

Ambient Pressure X-ray Photoelectron Spectroscopy Study of Formate Formation From CO₂ and H₂ on Brass

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Introduction

As a “clean” fuel, methanol attracts renewed attention recently. Methanol is industrially produced from a CO/CO₂/H₂O mixture gas using Cu/ZnO/Al₂O₃ as a catalyst. A rate limiting step of the synthesis is a reaction step from formate (HCO₂) to H₂CO, and the catalyst lowers the activation energy of this step. Activation sites are believed to exist on the Cu particles, on which Zn atoms migrate from ZnO to form a Cu-Zn complex [1]. Thus, surfaces of brass, a Cu-Zn alloy, are an ideal platform to study the elemental steps of the methanol synthesis.

In the present study, a reaction of CO₂ and H₂ on brass has been investigated by ambient-pressure X-ray photoelectron spectroscopy (APXPS). Although methoxy and methanol is not observed, formate and formic acid are detected on the brass surface as well as in the residual gas as reaction products.

Experimental

APXPS measurements were performed at BL-13A. A brass disc with a bulk composition of 75wt% Cu and 25wt% Zn was used as a substrate. The surface was cleaned by cycles of Ar⁺ sputtering and annealing. The surface Zn concentration was largely reduced after the cleaning procedure because of easy sublimation of Zn. CO₂ and H₂ gasses were introduced into the ultrahigh vacuum (UHV) chamber independently through variable leak valves. The substrate were kept at room temperature during the experiment.

Results and discussion

Among the elementary steps for the methanol synthesis from CO₂ and H₂, formate is a first stable intermediate on the catalyst surface. The formation of formate requires dissociative adsorption of H₂, and dissociated H migrates on the surface to interact with molecularly adsorbed CO₂ to form formate. However, when CO₂ is admitted to the UHV chamber before the H₂ introduction, the brass surface is packed by CO₂ with a narrow space for H₂ dissociation so that the formate formation is largely suppressed. On the other hand, a sufficient amount of formate is formed when H₂ is introduced into the chamber prior to the CO₂ introduction. Fig. 1 shows O 1s and C 1s core-level spectra measured in the mixture of the H₂ and CO₂ gasses (130 and 13 Pa, respectively). The O 1s spectrum bears two intense peaks at 531 and 537 eV. The latter is associated with

physisorbed CO₂, while the former peak contains contributions from the several species such as chemisorbed CO₂, ZnO and formate. The existence of the formate species is directly proved by the observation of C 1s peak at ~289 eV. This peak is not observed when the brass surface is exposed to the CO₂ gas. A detailed analysis of the O 1s and C 1s spectra suggests the existence of O, C, CO, CO₃ as other chemisorbed species and the formation of Cu₂O.

We have also made a residual gas analysis by mass spectroscopy. A result is shown in the inset of Fig. 1. Intensities of masses (m/e) of 45 and 46 are enhanced upon the introduction of CO₂. These masses are attributed to formate (HCO₂) and formic acid (HCOOH). Thus, formate is catalytically formed by an attachment of H to CO₂ on the brass surface, and a part of formate is further hydrogenated to formic acid, which should immediately desorb upon the formation.

Unfortunately, no direct evidence for methoxy and methanol species is obtained. This implies that the activation barrier between formate and H₂CO cannot be overcome in the reaction condition employed in the present study.

References

[1] J.-D. Grunwaldt et al., *J. Catal.* **194**, 452 (2000).

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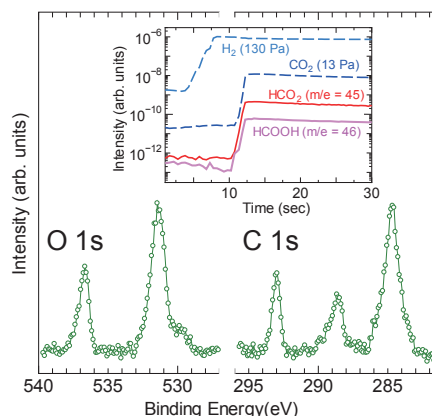


Fig. 1 O 1s and C 1s XPS spectra measured in an ambient condition of H₂ (130 Pa) and CO₂ (13 Pa). The inset shows time variation of partial pressures of masses of 2, 28, 45 and 46.