

Chemical state of copper in Pt-Cu catalysts synthesized by radiolytic process during preferential CO oxidation

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1 Introduction

Radiolytic process is a simple one-pot method to synthesize nanoparticles where the aqueous solution of metal salts is simply irradiated with electron beam for several seconds. Pt-Cu catalysts synthesized in this way consist of Pt-Cu alloy and CuO_x phases, which realize high activity and selectivity in preferential CO oxidation (PROX) in H₂-rich stream [1]. Our previous study revealed that the formation of metal-CeO₂ interface is suppressed by the presence of sulfate in the precursor solution, alloying of Pt-Cu is enhanced, and the selectivity to CO oxidation is improved [2]. However, the copper species effective for the improved performance was still unclear. To investigate the chemical state of copper during the reaction, Cu *K*-edge XAFS spectra were collected in-situ PROX atmosphere using a self-assembled in-situ cell for the fluorescence mode.

2 Experiment

The catalyst A and B were prepared by a radiolytic process where an aqueous solution containing 0.1 mM H₂PtCl₆, 0.1 mM CuSO₄ (or 0.1 mM CuCl₂ for the catalyst B), and CeO₂ powder dispersed in it was irradiated with 4.8 MeV of electron beam (20 kGy) at a commercial facility. The obtained powder was separated by filtration, washed, and dried at 80°C. The catalyst C was prepared similarly, but with five times of metal precursor concentrations without CeO₂ powder, and mechanically mixed with CeO₂ after the drying at 80°C.

X-ray absorption fine structure (XAFS) measurements were performed using a synchrotron radiation ring in fluorescence mode at PF-BL12C, PF-KEK. The data was analyzed by the software Athena. The FEFF calculations were conducted on Artemis.

3 Results and Discussion

Table 1 shows catalyst composition measured by ICP-AES and average oxidation states estimated from linear combination fitting of XANES from our previous study.

Table 1: Catalyst composition and oxidation state

| sample | Pt (wt.%) | Cu (wt.%) | oxidation state (Pt) | oxidation state (Cu) |
|--------|--------------|--------------|-------------------------|-------------------------|
| A | 2.7 | 1.0 | 0.76 | 1.6 |
| B | 2.4 | 0.82 | 2.12 | 1.7 |
| C | 2.3 | 0.54 | 0.33* | 1.2 |

* Value of samples from a different batch

Compared to the sample A, both Pt and Cu in sample B were more oxidic and those in sample C were more metallic. Thus, the presence of CeO₂ support oxidizes when Pt-Cu is immobilized on it in the synthesis stage. The more oxidic feature in sample B shows sulfate protects Pt-Cu from oxidation by CeO₂. The Cu *K*-edge XANES spectra of these catalysts collected in air at 25°C, in H₂ at 100°C, in PROX gas at 100°C are presented in Fig. 1. All the catalysts were significantly reduced in H₂ and PROX conditions. However, the copper were not completely metallic. The Fourier transform of EXAFS showed the presence of Cu-O bonds even in the PROX gas at 100°C. Since capping oxygen on the Pt-Cu alloy surface would be reduced easily, the strong Cu-O bond is of CuO_x phase possibly located on the alloy surface. From our recent reports that mechanical mixture of Pt-Cu and CeO₂ exhibits comparable PROX activity and higher CO₂ selectivity than CeO₂-supported Pt-Cu [3], CuO_x in contact with Pt-Cu alloy is suggested to be the active site on the Pt-Cu system. The in-situ cell is being modified for high S/N ratio for EXAFS analysis.

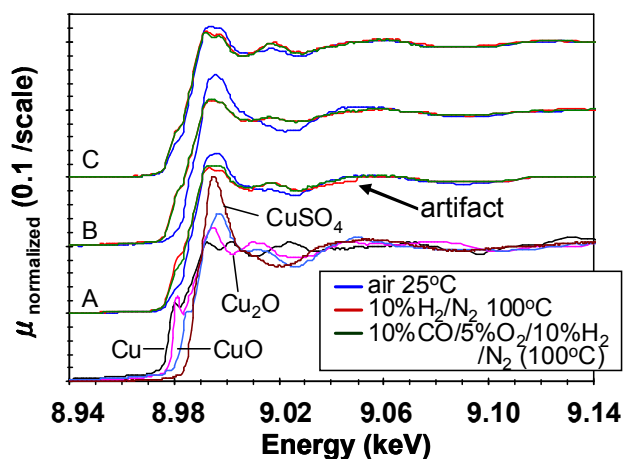


Fig. 1: In-situ Cu *K*-edge XANES spectra.

References

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