

Anisotropic distribution of reactive adsorbates on active metal sites of a model oxide-supported metal catalyst studied by *in situ* PTRF-XAFS technique

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1 Introduction

In heterogeneous catalysis, understanding the behavior and distribution of adsorbate species on a catalyst surface is crucial to unravel the origins of the catalytic performance. X-ray absorption fine structure (XAFS), more specifically, X-ray absorption near edge structure (XANES) is one of the promising techniques to obtain information about the reactive adsorbates during the catalytic reactions since it is sensitive to the type and amount of the adsorbates.^[1] However, when the powder catalysts are used as samples, it is hardly possible to detect the non-uniform distribution of the adsorbates, which is often proposed in oxide-supported metal catalysts, such as the case where the catalytic reaction proceeds preferentially at the metal-oxide interface and the distribution of the reactive adsorbates could be different depending on the metal sites. Polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS) may have the potential to detect such anisotropic distribution of the adsorbates on the active metal sites by measuring the polarization-dependent *in situ* XANES of the metal species deposited on an oxide single-crystal surface during the catalytic reactions.^[2-4]

In this study, *in situ* Pt L₃-edge PTRF-XANES of Pt nanoclusters deposited on an α -Al₂O₃(0001) surface were measured during CO oxidation reaction and polarization-dependent distribution of the reactive adsorbates was detected.

2 Experiment

Pt/ α -Al₂O₃(0001) model catalyst surface was prepared by vacuum deposition of Pt on an α -Al₂O₃(0001) surface in a separate UHV chamber. The Pt coverage was estimated to be 0.3 ML by the XPS measurements, where 1 ML was defined as the surface Al density (5.1×10^{14} cm⁻²). The sample was then transferred to the *in situ/operando* PTRF-XAFS cell. The cell was attached to the 5-axis goniometer and the Pt L₃-edge PTRF-XAFS measurements were performed after optimization of the total-reflection conditions for incident X-rays using the 5-axis goniometer. For the *in situ* measurements, CO and O₂ gases were introduced into the cell using the mass flow controller while the cell was continuously evacuated using the turbomolecular molecular pump and dry pump.

3 Results and Discussion

Figure 1 shows the Pt L₃-edge difference PTRF-XANES spectra of CO-covered, oxygen-covered, and oxidized Pt clusters on the α -Al₂O₃(0001) surface in *s*-polarization. The difference spectra clearly indicates that it is possible to distinguish these species. The difference PTRF-XANES

spectra in *p*-polarization also showed similar spectral features with those in *s*-polarization. Then, we measured the *in situ* PTRF-XANES during the CO oxidation reaction (CO: 0.33 mL/min, O₂: 1.00 mL/min, total pressure: 1.9 Pa) at different temperatures. At 473 K, only CO was visible in both *s*- and *p*-polarized XANES spectra, suggesting that the Pt was fully covered with CO. The CO oxidation activity measurement at 473 K showed a relatively high activation energy (~ 40 kJ/mol). On the other hand, at 503 K both CO and O were observed in *s*-polarization while only CO was visible in *p*-polarization. This result may indicate that the reaction mechanism changed and the metal-oxide interface worked more efficiently as the active sites. Indeed, the activation energy was decreased to ~ 6 kJ/mol at 503 K.

Our *in situ* PTRF-XANES measurements clearly showed the potential to detect the anisotropic distribution of the reactive adsorbates on the active metal sites. We are currently performing theoretical simulations on the obtained XANES spectra.

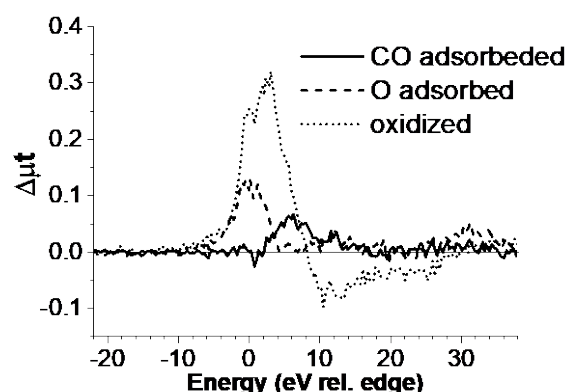


Fig. 1: Difference *s*-polarized Pt L₃-edge XANES spectra of CO-covered, oxygen-covered, and oxidized Pt clusters on α -Al₂O₃(0001) surface. The XANES of the adsorbate-free Pt clusters in *s*-polarization was used as the reference spectrum.

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References

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