

Development of *operando* PTRF-XAFS technique for elucidating 3D structure-activity relationship in heterogeneous catalysis

Satoru TAKAKUSAGI*, Lu BANG, Daiki KIDO and Kiyotaka ASAKURA
Hokkaido University, Sapporo, 001-0021, Japan

1 Introduction

Polarization-dependent total reflection fluorescence (PTRF)-XAFS is a powerful technique which can determine 3D structure of highly dispersed metal species deposited on a single-crystal surface by measuring polarization-dependent XAFS of the metal species. We have determined the precise 3D structures of single metal atoms and metal clusters deposited on single-crystal oxide surfaces such as $\text{TiO}_2(110)$ and $\text{Al}_2\text{O}_3(0001)$ by ultra-high vacuum (UHV) PTRF-XAFS apparatus in order to obtain fundamental aspects of metal/oxide-support interaction in heterogeneous catalysis.^[1,2]

In this project, we have developed a novel PTRF-XAFS technique which can measure PTRF-XAFS of active metal species dispersed on a single-crystal surface under reaction conditions (high temperatures and the presence of reactant gases). This “*operando* PTRF-XAFS technique” is then applied to CO oxidation reaction on a $\text{Pt}/\text{Al}_2\text{O}_3(0001)$ model catalyst surface. Our technique will offer a novel methodology to elucidate the relationship between 3D structure of active metal species and their catalytic performance in heterogeneous catalysis.

2 Experiment

$\text{Pt}/\text{Al}_2\text{O}_3(0001)$ model catalyst surface was prepared by vacuum deposition of Pt on an $\alpha\text{-Al}_2\text{O}_3(0001)$ surface in a separate UHV chamber (Pt coverage: $5.0 \times 10^{14} / \text{cm}^2$), and then transferred to the *operando* PTRF-XAFS apparatus (Fig.1) without exposure to air. The apparatus was attached to the 5-axis goniometer and PTRF-XAFS measurements (Pt L_3 -edge) were conducted after optimization of total-reflection conditions for incident X-rays using the 5-axis goniometer.

3 Results and Discussion

Fig.1 shows the schematic of our apparatus. It consists of a compact vacuum chamber connected to an inlet line for reactant gases and an outlet line for products analysis by a quadrupole mass spectrometer (QMS), and this chamber works as both the PTRF-XAFS cell and the batch-type reactor. The sample can be transferred to the chamber from another UHV chamber where the sample preparation (ion sputtering, annealing and metal deposition) and its surface characterization (LEED, XPS) are carried out. The sample in the PTRF-XAFS apparatus can be heated at high temperatures (< 800 K) in the presence of reactant gases.

Fig. 2 shows Pt L_3 -edge PTRF-XANES spectra of the $\text{Pt}/\text{Al}_2\text{O}_3(0001)$ surface measured at room temperature (RT), 353 K, 393 K, 423 K and 473 K in the presence of reactant gases ($\text{CO}+\text{O}_2$). The white line intensity decreased with increase of the temperature in both polarizations,

suggesting reduction of the Pt atoms probably due to partial desorption of CO and aggregation of the Pt atoms. CO_2 production was confirmed at $>473\text{K}$ by QMS, showing that creating vacant sites for oxygen adsorption by partial CO desorption might be needed to initiate CO oxidation reaction. Thus we have succeeded in measuring *operando* PTRF-XAFS spectra.

We also succeeded in obtaining PTRF-EXAFS spectra during CO oxidation reaction and the detailed 3D structure of the active Pt species will soon be reported.

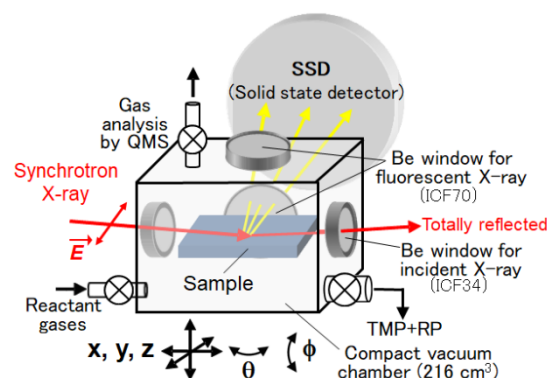


Fig. 1: Schematic of the *operando* PTRF-XAFS apparatus.

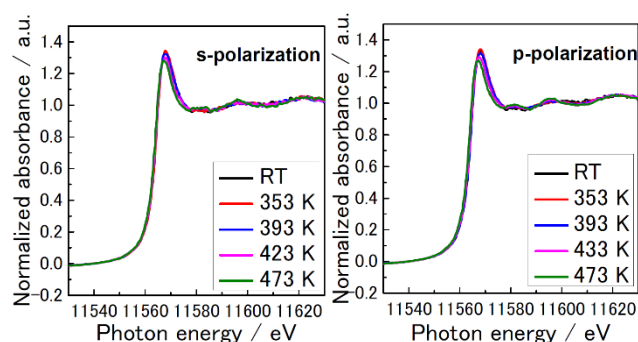


Fig. 2: Pt L_3 -edge PTRF-XANES spectra of the $\text{Pt}/\text{Al}_2\text{O}_3(0001)$ surface obtained at RT, 353K, 393K, 433 K and 473K in the presence of reactant gases ($\text{CO}:\text{O}_2:\text{Ar} = 0.3:1.0:0.1$, total pressure 100 Pa).

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References

- [1] S. Takakusagi et al., *Chem. Rec.* **18**, 1244 (2019).
- [2] S. Takakusagi et al., *Top. Catal.* **56**, 1477 (2013).

* takakusa@cat.hokudai.ac.jp