Operando ambient pressure HAXPES studies of Cu/ZnO(10-14) and Cu/ZnO(000-1) model catalysts for methanol synthesis

Heshmat Noei, Robert Gleißner, Robert Gleißner, Michael Wagstaffe, Christopher Goodwin, and Markus Soldemo

DESY NanoLab, Hamberg, Germany

The vicinal ZnO(10-14) facet recently gained scientific interest for its high density of surface steps and outstanding stability [1]. It has the lowest formation energy in comparison with other mixed-terminated facets such as (10-10) or (11-20) and therefor can be expected to play a distinct role in $Cu/ZnO/Al_2O_3$ powder catalysts [2]. We investigate the growth and morphology of the Cu nano particles on the vicinal ZnO surface under UHV conditions. In initial growth stages Cu nanoparticles adapt the height oscillations of the underlying stepped substrate closely and form elongated islands upon further growth. High energy surface x-ray diffraction as well as scanning tunneling microscopy reveals that the particle orient their <111> direction parallel to the <0001> direction of the ZnO(10-14) substrate, resulting in a unique interface relationship. The Cu particles present large area facets of high index as accessible sites for catalytic reactions. Additionally, sintering of the particles is inhibited by the substrate steps induced anisotropic diffusion over the surface.

Ambient Pressure XPS studies reveal the higher abundance of reaction intermediates for Cu/ZnO(10-14) in comparison to the Cu/ZnO(000-1) system on the surface of these model catalysts. Switching from CO/H_2 over $CO/CO_2/H_2$ to CO_2/H_2 conditions and vice versa revealed complete reversibility.

[1] H. Zheng, Phys. Rev. Lett. 2013, 111, 086101.
[2] K.S. Chan, Appl. Phys. Lett. 2015, 106, 212102.