

# PTRF-XAFS study on 3D structure and catalytic activity of single Cu atoms formed on an $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface

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## 1 Introduction

Single atom catalysts (SACs), which consist of isolated single metal atoms dispersed on oxide support surfaces, have attracted much attention due to their high catalytic activity and drastic cost reduction [1]. Since catalytic performance of the SACs significantly depends on the coordination environments around the active metal site. i.e., metal-O bond distance, metal-O coordination number, coordination symmetry, and valence state of the metal atoms etc., unraveling the precise 3-dimensional (3D) structure and valence state of the active metal site is essential to understand the origins of the high catalytic performance and for development of further active SACs. In this study, single Cu atoms were prepared on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface, and their structure was analyzed by polarization-dependent total reflection fluorescence (PTRF)-XAFS technique.

## 2 Experiment

Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface was prepared by vacuum deposition of Cu on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface in a separate UHV chamber. The Cu coverage was estimated to be 0.19 ML by the XPS measurements, where 1ML was defined as surface Al density ( $5.1 \times 10^{14}$  /cm<sup>2</sup>). And then the sample was transferred to the compact vacuum chamber, termed an *operando* PTRF-XAFS cell which was recently developed by our group [2]. The cell was attached to the 6-axis goniometer, and the PTRF-XAFS measurements (Cu K-edge) were conducted under vacuum conditions ( $\sim 10^{-6}$  Pa) after optimization of total-reflection conditions for incident X-rays using the 6-axis goniometer.

## 3 Results and Discussion

Fig. 1 shows the Cu K-edge PTRF-XANES spectra of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface measured at room temperature (RT). The XANES spectra showed different features from that of Cu foil, which suggests the formation of a non-metallic Cu species. The mid-edge features observed at around 8983 eV for *s*- and *p*- polarizations could be assigned to the 1s - 4p $\pi^*$  transition, as determined from the previous XANES results and *ab initio* calculation [3, 4]. The inflection points of the edge appeared at around 8981 eV for both polarization directions. Considering that the respective inflection points for Cu foil, Cu<sub>2</sub>O, CuO appeared at 8979.5, 8980.6, 8984.5 eV, the oxidation state of the Cu species is monovalent.

Fig. 2 shows the Cu K-edge PTRF-EXAFS spectra of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface measured at RT. Curve fitting results showed the presence of Cu-O interaction ( $0.225 \pm 0.002$  nm), and no Cu-Cu interaction or Cu-Al interaction was detected.

These results indicate that Cu was atomically dispersed and present as a single atom catalyst on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface by making bonds with the O atoms of the Al<sub>2</sub>O<sub>3</sub> surface. We are now trying to determine the precise 3D structure of the Cu species by theoretical simulation of the EXAFS oscillations using the FEFF code [5], and plan to conduct the simultaneous measurements of PTRF-XAFS and catalytic activity by using the *operando* PTRF-XAFS technique.

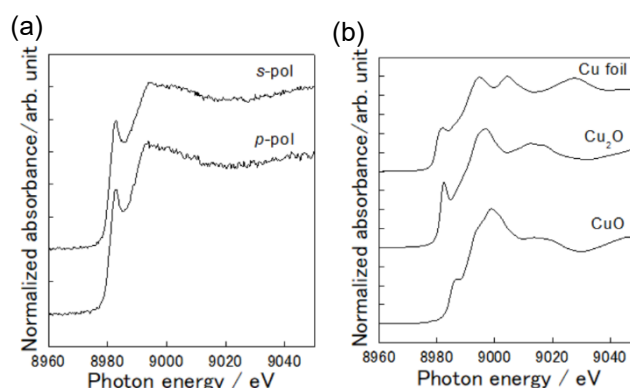


Fig. 1: (a) Cu K-edge PTRF-XANES spectra of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface. (b) XNAES spectra of reference compounds.

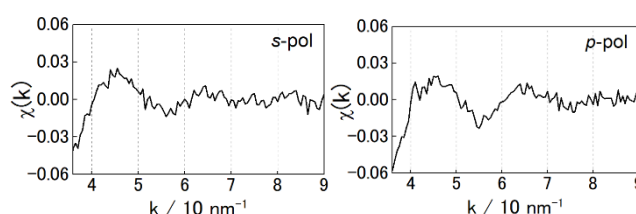


Fig. 2: Cu K-edge PTRF-EXAFS spectra of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface.

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## References

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