In situ / *operando* spectroscopic measurements for understanding surface functional materials under working conditions

Ryo Toyoshima
Department of Chemistry, Keio University

Abstract

Chemical reactions at surfaces have been widely used for chemical processes such as catalytic synthesis, energy conversion, environmental clean-up, and sensor. Surface science techniques enable us to understand fundamental physicochemical processes on surfaces. However, a drawback of such surface science techniques is that those experiments are carried out under vacuum in many cases. In recent decades, some advanced experimental techniques have been developed to overcome such pressure gap problem, which are so called in situ / operando techniques.

We have developed some experimental techniques for in situ / operando observations of surface reactions on liquid/solid and gas/solid interfaces in energy range from infrared to soft X-ray. Here, we present our recent results obtained by ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and X-ray absorption spectroscopy (AP-XAS). The experiments were carried out at a soft X-ray beamline BL-13 at the Photon-Factory of High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan. The AP-XPS system is consisted of a high-pressure chamber with a differential pumping system, preparation chamber and load-lock chamber. The XAS system is consisted two sections: high-vacuum front-end and ambient pressure reaction cell. A Si3N4 membrane is sandwiched between the front-end and reaction cell. Further details of our experimental techniques are described elsewhere [1,2].

Figure 1 shows a result of operando AP-XPS measurement for H2 sensing Pt-Rh thin-film sensor. The Pt-Rh sensor detects the atmospheric concentration of H2 gas by changing in electric resistivity. Figure 1(a) shows time evolution of relative electric resistivity (ΔR/R). The resistivity decreases with exposing H2 gas to the sensor surface, whereas it increases with exposing O2 gas. Figure 1(b) shows corresponding Rh 3d and Pt 4f XPS. Before the gas dosing (i), the surface was dominated by Rh oxide. When the surface was exposed to the H2 gas, the chemical state clearly changed. The Rh oxide was completely reduced to the metallic state. When, the surface was exposed to the O2 gas, the oxygen-induced species grew up again. Those findings indicate the surface chemical state strongly relate to the material functions (i.e. electric resistivity).

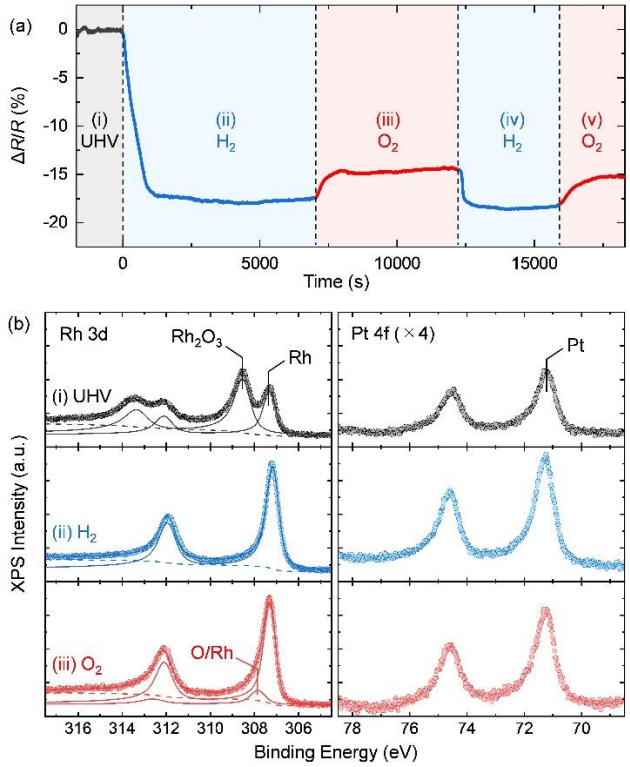

Figure 1. *Operando* AP-XPS analysis of Pt–Rh thin-film sensor surface under working conditions. (a) Evolution of resistivity and (b) Rh 3d and Pt 4f AP–XP spectra taken under UHV (i) and at working conditions (ii and iii). (Ref. 1)

References

[1] Toyoshima, R. et al. J. Phys. Chem. Lett. 2022, 13, 8546–8552.

[2] Shimizu, H. et al. Phys. Chem. Chem. Phys. 2022, 24, 2988–2996.