

Operando characterization of copper-zinc-alumina catalyst for methanol synthesis by ambient-pressure hard X-ray photoelectron spectroscopy

The conversion of carbon dioxide (CO₂) into chemicals is essential for the recycling of carbon resources. Methanol synthesis via the hydrogenation of CO₂ has been particularly investigated, and industrial plants for methanol production have already been developed worldwide. Copper-zinc-alumina (CZA) catalysts are widely used for the synthesis of methanol from CO₂ and H₂. Metallic Cu nanoparticles formed on the surface during the catalytic activation process are considered to be the active sites for methanol synthesis. To reveal the reaction mechanism, we investigated the surface chemistry of CO₂ on the Cu surface [1-3]. The *operando* observation of working catalysts is highly desirable for understanding the nature of active sites in heterogeneous catalysis. In this study, the reduction of CO₂ over a CZA catalyst was investigated using ambient-pressure hard X-ray photoelectron spectroscopy (AP-HAXPES). XPS measurements of gas–solid interfaces can provide quantitative information on the electronic states of heterogeneous catalysts and reaction intermediates under reaction conditions as well as catalytic reactivity/selectivity by mass spectrometry of the desorbed products. This study aims to reveal the surface chemical states of methanol-synthesis catalysts under catalytic working conditions. Using hard X-rays as the excitation source, XPS can be performed at a higher gas-phase pressure than soft X-ray AP-XPS, which is advantageous for the *operando* spectroscopy of the catalytic conversion of inert molecules such as CO₂.

Operando AP-HAXPES experiments were conducted at SPRING-8 BL36XU [4]. The HAXPES apparatus consisted of a differentially pumped pre-lens, lens, and hemispherical electron analyzer. At the entrance of the pre-lens, a front cone with a micrometer-order aperture was installed to prevent a pressure increase in the lens/analyzer chamber. The system specifications are listed in Table 1.

The as-received CZA catalyst was insulating and

severely charged upon irradiation with hard X-rays under vacuum. However, AP-HAXPES measurements of the as-received catalyst were successfully performed in the presence of 17 kPa Ar gas to compensate for sample charging by ions and electrons generated from the photoionization of Ar atoms in the gas phase. The as-received CZA catalyst consisted mainly of CuO, Al₂O₃, and ZnO with adsorbates (Fig. 1). The CZA catalyst was activated by heating it to 563 K in the presence of hydrogen gas (37 kPa) before methanol synthesis. AP-HAXPES spectra were measured during the reduction process and showed the complete reduction of Cu and partial reduction of ZnO to Zn migrating into metallic Cu particles. Based on the relative intensity of the Zn 2*p* peaks of each component, 8% of the total Zn atoms in the interfacial region detectable by HAXPES were reduced to the metallic state. The chemical state of Al also changed significantly because of reduction. The new peak at 1561.7 eV could be attributed to Al atoms embedded in ZnO.

After the reduction process, the catalytic reactivity was investigated in the presence of CO₂ and H₂ using quadrupole mass spectrometer (QMS) in a differentially pumped lens chamber (Fig. 2(a)). The temperature-programmed reaction spectrum of the produced methanol (*m/z* = 31) exhibited a peak at 480 K, which then decreased at 490–530 K. The coverage of the reaction intermediates was estimated from the C 1*s* AP-HAXPES experiments (Fig. 2(b)). At 470 K, the peak intensity of the formate adsorbed on the ZnO surface increased significantly. After heating to 533 K, the coverage of the formate on ZnO decreased, indicating that the formate species was further hydrogenated to form methoxy groups or decomposed into CO₂ and hydrogen at this temperature. The temperature dependence of the formate species correlated with an increase in the methanol production rate (Fig. 2(a)). These results indicate that formate on ZnO is an important reaction intermediate in the methanol synthesis.

Table 1. Specifications for the AP-HAXPES system at BL36XU[#]

Analyzer	Gas pressure	Sample temperature	Gas-analysis method	Application examples
Scienta-Omicron R4000 HiPP-2	0.1 – 10 ⁵ Pa	300 – 700 K	Quadrupole mass spectrometry	Heterogeneous catalyst Liquid samples Electrochemistry Fuel cell

[#]This system has been in operation at BL46XU since FY2023.

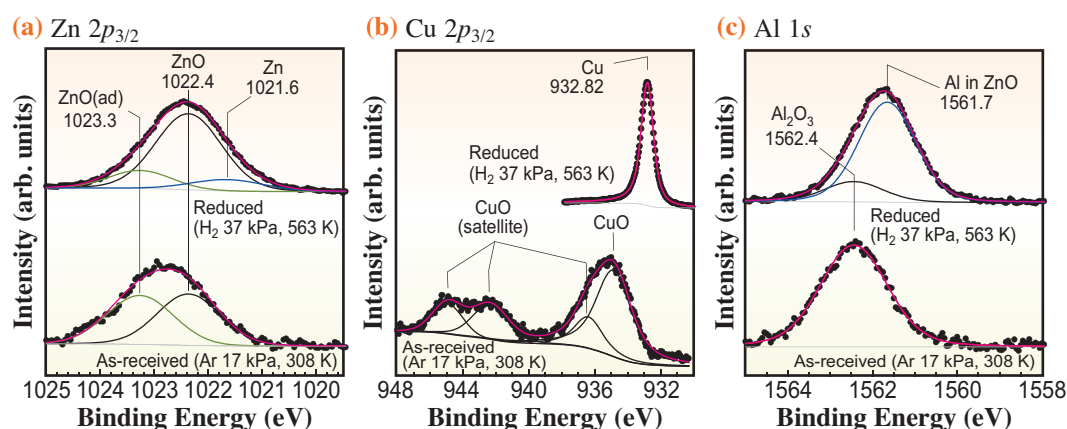


Fig. 1. Ambient-pressure HAXPES spectra of the as-received methanol synthesis catalyst (bottom) and reduced catalyst (top) for (a) Zn $2p_{3/2}$, (b) Cu $2p_{3/2}$, (c) Al $1s$. [3]

The chemical states of Zn and Al in the catalyst depend on the reaction temperature and gas-phase composition, indicating that the catalytic surface is not static, but dynamic under the catalytic operating conditions. The Cu/ZnO interface was responsible for methanol synthesis under the present near-ambient pressure conditions. One of the roles of ZnO was the stabilization of reaction intermediates such as the formate and methoxy species. The present *operando* AP-HAXPES measurements demonstrated the

importance of *in situ*, real-time characterization of the active catalyst under working conditions to reveal the nature of the reaction sites.

The AP-HAXPES system used in this study was moved to the renovated BL46XU, which is a dedicated beamline to HAXPES. The optical equipment was optimized to increase the beam intensity and reduce the beam size compared with BL36XU, resulting in highly effective *operando* AP-HAXPES measurements, even under atmospheric pressure.

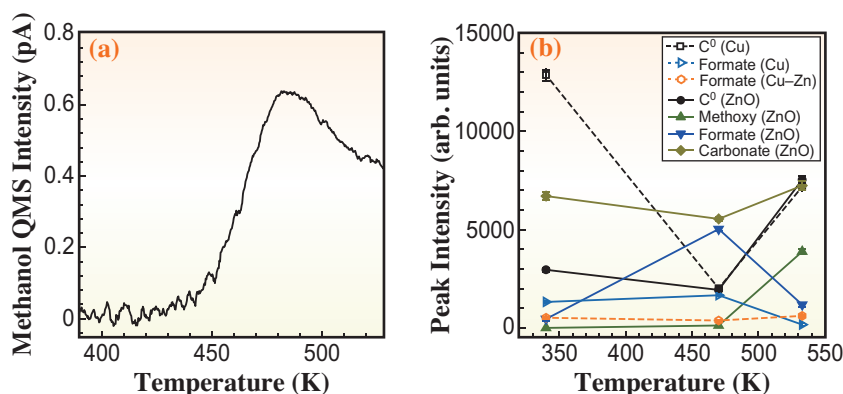


Fig. 2. (a) Temperature-programmed reaction spectroscopy of produced methanol in the presence of 36 kPa H_2 and 17 kPa CO_2 gases with a heating rate of 0.1 K/s. (b) C $1s$ peak intensity of adsorbates as a function of temperature. [3]

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