

In-situ study of trimetallic catalysts Pd-Cu-Zn/SiC and Pd-Cu-Zn/TiO₂ for CO₂ hydrogenation by Ambient Pressure X-ray Photoelectron Spectroscopy

Ying-Chih Lo¹, Chia-Hsin Wang^{1*}, Yaw-Wen Yang^{1,2}

¹National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan

²Department of Chemistry, National Tsing-Hua University, Hsinchu, 30013, Taiwan

Abstract

The conversion of CO₂ to value-added chemicals efficiently plays an important role in reducing CO₂ emissions. Pd-Cu-Zn catalysts have the potential for CO₂ hydrogenation. Pd-Cu-Zn/SiC was prepared by the impregnation method and Pd-Cu-Zn/TiO₂ was prepared by the solvent free chemical vapor impregnation method, respectively. Both catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and ambient pressure X-ray photoelectron spectroscopy (APXPS). The broad peak between two theta of 41° and 45° was suggested that the formation of alloy in trimetallic catalyst. The particles size distribution of Pd-Cu-Zn/SiC and Pd-Cu-Zn/TiO₂ catalysts is around 10- 20 nm and 5- 6 nm, respectively. In this study, we study the reaction mechanism of CO₂ hydrogenation on Pd-Cu-Zn catalysts at the different substrates at the pressure of 0.5 mbar with a mixing gas (CO₂ : H₂=1:3) and then carry out at the temperature from room temperature (RT) to 573 K via APXPS at TLS BL24A. The catalysts were cleaned by Ar⁺ sputtering and atomic hydrogen treatment first to reduce carbon and oxygen contamination. APXPS revealed the change in the composition of carbon species at the catalysts during the reaction process. In the presence of a mixing gas (CO₂ : H₂=1:3) under 0.5 mbar at room temperature, the C1s signal shows an additional peak assigned to chemisorbed CO₂ at the binding energy of 288.6 eV on the surface of Pd-Cu-Zn/SiC compared to that in the vacuum. After the reaction temperature reaches 523 K, the C-H signal at the binding energy of 284.6 eV was enhanced, and the chemisorbed CO₂ peak has vanished. In the case of Pd-Cu-Zn/TiO₂ catalyst, the C1s spectrum shows the chemisorbed CO₂ at the binding energy of 288.0 eV, and the peak of carbonated at the binding energy of 289.3 eV have been enhanced on the surface of catalyst in the presence of a mixing gas (CO₂ : H₂=1:3) under 0.5 mbar at room temperature. Both chemisorbed CO₂ and carbonated signals decrease gradually, and the C-H (B. E. 284.6 eV) and C-O (B. E. 285.4 eV) were slightly increased at the reaction temperature of 473 K. The C-H signal was dramatically increased at the reaction temperature of 573 K. This crucial real-time reaction information helps us figure out the possible reaction mechanism of CO₂ hydrogenation on Pd-Cu-Zn catalysts at the different substrates. More detailed information will be discussed in this study.

Keywords – APXPS; CO₂ hydrogenation; methanol synthesis