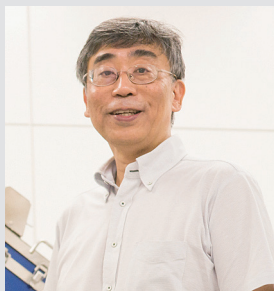


# Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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### Keywords

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For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage. Recently, assistant professor Kohei Yamamoto is developing the reflectance soft x-ray magnetic circular dichroism system for the clarification of depth resolved magnetism of magnetic thin films with the atomic layer resolution scale.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although photoelectron spectroscopic measurement is

usually done under high vacuum, recent material science often requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure ( $10^5$  Pa) HAXPES measurements for the first time in the world using Beamline 36XU of SPring-8. Moreover, we designed and constructed the subsecond time resolved AP-HAXPES measurement system, and successfully investigated electrochemical reaction dynamics for the cathode Pt oxidation/reduction and the  $S^2$ -adsorption/desorption processes upon an abrupt step of the cathode-anode bias voltages. These works were supported by the NEDO Fuel Cell project. More recently, assistant professor, Takanori Koitaya, has been investigating various kinds of surface chemical reactions such as methane activation and  $CO_2$  hydrogenation using the AP-HAXPES system combined with the near ambient pressure soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8.

The third subject is the x-ray absorption fine structure (XAFS) investigation. This includes femto- and picosecond time resolved XAFS measurements using the x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Moreover, conventional temperature dependent extended x-ray absorption fine structure (EXAFS) spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of alloy systems.

### Selected Publications

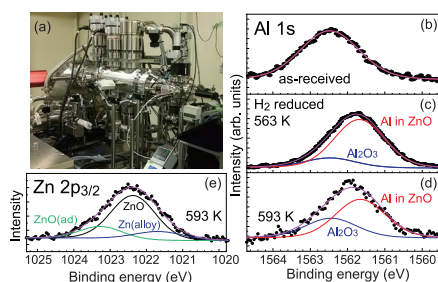
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## 1. Operando Characterization of Copper-Zinc-Alumina Catalyst for Methanol Synthesis from CO<sub>2</sub> and H<sub>2</sub> by AP-HAXPES<sup>1)</sup>

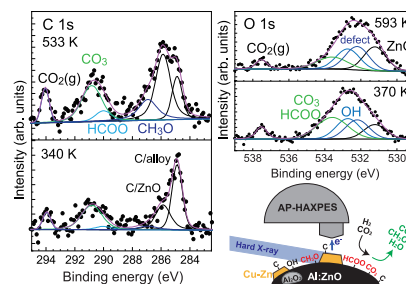
*Operando* spectroscopy is a very powerful tool for the characterization of heterogeneous catalysts under working conditions. In this study, an AP-HAXPES investigation of an industrial copper-zinc-alumina methanol synthesis catalyst was performed using our AP-HAXPES system shown in Figure 1(a) to reveal surface chemical states of the catalyst and adsorbed intermediates during the catalytic reaction. The reaction activity of the present catalyst is quite important because of the significance of the CO<sub>2</sub> circulation. *In-situ* formation of metallic Cu-Zn particles was detected during the reduction process of the catalyst under hydrogen atmosphere. More interestingly, a significant amount of Al atoms was found to be incorporated into ZnO during H<sub>2</sub> reduction and also CO<sub>2</sub> hydrogenation chemical reaction as seen in Figures 1(b) and 1(c).

In this study, we also installed a quadrupole mass spectrometer installed in the differentially pumped electron lens chamber to observe the reaction products in the presence of near ambient-pressure CO<sub>2</sub> and H<sub>2</sub> gases. The formation of CO and methanol was actually observed very clearly. Temperature dependence was found to differ between rWGS (reverse water-gas shift to form CO) reaction and methanol synthesis; the reaction products of rWGS monotonically increased as a function of the sample temperature between 420 K and 593 K, whereas the rate of the methanol synthesis reached a local maximum at 480 K, and decreased at 593 K. The observed temperature-dependence of methanol synthesis correlates well with the dynamic changes in the chemical states of the catalyst and adsorption intermediates during the reaction observed in the AP-HAXPES.

Figure 2 shows the C 1s and O 1s HAXPES during the CO<sub>2</sub> hydrogenation reaction. The total environmental pressure amounts 53 kPa. Although the C 1s spectra measurement was



**Figure 1.** (a) Our AP-HAXPES system installed at BL36XU in SPring-8, (b–d) Al 1s HAXPES ( $h\nu = 7.94$  keV) from the CuZn/Al<sub>2</sub>O<sub>3</sub> catalyst: (b) as-received, (c) during H<sub>2</sub> reduction at 563 K, and (d) in the 36 kPa H<sub>2</sub> and 17 kPa CO<sub>2</sub> atmosphere at 593 K, together with (e) Zn 2p<sub>3/2</sub> HAXPES in the same condition as (d). The Al atoms are found to be incorporated in ZnO in CO<sub>2</sub> hydrogenation reaction, which is a key role for the catalytic activity in this system.



**Figure 2.** (left) C 1s HAXPES during the CO<sub>2</sub> hydrogenation reaction (8 kPa H<sub>2</sub> and 5 kPa CO<sub>2</sub> at 340 and 533 K) and (right) O 1s HAXPES during the reaction (36 kPa H<sub>2</sub> and 17 kPa CO<sub>2</sub> at 370 and 593 K). Reaction intermediate species as CO<sub>3</sub>(a), HCOO(a), and CH<sub>3</sub>O(a) are seen, implying successful direct observation in the present catalytic reaction. Schematic surface reaction model is also shown in the figure.

rather difficult due to the small C 1s photoionization cross section, important reaction intermediate species such as CO<sub>3</sub>(a), HCOO(a), CH<sub>3</sub>O(a) were observed. The present AP-HAXPES measurements clearly show the importance of *operando* characterization of the dynamic nature of heterogeneous catalysts.

## 2. Exploitation of Reflectance Soft X-Ray Magnetic Circular Dichroism System for the Clarification of Layer-Resolved Magnetic Structures

Magnetic thin films/multilayers with complex depth structures exhibit a wide variety of magnetic phenomena due to the interactions between layers. Furthermore, multilayer structures have been used to realize useful properties in recording media, which is an important application of magnetic materials. Direct observation of the magnetic distribution in the depth direction of such magnetic multilayers has been used to elucidate the mechanism of evolution of magnetic structures in thin films. We installed an experimental setup for reflectance x-ray magnetic circular dichroism (XMCD) method in the soft X-ray regime at UVSOR BL4B and experiments were performed on test samples. The sample was CoFeB and an oscillating structure was observed due to the interference of the cap layer and the underlying layers. We observed the difference corresponding to XMCD by changing the direction of magnetic field, which is consistent with the simulation results. We also conducted spectroscopic measurements and obtained photon energy and reflection angle dependence to analyze the depth-resolved magnetization information. We will test the silicon drift detector for getting information of higher angle regions and eliminating the fluorescence effect with energy selectivity.

### Reference

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