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Asymmetric Structure Determination of Copper Oxide on α-Quartz(0001) Surface by Polarized Total-Reflection Fluorescence Extended X-Ray Absorption Fine Structure Spectroscopy

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Cu oxides were supported on α-quartz(0001) by CVD of $Cu(DPM)_2$ (DPM: dipyvaloylmethanate) and the subsequent calcination. The structure of the Cu species in the submonolayer was determined by polarized total-reflection fluorescence extended X-ray absorption fine structure (EXAFS) spectroscopy. Both s- and p-polarized EXAFS data revealed that Cu atoms were dispersed in a monomer form on the three-fold hollow sites of the quartz surface with the Cu-O distance of 0.201 nm.

Attached metal/metal oxide catalysts prepared by the reaction between organometallic precursors and surface functional groups of inorganic oxides have shown unique catalytic activities and selectivities derived from their surface structures.[1,2] EXAFS (extended X-ray absorption fine structure) spectroscopy is one of the most useful techniques to provide structural information on kinds of surrounding atoms, bond distances and coordination numbers.[3] While attached catalysts have been well characterized by means of EXAFS,[1,2] metal sites are usually dispersed on powder oxides with high surface areas, so that the structural information obtained from a conventional EXAFS analysis is averaged over all directions around a particular element. If one can determine surface structures in two different directions, i.e. parallel and perpendicular to the surface, independently, the structure and behavior of active metal sites at surfaces will be understood more clearly. This new way of structure determination is referred as asymmetric structure determination.[4] K-edge EXAFS

amplitude depends on $\cos^2\theta$, where θ is the angle between a bond vector and the electronic field vector of a polarized X-ray. When metal species are supported on a flat substrate, therefore, asymmetric structure information is obtained by the polarized EXAFS technique changing the angle. In order to obtain surface sensitive EXAFS signals, we adopted a total-reflection fluorescence method that has the following advantages.[5] The penetration depth of X-ray in total reflection conditions is very small (1-2 nm), which minimizes the contribution from the bulk material.[6] Moreover, the fluorescence detection technique is possible to get a large S/B ratio to detect small amounts of surface metal species, and to obtain EXAFS oscillations in air or in-situ conditions unlike electron detection methods. In this article the location and structure of Cu ions on α–quartz(0001) surface were at first determined by the polarized total-reflection fluorescence EXAFS technique.

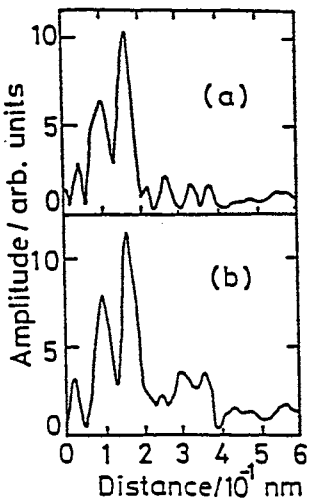

Fig. 1. Fourier transforms of the EXAFS data for Cu/SiO_2; (a) 0-deg and (b) 90-deg.

Sample preparation was carried out as follows. After a α–quartz(0001) substrate was treated at 393 K for 2 h in air, $Cu(DPM)_2$ vapor (DPM: dipyvaloylmethanate(2,2,6,6-tetramethyl-3,5-heptadione)) was deposited on the quartz surface for 4 h by a chemical vapor deposition (CVD) method (temperature of the vaporization: 373 K, deposition temperature: 473 K, carrier gas: dried air, and flow rate: 20 ml/min). Then, the sample was calcined at 673 K for 2 h. The treatment of the sample at 673 K may transform α–quartz(0001) to the β-type (at least at the surface layers) which has a more ordered structure. The ratio of Cu atom to surface oxygen atom on the quartz surface was estimated to be 0.4 ± 0.2 by an ICP analysis. Polarized total-reflection fluorescence EXAFS spectra were measured at BL-14A of Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) (proposal No. 89-146).[7] A four-axis goniometer equipped at the BL-14A was used for setting the sample at a particular orientation against the polarization direction of synchrotron and at a total reflection angle. The angle between the crystal surface and the polarized X-ray was chosen to be 90- and 0-deg. Hereinafter 0-deg and 90-deg are denoted as s-polarization and p-polarization,

Table 1. Curve-fitting results and effective coordination numbers

Polarization	Distance/nm	Coordination number			
		Observed	Calculated		
			On-top	Bridge	Three-fold
CuO(bulk)	0.196	4			
0 deg (s)	0.200[a)]	3.2[b)]	0	1.3	2.5
90 deg (p)	0.202[a)]	3.7[b)]	3	3.5	3.9
ratio (p/s)		1.2	∞	2.7	1.6

a) ±0.002. b) ±0.5.

respectively. The incident X-ray was monitored by an ion chamber filled with N_2. The fluorescence from the sample was detected by a NaI scintillation counter.

The effective coordination number (Ni^*) of the ith shell was calculated based on the relation (1).

$$Ni^* = 3\cos^2\theta \quad (1)$$

The Fourier transforms of s- and p-polarized EXAFS spectra showed one peak between 0.1-0.2 nm which is assigned to Cu-O bond (Fig. 1). This was confirmed by a curve-fitting analysis and the Cu-O bond distance was determined as 0.201 nm (±0.002 nm) for s- and p-polarization (Table 1). Cu-Cu bond was not observed in both direction analyses. It means that Cu atoms were supported on α–quartz(0001) in a monomer form.

The curve-fitting analysis revealed that the Ni^*'s of Cu-O are 3.2 and 3.7 for s- and p-polarization, respectively. The ratio is 1.2 (Table 1). There are three typical locations of Cu atoms on the quartz(0001), that is, "a-top", "bridge site", and "three-fold hollow site" as shown in Fig. 2. The Ni^*'s for these arrangements can be calculated by Eqs. 2 and 3.

$$Ni^*/3 = 2\cos^2\alpha\cos^2\beta + 2\sin^2\alpha\sin^2\beta\cos^2\phi \quad \text{(bridge site)} \quad (2)$$

$$= 3\cos^2\alpha\cos^2\beta + 1.5\sin^2\alpha\sin^2\beta \quad \text{(three-fold hollow site)} \quad (3)$$

The electric field vector E is characterized by spherical coordinates α from the surface normal and φ in the surface plane, and β is the bond angle with the surface normal.[8)] For the bridge site $\cos^2\phi$ was integrated in every directions because of equivalent positions (see Fig. 2). For the on-top position the EXAFS oscillation parallel to the surface should not appear.

Assuming the ideal surface structure with the O-O distance of 0.267 nm for the quartz.[9)] and using Cu-O bond length (0.201 nm) determined by the EXAFS analysis, we calculated the N^* of Cu-O bond in Table 1. The experimental values are in agreement with only the

calculated values based on the three-fold hollow site model. Particularly, the p/s ratio was reproduced by three-fold hollow site model, not by on-top and bridge models.

So far as we know, the asymmetric structure analysis for supported metal systems by both s- and p-polarized total-reflection fluorescence EXAFS has not been reported. It is demonstrated from the bond distance and the N^* ratio that Cu atoms in the submonolayer are preferentially located at the three-fold hollow sites of the quartz(0001) plane. The asymmetric structure change of supported metals in ambient gases by this technique is under investigation.

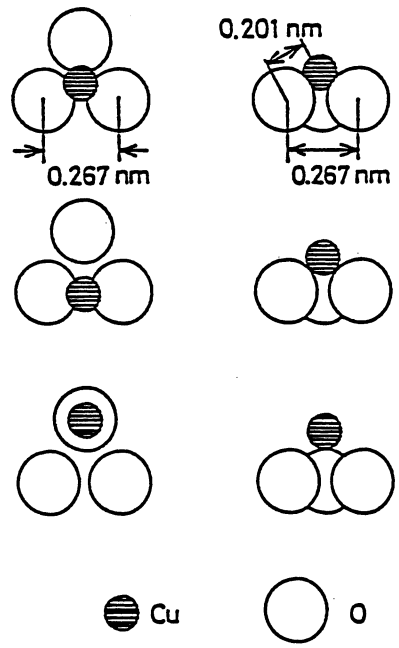

Fig. 2. Models for Cu atoms on three sites of α–quartz(0001).

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