

## Local Structures of Au(III) species Adsorbed on Cerium Oxide Using XAFS

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### Introduction

We have found in the previous studies that Au(III) complex ions adsorbed on the surface of the powders for aluminum, titanium, and manganese oxides were spontaneously reduced to atomic gold without a specific reducing agent or heat treatment, and consequently formed gold particles on each oxide[1]. However, the reduction of Au(III) complex ions did not occur on the surface of the powder of cerium oxide as studied by <sup>197</sup>Au Mössbauer measurements, although it has the adsorption capacity as well as the powder of manganese oxide. This phenomenon for cerium oxide is useful in studying on the local structures of Au(III) complex ions on a metal oxide in the first step of the adsorption. In the case of a metal oxide on which the reduction occurred like manganese oxide, on the other hand, it is difficult to study on it because the adsorption behavior is not distinguishable from the reduction behavior. In the present study, XAFS measurements were carried out for Au(III) complex ions adsorbed on the powder of cerium oxide to examine their local structures.

### Experimental

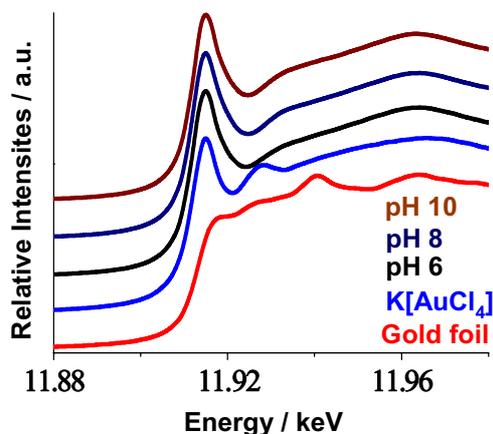
The adsorption experiments were carried out at ambient condition. A 0.5 dm<sup>3</sup> of Au(III) sample solutions (5 mg dm<sup>-3</sup> for Au) with a constant ionic strength (0.12 M NaCl) were prepared by diluting an H[AuCl<sub>4</sub>] standard solution with deionized water. 50 mg of cerium oxide powder ( $S_{\text{BET}} = 166 \text{ m}^2 \text{ g}^{-1}$ ) was added to the sample solution, and the suspended solution was then adjusted to pH 6, 8, or 10 with a NaOH aqueous solution. After stirring for 24 and 48 h, each suspension was filtered with a 0.45  $\mu\text{m}$  membrane filter and dried under the vacuum for 24 h. The adsorption rate of gold was ca. 99 %. The obtained sample powders were hardened on a piece of acryl board using a press machine to make a flat surface.

XAFS data for Au L<sub>3</sub>-edge were collected at ambient condition by a fluorescence mode. The fluorescence X-rays were detected by 19-elements Ge-SSD. Data accumulation time was 5 s / step. Data analysis was performed using the WinXAS ver. 2.1 package and FEFF6 code for the theoretical backscattering amplitudes and phase shifts. The curve fittings were carried out for the first-shell filtered data obtained by an inverse Fourier transform range of 0.9 – 2.2 Å.

### Results and Discussion

Figure 1 shows the Au L<sub>3</sub>-edge XANES spectra for the powder samples of Au(III) complex ion adsorbed on the cerium oxide together with those for H[AuCl<sub>4</sub>] and gold foil. The spectra indicate that most of gold adsorbed on cerium oxide at pH 6, 8, or 10 for 48 h exist as Au(III) species.

Table 1 shows the result of the curve fitting of an EXAFS spectrum for the powder samples of Au(III) complex ion adsorbed on cerium oxide at pH 6 for 24 h. This result suggests that there are two different Au(III) species as the adsorption structure on cerium oxide; one is coordinated by –OH and –Cl, and another is coordinated only by –OH. Existence of the two different Au(III) species have been also observed by <sup>197</sup>Au Mössbauer spectroscopy.



**Fig. 1.** Au L<sub>3</sub>-edge XANES spectra for the powder samples of Au(III) ion adsorbed on the cerium oxide at pH 6, 8, or 10 for 48 h, H[AuCl<sub>4</sub>], and gold foil.

**Table 1:** Result of curve fitting of EXAFS spectrum using two atomic pairs: sample prepared at pH 6 for 24 h

	CN	$r / \text{\AA}$	$\sigma^2 / \text{\AA}^2$	$E_0 / \text{eV}$
Au-O	3.3	1.96	0.0058	4.59
Au-Cl	0.7	2.30	0.0075	15.73

### Reference

[1] S. Matsuo et al., X-ray Spectrom. 32, 158 (2003).

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