Three-dimensional analysis of the local structure of Cu on TiO_2(110) by *in situ* polarization-dependent total-reflection fluorescence XAFS

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Cu K-edge XAFS of Cu/TiO_2(110) was measured by polarization-dependent total-reflection fluorescence XAFS technique. XAFS of [001], [1$\bar{1}$0], and [110] directions were measured to elucidate the three dimensional structure of Cu species on the TiO_2(110) surface prepared by the deposition of $Cu(DPM)_2$ followed by reduction with H_2. Simulation of the EXAFS functions as well as conventional curve fitting analysis revealed that plane $Cu_{3\text{-}4}$ small clusters with similar structure to Cu(111) plane were formed by the reduction at 363 K. The small clusters converted into spherical metallic Cu particles by the reduction at 473 K.

Keywords: total-reflection XAFS, polarization-dependent XAFS, surface structure, Cu-clusters, TiO_2(110)

1. Introduction

Understanding and controlling the metal-oxide interfaces are important issues for investigating the genesis and origin of catalysis and the relationship between structure and reactivity, and developing new catalytic systems. In supported metal catalysts, the support not only disperses the metal on its surface but also affects the selectivity and activity of the catalysts through the metal-support interaction, which changes the electronic structure, orientation and morphology on the surface. In general, the metal-support interaction at the interface and structure of supported metal or metal oxides are anisotropic and asymmetrical. Thus it is difficult to clarify the metal-support interaction by conventional XAFS technique, though there are some examples which have proposed metal-support interactions by conventional EXAFS (Iwasawa, 1996).

The EXAFS oscillation $\chi(k)$ depends on the angle θ_i between the ith bond direction and the polarized electric-field vector of the incident X-rays as shown in Eq. (1);

$$\chi(k) = \sum \chi_i(k) \cos^2 \theta_i, \qquad (1)$$

where $\chi_i(k)$ is an EXAFS oscillation accompanying the *i*th bond. When a single crystal oxide is used as a support, structural information on the bonds both parallel and normal to the surface can be independently obtained. However, there are two problems in applying the polarization dependent XAFS to species on a flat substrate. First, concentration of the surface species is very low, thus, we must measure them in a fluorescence yield mode. Second, incident X-rays penetrate deeply into the bulk, yielding a large amount of scattering X-rays which hinder detecting the fluorescence X-rays from the surface species. In order to improve the surface sensitivity, we adopted the measurement under a total-reflection condition.

This technique is called as polarization-dependent total-reflection fluorescence XAFS (PTRF-XAFS) method hereinafter. We have determined the asymmetric structure of supported metals and metal oxides structure such as Pt on α-Al_2O_3(0001) and dimeric Mo-oxide on TiO_2(110) (Chun, et al., 1998, Asakura, et al., 2000).

Rutile TiO_2(110) has an anisotropic structure with an alternative alignment of bridging oxygen ridges and five-fold coordinated Ti^{4+} rows along the [001] axis (Onishi, et al., 1995). Therefore, formation of an anisotropic structure of copper on the surface is expected. TiO_2-supported copper is important as catalysts for the reduction of NO(Aritani, et al., 1996, 1997). In this study, we have applied PTRF-XAFS spectroscopy to probe the morphology change of the Cu/TiO_2(110) before and after the reduction by H_2.

2. Experimental

The sample was prepared by depositing a diethyl ether solution of $Cu(DPM)_2$ (DPM = 2,2,6,6-tetramethyl-3,6-heptadionate) on a

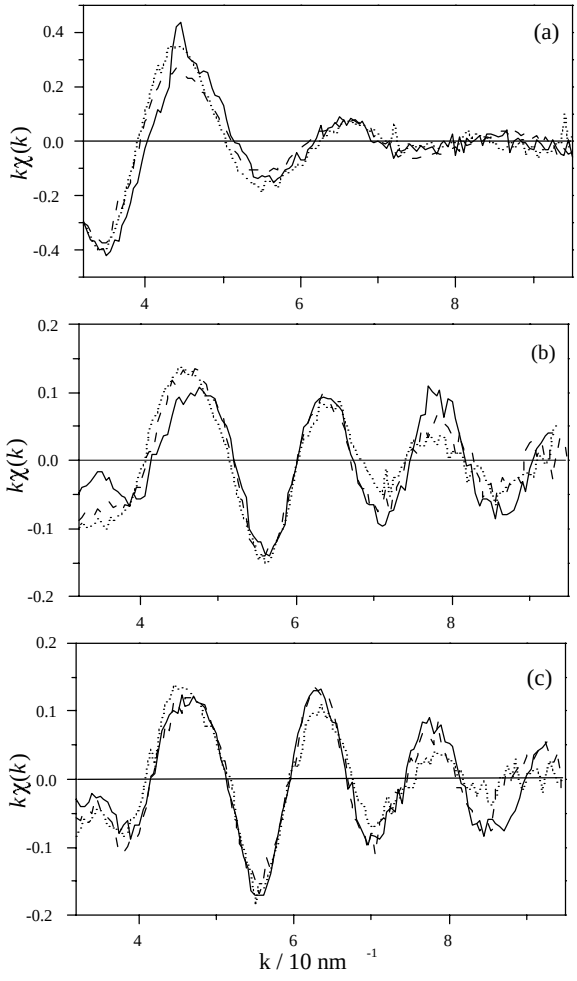

Figure 1

k^1 weighted Cu K-edge EXAFS functions of $Cu(DPM)_2/TiO_2$(110) before (a) and after reduction at 363 K (b) and 473 K (c). Solid, broken, and dotted lines represent EXAFS for the [001], [1$\bar{1}$0] and [110] directions, respectively.

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TiO_2(110) surface, which was pre-calcined at 673 K in air. The loading of Cu was 5×10^{14} atoms/cm^2, which was estimated by XPS. The obtained sample was mounted in a vacuum chamber equipped with a 6-axis goniometer, a solid state detector (or a scintillation counter), and a heating device. The sample was reduced at given temperatures by H_2 (2 Torr) in the chamber and PTRF-XAFS spectra were measured.

The measurement was done at BL-12C at KEK-PF. The energy and current of the electrons in the storage ring were 2.5 GeV and 250-400 mA, respectively. A Si(111) double crystal was used to monochromatize the X-rays. The X-rays were focused at the sample by a cylindrical mirror. The intensity of the incident X-rays (I_0) and that of fluorescence X-rays from the sample (I_f) were monitored by an ion chamber filled with N_2 gas and a NaI(Tl) scintillation counter, respectively. Each scan took 1 h, and we scanned 5-8 times. The sample was rotated by the goniometer to measure X-ray absorption spectra in three different directions where the electric vectors of the incident X-rays were adjusted parallel to the [001], [1$\bar{1}$0], and [110] axes of TiO_2(110). The X-ray absorption spectra were represented by the ratio of I_f and I_0 against X-ray energy without any correction for self-absorption because all the absorbing atoms were located on the surface.

The spectra were analysed by the UWXAFS package (Stern, et al., 1995). After background subtraction, k^1 weighted EXAFS functions were Fourier transformed into R-space and the curve fittings were done in the R-space. The k range of the Fourier transformation was 30-90 nm^{-1} and the fitting R range was 0.10-0.20 nm for the sample before reduction and 0.10-0.30 nm for reduced samples at 363 K and 473 K. The Fourier transformed EXAFS functions were fitted by Cu-O, Cu-Cu and/or Cu-Ti contributions. The backscattering amplitude and phase shift were calculated by the FEFF8 code (Ankudinov, et al., 1998). The fitting parameters were interatomic distances (R), effective coordination numbers (N^*) and Debye-Waller factors (σ) for each shells and the correction of edge energy (ΔE_0). The number of free parameters was smaller than the number of independent parameters calculated by the Niquest law (Stern, 1993).

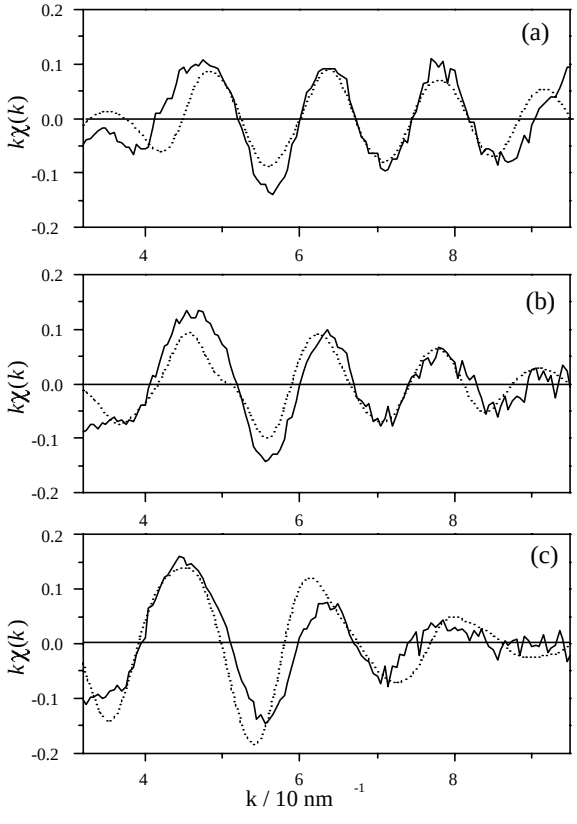

Figure 2

k^1 weighted EXAFS functions of Cu/TiO_2(110) reduced at 363 K (solid lines) with calculated results (dotted line) for a model structure proposed in Figure 3 : (a) [001], (b) [1$\bar{1}$0] and (c) [110].

Table 1

Structural parameters for the Cu species on the TiO_2(110) surface in the [001], [1$\bar{1}$0], and [110] directions, obtained by the curve fitting analysis. (a): after reduction at 363 K, (b): after reduction at 473 K.

(a)

	R / 0.1 nm	N*	σ^2 / 10^{-2} nm^2	ΔE_0 / eV
[001] Cu-Cu	2.43	2.1	0.0040	
Cu-O	1.75	0.5	0.0035	-11.2
[1$\bar{1}$0] Cu-Cu	2.44	1.8	0.0040	
Cu-O	1.77	0.8	0.00065	-10.0
[110] Cu-Ti	2.48	0.9	0.0012	
Cu-O	1.79	1.1	0.0023	-10.0

(b)

	R / 0.1 nm	N*	σ^2 / 10^{-2} nm^2	ΔE_0 / eV
[001] Cu-Cu	2.47	3.6	0.0083	
Cu-O	1.81	1.1	0.0166	-7.0
[1$\bar{1}$0] Cu-Cu	2.48	4.15	0.0109	
Cu-O	1.81	0.75	0.0050	-7.0
[110] Cu-Cu	2.48	4.68	0.0154	
Cu-O	1.83	1.2	0.0066	-7.0

3. Results and discussion

Figure 1 (a)-(c) shows k^1 weighted EXAFS functions in the [001], [1$\bar{1}$0], and [110] directions of Cu(DPM)$_2$/TiO_2(110) before and after reduction at 363 and 473 K. The quality of the spectra was reasonably good until 90 nm^{-1}. In the sample reduced at 363 K, strong polarization dependence was observed and the EXAFS functions in the three directions were substantially different from each other. In the [001] direction, EXAFS oscillation in the higher k range was stronger than those in the other directions, which suggests that the absorber was surrounded by heavier atoms in the [001] direction. Another characteristic feature of this direction is that a large amplitude oscillation appear at 30-40 nm^{-1}, which also appeared in the EXAFS of Cu foil. From these results, Cu-Cu bondings were preferably formed along the [001] axis. On the other hand, the EXAFS oscillation in the [110] direction damped quicker than the other directions with k values. Thus the absorber was coordinated by a different kind of atoms in the [110] direction (perpendicular to the surface) from the coordinating atoms in other

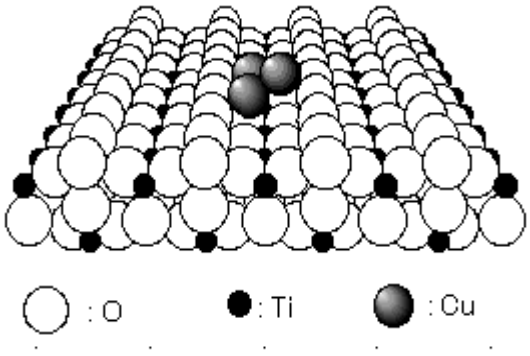

Figure 3

A structure model for Cu clusters formed by the reduction at 363 K.

directions (parallel to the surface). Probably the absorber was coordinated by the surface atoms of the TiO_2(110) surface. From these features of the EXAFS functions measured in the three directions, the formation of Cu cluster along the [001] direction is suggested. Table 1 shows the structural parameters in the [001], [1$\bar{1}$0] and [110] orientations of the Cu species on the TiO_2(110) surface after the reduction at 363 K obtained by the curve fitting analysis.

In the sample before the reduction, Cu-O bonds were observed at 0.192 nm in all three directions. There was no resemblance in XANES spectra between $Cu(DPM)_2$ complex and the $Cu(DPM)_2/TiO_2$. These results indicate that the framework of $Cu(DPM)_2$ complex was broken.

In the sample reduced at 473 K, Cu-Cu bonds were observed at 0.247-0.248 nm (Table 1). The distances were similar to that of metallic Cu-Cu. The N^* values were similar in all the directions. Thus, spherical Cu metal particles were formed at this temperature. From the N^*, the particle size was small ($Cu_{6\text{-}13}$). In addition to the Cu-Cu bond, Cu-O bonds at 0.181-0.183 nm were observed. However, the observed coordination number of Cu-O was as small as 0.7-1.2. It implies that a part of the $Cu_{6\text{-}13}$ atoms interact with the surface oxygen atoms.

In the sample reduced at 363 K, Cu-Ti bond was observed in the [110] direction perpendicular to the surface, while Cu-Cu bond instead of Cu-Ti was observed in the directions parallel to the surface ([001] and [1$\bar{1}$0]). The result suggests that plane Cu clusters were formed on the TiO_2 surface.

To investigate the structure of the reduced Cu species in more detail, we simulated the EXAFS spectra of the sample reduced at 363 K by the FEFF8 code. Figure 2 (a)-(c) shows the calculated EXAFS functions for a Cu_3 model shown in Fig. 3. As shown in Fig. 2 (a)-(c), the calculated spectra for the Cu_3 model reproduced the observed spectra in all the directions. The results of the simulation are summarized as below:

1) The Cu clusters consist of Cu_3 close-packed structure with the Cu-Cu distance at 0.25 nm.
2) The Cu clusters were tilted by 15 degree as shown in Fig. 3.
3) The Cu atoms in the cluster are nearly located on the three-hold hollow sites of surface oxygen atoms.

Some Cu_3 clusters may catch additional atoms to grow into Cu_4 clusters. However, bigger Cu clusters than Cu_4 with similar structure could not reproduce the experimental data.

The curve fitting results and the results of the simulation is somehow different from each other, especially in the [110] direction (perpendicular to the surface). This may be because of the limited information of the EXAFS spectra. As shown in Fig. 3, the structure in the [110] orientation is complicated and cannot be reproduced by one or two shells. As the Cu clusters may have a similar structure to that of closed-packed Cu(111) plane, which is suggested from the curve fitting results in [001] and [1$\bar{1}$0] orientations, we put the clusters in different positions on the TiO_2(110) surface and simulated EXAFS functions to know which structure reproduces well the observed spectra. Although the Cu_3 model reproduced the observed data in the three directions, we cannot exclude other possibilities for the structure shown in Fig. 3 at present. Our model is also supported by previous studies (Diebold, et al., 1993, Pan, et al., 1993) which showed that Cu clusters with (111) plane were formed on a TiO_2(110) surface. A Cu-Ti bonding was suggested from both the curve fitting and the simulation, which implies that the mobility of the clusters on the surface is restricted. On the other hand, STM study (Chen, et al., 2000) showed that clusters move frequently. This disagreement cannot be explained, but there may be a tip effect in the STM results. The EXAFS results indicate that the majority of the Cu species are trapped at the stable site.

It has been demonstrated that PTRF-XAFS is a good compliment of STM and precise local structural information can be obtained from this technique. Especially, the PTRF-XAFS technique has an advantage in investigating the chemical interaction between the deposited species and the substrate.

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