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Anisotropic Effects of ZnO on Electron Transfer to Copper Sites during Preferential Photooxidation of Carbon Monoxide in Hydrogen

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1 Introduction

Purification of hydrogen is a key technology to realize hydrogen society based on fuel cells. The activity of preferential photooxidation (photo-PROX) of carbon monoxide depended on the exposed crystal face distribution of ZnO [1]. To investigate the anisotropic effect of ZnO on electron diffusion, Cu K-edge XAFS spectra were measured under preferential photooxidation conditions over Cu–adsorbed ZnO.

2 Experiments

Cu K-edge XAFS spectra were measured on a beamline 9C. Rod-like ZnO grown in [0001]-direction and disc-like ZnO grown in the perpendicular plane to [0001]-direction were synthesized and Cu ions were adsorbed on each of them. The sample discs were set in a batch Pyrex cell equipped with polyethylene naphthalate windows. The sample under CO (2.2 μmol), O_2 (5.7 μmol) and H_2 (22 mmol) gases was illuminated with UV-visible light from the direction perpendicular to the X-ray beam path.

3 Results and Discussion

The normalized Cu K-edge XANES spectra for Cu–rod-like ZnO (Figure 1A-a) and Cu–disc-like ZnO (Figure 1B-a) were for Cu(II) valence state [1]. For Cu–rod-like ZnO (panel A), a shoulder peak at 8984.3 eV appeared and increased gradually by as much as 0.17 in 3 h, demonstrating the reduction of Cu(II) to Cu(I). Cu–O peak appeared in the Fourier transform (FT) of EXAFS before irradiation (Figure 2A). By the 3 h irradiation, Cu–O interatomic distance changed from 0.194 to 0.192 nm (Figures 2A, B), supporting the transformation from Cu(II) to Cu(I).

In Cu–disc-like ZnO, the intensity of shoulder peak at 8984.3 eV reached 0.32 at only 8 min. A whiteline peak intensity at 8999.0 eV gradually decreased and the energy shifted to 8998.4 eV during 2 h of irradiation (Figure 1Ba→d) due to the formation of Cu metal. In the FT of EXAFS, Cu–Cu peak also appeared (Figure 2D). The XANES in 3 h was fitted with the spectrum of Cu metal and that of Cu(I)–ZnO standard spectrum [1] by changing the mixing ratio from 9:1 to 1:9. The fit was best when the ratio was 5:5, demonstrating population ratio of Cu(0) to Cu(I) nearly one.

In summary, charge separation took place both in rod-like and disc-like ZnO under light, but the diffusion to Cu(II) sites at surface was by far faster for disc-like ZnO based on the shoulder peak growth at 8984.3 eV in 8 min. The Cu(I) sites on major face of disc-like ZnO, i.e. (0001) face, were further reduced to Cu(0) nanoparticles in 2 h of irradiation based on the whiteline peak at 8999.0 eV and EXAFS.

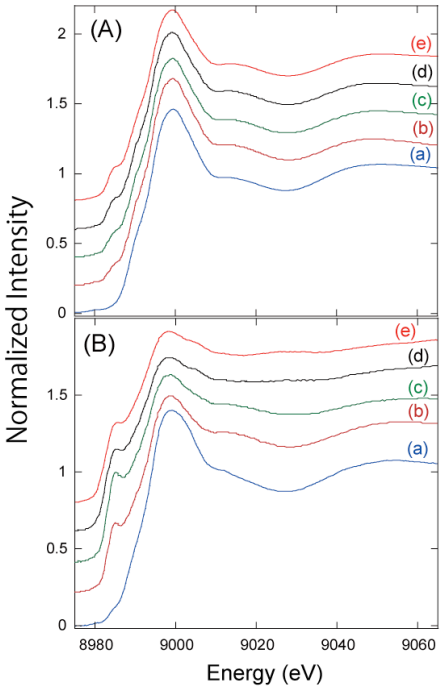

Figure 1. Normalized Cu K-edge XANES spectra for Cu–rod-like ZnO (A) and Cu–disc-like ZnO (B) before illumination (a) and at 8 min (b), 1 h (c), 2 h (d), and 3 h of illumination (e).

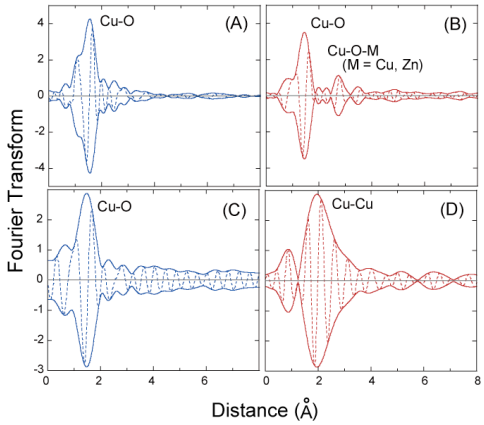

Figure 2. Cu K-edge EXAFS spectra of Cu–rod-like ZnO before (A) and at 3 h of illumination (B) and Cu–disc-like ZnO before (C) and at 3 h of illumination (D).

Reference

[1] Y. Yoshida, Y. Mitani, T. Itoi, Y. Izumi, *J. Catal.* **287,** 190-202 (2012).

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