

# Monitoring of Photocatalytic Reduction Sites of Preferential Oxidation of Carbon Monoxide in Hydrogen

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## 1. Introduction

Hydrogen energy is advantageous because it does not produce CO<sub>2</sub> when the chemical energy is transformed to electricity. In this study, the reduction sites of inexpensive preferential oxidation (PROX) photocatalyst of CO [1] for purification of hydrogen were investigated using Cu K-edge XANES.

## 2. Methods

Cu K-edge XAFS spectra were measured on a beamline 9C and 7C in KEK-PF and also on a beamline 01B1 at SPring-8. The sample disk was set in a cell equipped with polyethylene naphthalate windows. The sample was illuminated with an Xe arc lamp placed perpendicular to the X-ray beam path with the CO, O<sub>2</sub>, and H<sub>2</sub>.

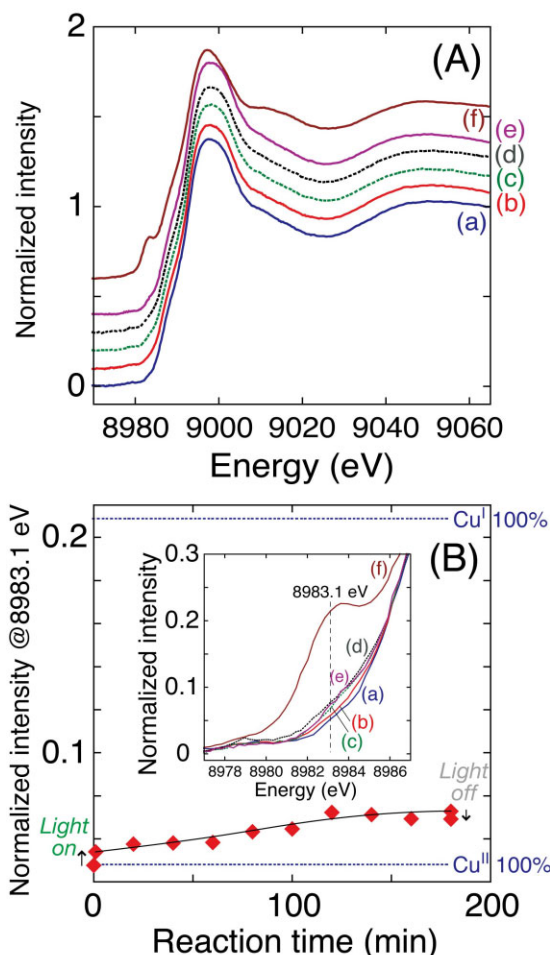
## 3. Results and Discussion

The Cu K-edge XANES spectrum for the fresh Cu–spheroidal ZnO catalyst is shown in Figure 1A-a. The Cu valence state was II in fresh Cu–spheroidal ZnO. After illumination for 1 min under UV–visible light, a weak shoulder peak began to appear at 8983.1 eV (Figure 1A-b). The shoulder peak intensity grew gradually to 0.0727 under the illumination for 3 h (Figure 1A-d). One minute after the UV–visible light was removed, the peak intensity at 8983.1 eV reduced by 0.0035 (Figure 1A-e).

The shoulder peak at 8983.1 eV originated from Cu<sup>I</sup> sites. The Cu K-absorption edge energy negligibly changed when the Cu<sup>II</sup> sites were reduced to Cu<sup>I</sup> sites. Therefore, the Cu<sup>I</sup>-site ratio in the sample was approximated using the following equation:

$$\frac{\text{Peak intensity@8983.1 eV} - 0.048 (\text{for Cu}^{\text{II}} 100\%)}{0.21 (\text{for Cu}^{\text{I}} 100\%) - 0.048 (\text{for Cu}^{\text{II}} 100\%)}$$

Based on this approximation, 3.9% of Cu<sup>I</sup> sites were formed in the initial 1 min, and this population gradually increased to 15.6% after 3 h of illumination. When the illumination was removed, the Cu<sup>I</sup> population dropped to 13.4%. Cu<sup>II</sup> and Cu<sup>I</sup> sites were in a dynamic equilibrium in a steady-state population of transmitted electrons that were photogenerated and did not recombine with holes



**Figure 1.** (A) Normalized Cu K-edge XANES spectra for Cu–spheroidal ZnO before illumination (a), at 1 (b), 80 (c), and 180 min (d) of illumination in CO (135 Pa), O<sub>2</sub> (270 Pa), and H<sub>2</sub> (13 100 Pa), and at 1 min after the illumination (e) for Cu–spheroidal ZnO-reduced (f). (B) The intensity change of a shoulder peak at 8983.1 eV during the illumination of UV–visible light.

during the diffusion to surface. The Cu ions were active for CO reduction in the PROX reaction.

$$K = \frac{[\text{Cu}^{\text{I}}]}{[\text{Cu}^{\text{II}}][e^-_{\text{diffused to surface}}]}$$

## Reference

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

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