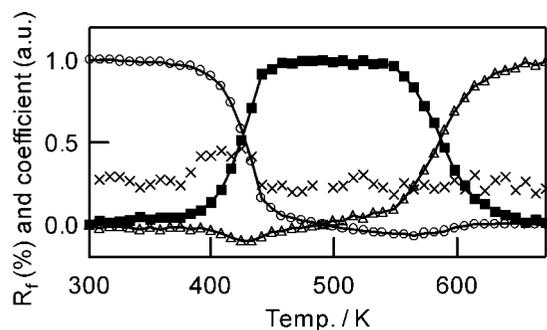


Figure 4 The proportion of Cu^{2+} , Cu^+ and Cu^0 (c_2 , c_1 and c_0 respectively) and the residual factor (R_r) against reduction temperature; \circ : c_2 ; \blacksquare : c_1 ; \triangle : c_0 ; \times : R_r .

results of figures 3 and 4 show that the transformation of Cu^{2+} to Cu^+ takes place more quickly than that of Cu^+ to Cu^0 , because the temperature range of the former conversion (400–450 K) is narrower than that of the latter conversion (550–650 K). This can be explained by the idea that the isolated Cu^{2+} species can be reduced to isolated Cu^+ without migration in the ZSM-5 channels, while the isolated Cu^+ species must migrate to form Cu^0 particles.

We can estimate the size of Cu metal particles by using the CN determined by the EXAFS analysis which is averaged one over all Cu atoms in the sample and by using the proportion of Cu^0 species determined by the XANES analysis. The CN's of Cu metallic particles are calculated by dividing observed CN for Cu-Cu by the proportion of Cu^0 .

As shown in figure 5, the CN of Cu metallic particles was 3 at 550 K. It is likely from CN = 3 that Cu_4 clusters are formed at the initial stage of Cu^+ reduction. The CN increased gradually during the TPR and reached 7.8 at 670 K. The diameter of the channels is ca. 0.56 nm and the channels can accommodate only small clusters, like Cu_{4-6} clusters. Thus it is suggested that Cu_4 clusters are formed at the initial stage of the $\text{Cu}^+ \rightarrow \text{Cu}^0$ reduction and grew to Cu_{4-6} clusters in the channels, and a part of them migrated to the outer-surfaces of ZSM-5 on which they merged to form Cu particles. TEM photograph for Cu-ZSM-5 after the TPR shows 10–20 nm Cu metal particles on the outer surfaces of ZSM-5.

4. Conclusion

Isolated Cu^{2+} species in the channels of ZSM-5 were reduced stepwise, $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$. The Cu^{2+} ions were reduced to isolated Cu^+ ions at 400–450 K and the Cu^+ ions were reduced to Cu^0 metallic state at 550–650 K. The reduction of Cu^{2+} to Cu^+ proceeds faster than that of Cu^+ to Cu^0 . At the initial stage of reduction of Cu^+ , small clusters Cu_4 were formed and then grew to Cu_{4-6} clusters. At 670 K a small number of them went out to the outer surfaces of the ZSM-5 to form Cu particles.

We have succeeded in observing the time-resolved DXAFS spectra for Cu-ZSM-5 catalysts during TPR processes in 1 s time scale. It has been demonstrated that DXAFS is a powerful technique to characterize the dynamic behavior of metal sites dispersed in zeolites during reduction. The dynamic structural transformations of Cu species in ZSM-5, which cannot be obtained by other techniques, are elucidated by the DXAFS technique.

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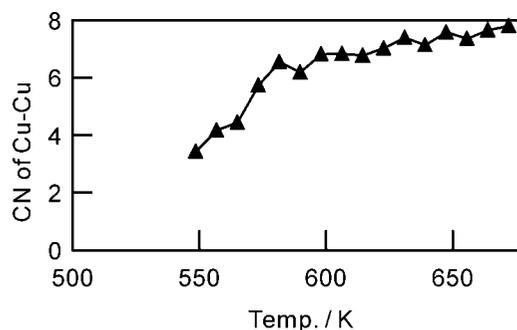


Figure 5 The CN of Cu-Cu bond in the Cu metal particles against reduction temperature.

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