Site-selective XAFS spectroscopy tuned to surface active sites of Cu/ZnO and Cr/SiO$_2$ catalysts

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XAFS (X-ray absorption fine structure) spectra were measured by using the fluorescence spectrometer for the emitted X-ray from sample. The chemical shifts between Cu^0 and Cu^I and between Cr^{III} and Cr^{VI} were evaluated. Tuning the fluorescence spectrometer to each energy, the Cu^0 and Cu^I site-selective XANES for Cu/ZnO catalyst were measured. The first one was similar to the XANES of Cu metal and the second one was the 5 : 5 average of XANES for Cu^I sites + Cu metal. The population ratio of copper site of the Cu/ZnO catalyst was found to be Cu metal : Cu$_2$O : Cu^I atomically dispersed on surface = 70($\pm$23) : 22($\pm$14) : 8($\pm$5). Site-selective XANES for Cr^{III} site of Cr/SiO$_2$ catalyst was also studied.

Keywords: site selective, XAFS, fluorescence spectroscopy, energy resolution, active site

1. Introduction

When XAFS spectroscopy is applied to sample which consists of more than one kind of site, obtained information is the average for all sites in the sample. Heterogeneous catalysts are typical examples that consist of several kinds of sites. To overcome this problem, a fluorescence spectrometer was designed to analyze fluorescence X-rays from samples in the XAFS measurements. XAFS spectra will be site-selective (selection of species or state for the X-ray absorbing atom) when the fluorescence spectrometer is tuned to the Kα or Kβ peak energy corresponding to each site based on the chemical shift of each site.

Supported Cu/ZnO catalysts consist of several sites of Cu^0 and Cu^I under the reaction conditions of methanol synthesis. Supported Cr/SiO$_2$ catalysts consist of monochromate, dichromate, and polychromate Cr^{VI} species, the corresponding reduced species, and α-Cr$_2$O$_3$ like phase. In both cases, it is important to obtain independent local structure and electronic state information for each site to understand the surface catalytic process.

2. Experimental

2.1. Design of fluorescence spectrometer

A Johansson-type fluorescence spectrometer (Fig. 1) was designed to realize higher Bragg angle reflection 55.6 - 83.9° to be applicable to many fluorescence lines (Kα and Kβ of K - As) by frequently-prepared Ge or Si crystal-face diffractions, such as (333), (440), or (800). The details of the fluorescence spectrometer were described
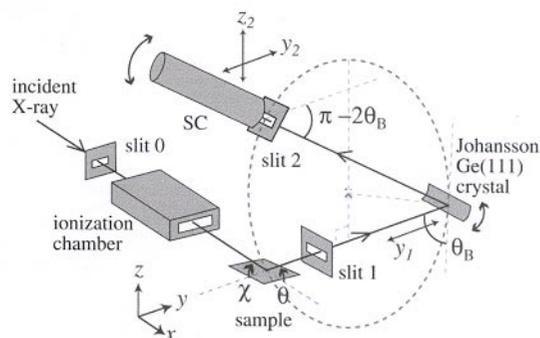

Figure 1
Configuration of the fluorescence spectrometer.

in Izumi *et al.* (2000). Multichannel control was for more precise determination of crystal and detector positions compared to the spectrometer by Stojanoff *et al.* (1992).

Sample was placed on a plane tilted from horizontal plane and the Rowland circle was in the vertical plane. The top surface of sample can be tilted by micrometer to the direction of the incident X-ray from the horizontal plane (angle θ; Fig. 1) and also to the direction perpendicular to incident X-ray and in the same horizontal plane (angle χ; Fig. 1). The angles θ and χ was 6 - 13° and 7 - 13° during measurements.

Cylindrically-bent Johansson-type Ge(111) crystal [50(H) $\times$ 25(V) mm^2, R = 220($\pm$1) mm, Crismatec] moves in the *y*-direction and rotates by PC control. The geometry of small angles of θ and χ is superior to the geometry of beam entrance 45° and exit 45° in terms of signal/noise ratio. A receiving slit was placed between sample and bent crystal, 100 mm apart from the sample (slit 1; Fig. 1). The NaI(Tl) scintillation counter (SC, SP-10) and the slit 2 move in *y*- and *z*-directions and rotate by PC control. The centers of sample, bent crystal surface, and slit 2 were always on the Rowland circle during spectrum scan. Independent control of these positions enabled free choice of Rowland radii 127.7 - 240.9 mm. The configuration in Fig. 1 effectively focuses the divergence which originated from the incident X-ray beam, polarized horizontally.

Additional optimization of X-ray intensity at SC was carried out by the adjustment of micrometers for *x*, *y*, *z*, and rotation around the axis in the crystal surface and perpendicular to the θ_B rotation axis of bent crystal.

2.2. Sample preparation

A Cu/ZnO catalyst was prepared by the co-precipitation method (Izumi & Nagamori, 2000). Copper and zinc nitrates were dissolved in water, and co-precipitated by adding a sodium carbonate solution. Filtrated and washed powder was dried at 393 K and calcined at 623 K. The Cu content was 5 wt%. The sample was heated in H$_2$ (53 kPa) at 523 K and in CO (27 kPa) + H$_2$ (27 kPa) at 523 K. A Cr/SiO$_2$ catalyst was prepared by the incipient wetness method (Izumi & Nagamori, 2000). A CrO$_3$ solution was reacted with SiO$_2$ (Davison 952). The Cr content was 15 wt%. The sample was evacuated at 293 K and interacted with ethanol (10 kPa) at 373 K. Thus-activated catalysts were transferred to an *in-situ* Pyrex cell

capped by Kapton windows. The activities of catalysts were reproduced after use for site-selective XAFS measurements.

2.3. Emission and XAFS spectrum measurements

The Cu Kα and Cr Kβ emission spectra and the Cu and Cr K-edge site-selective XAFS spectra were measured at the Undulator beamline 10XU of SPring8 (Proposal Nos. 1999B0220-NX-np and 1998A0295-NX-np) and Bending magnet beamline 7C of KEK-PF (Proposal Nos. 99G060 and 98P025). In both beamlines, Si(111) double crystal monochromator was used. Cu Kα emission was monitored with Ge(444) reflection. The excitation energy was 9000.1 eV. Spectrum scan step was 0.01° of Bragg angle (≈ 0.5 eV) and an emission spectrum consists of 80 steps. Accumulation time of a step was 60 s. Cr Kβ emission was monitored with Ge(333) reflection. The atomosphere in acrylic house, which covers completely the spectrometer, was purged with helium. The excitation energy was 6020.9 eV. Spectrum scan step was 0.01° of Bragg angle (≈ 0.3 eV) and an emission spectrum consists of 120 steps. Accumulation time of a step was 60 s.

Site-selective Cu K-edge XAFS spectra were measured by tuning the fluorescence spectrometer at 8046.6 eV ($\theta_B = 70.654°$) and 8050.9 eV ($\theta_B = 70.567°$) for Cu/ZnO. The accumulation time of a step was 10 - 100 s, and the summation of several good spectra were done. Site-selective Cr K-edge XANES spectra were measured by tuning the fluorescence spectrometer at 5947.5 eV ($\theta_B = 73.218°$) for the Cr/SiO$_2$. The accumulation time of a step was 60 s.

3. Results and Discussion

3.1. Chemical shift and line width of the emission spectra

Cu Kα emission spectra were measured for Cu metal, CuCl, and CuCl$_2$. The peak top and FWHM (full width at a half maximum) was evaluated based on the fitting with a Gaussian for each peak of
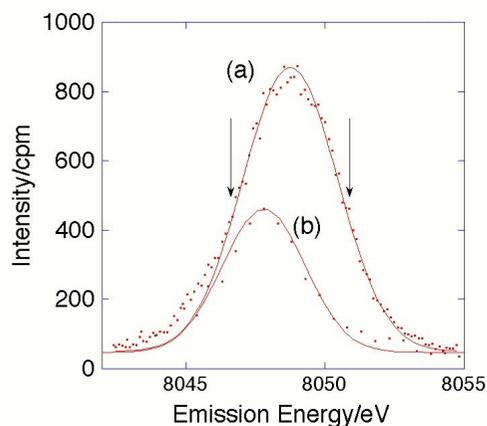
Figure 2
Cu Kα$_1$ emission spectra for activated Cu/ZnO catalyst (a) and Cu metal (b). The experimental data are plotted as points and the Gaussian fittings are drawn as solid lines. Two arrows indicate tune energies for site-selective XAFS measurements.

Kα$_1$ and Kα$_2$ and flat background. The peak top energy shifted by +1.6 eV on going from Cu^0 to Cu^I and by –0.6 eV on going from Cu^I to Cu^{II} both for Kα$_1$ and Kα$_2$ peaks. The HWHM values varied according to the changes of slit length (horizontal) of slit 0 and of

slit length (vertical) of slits 1 and 2 (Fig. 1). The FWHM was as small as 3.0 eV when the sizes of slits 0 – 2 were 2.0(H) × 1.0(V), 8.0(H) × 0.5(V), and 8.0(H) × 0.5(V), respectively.

Figure 2 illustrates the Cu Kα emission spectra for Cu/ZnO catalyst activated in CO + H$_2$ at 523 K. The Kα$_1$ peaks shifted by +0.9 eV, from Cu metal. The shift corresponds to Cu^I site, however, wider peak width (4.0 eV for Cu/ZnO *v.s.* 3.5 eV for Cu metal; Fig. 2) suggests the Cu/ZnO consists of Cu^0 and Cu^I sites and the emission spectra were the convoluted peak.

Cr Kβ emission spectra were measured for Cr metal, Cr$_2$O$_3$, and K$_2$CrO$_4$. The peak top and FWHM was evaluated based on the fitting with two Gaussians for main and weaker shoulder peaks. The Kβ$_1$ peak energy shifted by +0.8 eV on going from Cr^0 to Cr^{III} and –1.6 eV on going from Cr^{III} and Cr^{VI}. The Kβ peak of Cr/SiO$_2$ catalyst interacted with ethanol shifted by +0.6 eV from Cr metal, suggesting the Cr^{III} site was major in the reaction condition.

The energy resolution of this fluorescence spectrometer equipped with bent crystal was estimated based on the formula by Georgopoulos & Knapp (1981). The energy resolution is calculated to be 2.5 eV under the condition that the Cu Kα peak width was 3.0 eV. The slit size effects were larger than those of Rowland radius and X-ray penetration depth into the bent crystal. The convolution with the lifetime width for Cu Kα 2.11 eV is ≈ 2.4 eV, smaller than experimental FWHM 3.0 eV. In the case of Cr Kβ$_1$ peak, the convolution of theoretical energy resolution 1.8 eV and lifetime width ≈ 1.1 eV is ≈ 1.5 eV. Thus, the difference of tune energies of site-selective XAFS should be taken larger than the chemical shift (Fig. 3). 67 and 71% of site selection is expected for Cu and Cr K-edge, respectively. The site selection increases as the energy resolution is improved and the edge energy decreases toward soft X-rays.
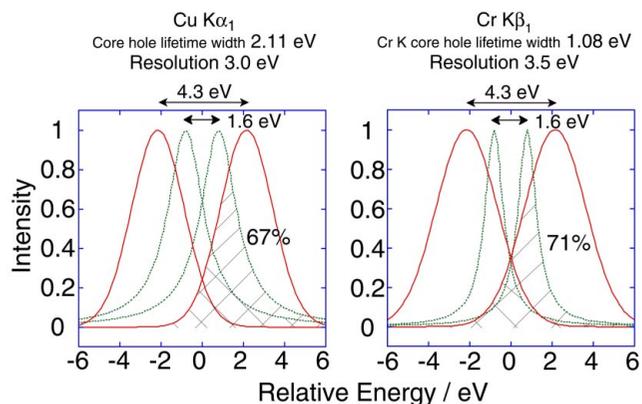
Figure 3
The estimation of site selection of Cu Kα$_1$ (left) and Cr Kβ$_1$ (right). Two emission peaks (Gaussian) separated by 4.3 eV and two peaks of core hole lifetime width (Lorentzian) separated by 1.6 eV are drawn.

3.2. Site-selective Cu K-edge XANES

The conventional fluorescence XANES spectrum for the Cu/ZnO catalyst (Fig. 4c) did not have a shoulder at 8988 eV nor a peak top at 9000 eV, which were typical for CuO (Fig. 4h). Hence, site-selective XAFS of Cu^0 and Cu^I were measured. The tune energies were 8046.6 and 8050.9 eV, as arrows in Fig. 2.
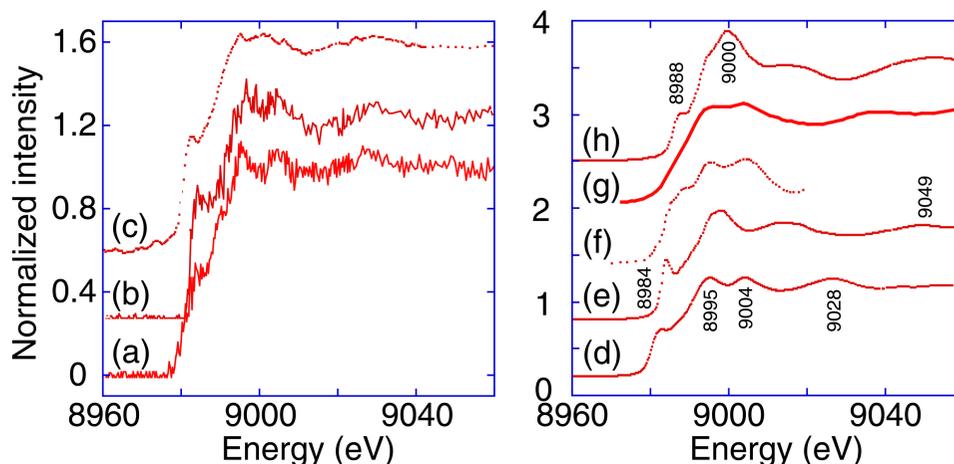
Figure 4

Site-selective XANES spectra for Cu/ZnO catalyst tuned to 8046.6 eV (a) and to 8050.9 eV (b). Conventional XANES spectra for Cu/ZnO (c), Cu metal (d), Cu_2O (e), [Cu(tepa)][BPh$_4$] (f), and CuO (h). XANES for Cu^I atomically dispersed on ZnO generated by FEFF8 (g).

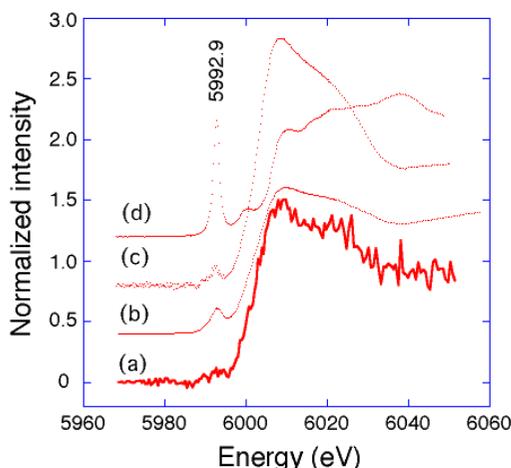**Figure 5**

Site-selective XANES spectra for Cr/SiO$_2$ catalyst. Fluorescence spectrometer was tuned to 5947.5 eV (a). Conventional XANES for Cr/SiO$_2$ (b), Cr$_2$O$_3$ (c), and K$_2$CrO$_4$ (d).

The site-selective XANES tuned to 8046.6 eV (Fig. 4a) resembled the XANES of Cu metal (Fig. 4d). The rising-edge position shifted to higher energy for site-selective XANES tuned to 8050.9 eV (Fig. 4b) compared to Fig. 4a, demonstrating the contribution from the Cu^I site. The peak top position at 8984 eV was the same as that of Cu$_2$O (Fig. 4e). The region of 8993 - 9008 eV was intense, similar to the case of Cu$_2$O, though the peak split into two peaks. The peak position 9028 eV was the same as that of Fig. 4d (Cu metal).

Based on obtained site-selective spectra (Fig. 4) and the estimation of site selection (Fig. 3), the conventional XANES (Fig. 4c) was fit by two site-selective XANES, and site-selective XANES was fit by standard spectra in Fig.4d - h. Note that the XANES of Cu^I site atomically dispersed on wurzite ZnO(0001) surface (Fig. 4g) was generated by FEFF8 for a model cluster within 6Å from the Cu center in a SCF and multiple scattering modes (Ankudinov et al.,

1998; Rehr et al., 1991). The theoretical XANES was similar to XANES of model complex [Cu(tepa)][BPh$_4$] (tepa = N(CH$_2$CH$_2$-2-pyridyl)$_3$). The fit was evaluated based on R_f.

$$R_f = \int |\chi(ex) - \chi(fit)|^2 \, dE / \int |\chi(ex)|^2 \, dE$$

Conventional XANES was best fitted with 7 : 3 mixture of Cu^0 and Cu^I site-selective XANES. Cu^0 and Cu^I site-selective XANES were best fitted with 8 : 2 mixture of XANES for Cu metal + Cu$_2$O and 50 : 25 : 25 mixture of XANES for Cu metal + Cu$_2$O + Cu^I site atomically dispersed on ZnO, respectively. Hence, the Cu site ratio is estimated to be Cu metal : Cu$_2$O : Cu^I atomically dispersed on ZnO = 70($\pm$23) : 22($\pm$14) : 8($\pm$5) for activated Cu/ZnO catalyst.

3.3. Site-selective Cr K-edge XANES

Site-selective Cr K-edge XANES for Cr/SiO$_2$ interacted with ethanol was measured by tuning the fluorescence spectrometer 5947.5 eV (Fig. 5a). The XANES pattern is similar to that of Cr$_2$O$_3$ (Fig. 5c). Based on the pre-edge peak intensity at $\approx$5993 eV for Fig. 4a, b, and d, site-selective XANES consisted of a contribution of 94($\pm$3)% from the Cr^{III} site, whereas the conventional XANES (Fig. 4b) consisted of 78($\pm$2)% of the Cr^{III} contribution.

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