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 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 liner combination fitting of XANES from our previous study.

<table>
<thead>
<tr>
<th>Table 1: Catalyst composition and oxidation state</th>
<th>sample</th>
<th>Pt (wt.%)</th>
<th>Cu (wt.%)</th>
<th>oxidation state (Pt)</th>
<th>oxidation state (Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.7</td>
<td>1.0</td>
<td>0.76</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.4</td>
<td>0.82</td>
<td>2.12</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.3</td>
<td>0.54</td>
<td>0.33</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

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 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 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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