

# The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> System – Insights into the ZnO<sub>x</sub> Dynamics by *Operando* Electron Microscopy

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Multinary Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have been used industrially since the mid-1960s for both the water-gas shift (WGS) reaction and methanol synthesis. In addition, methanol produced from CO<sub>2</sub> and H<sub>2</sub> is considered an important storage molecule on a prospective renewable energy landscape [1].

In general, the catalyst is reductively activated, which promotes the formation of a partially reduced ZnO<sub>x</sub> overlayer over Cu nanoparticles (NPs) through the formation of strong metal-support interactions (SMSI) or the formation Cu-Zn surface alloys.[2] The SMSI state has been described *ex situ* in the activated catalyst after reductive activation as a thin ZnO layer encapsulating the metallic Cu particles.[3] This overlayer transformed to thermodynamic stable ZnO phases decorating the Cu NPs after long-term experiments causing deactivation.[4] However, its evolution and participation in the catalytic reaction has yet not been investigated in real time. Here we focus on an *operando* transmission electron microscopy (OTEM)[5] approach to unravel the dynamics the ZnO<sub>x</sub> species in a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst during activation and CO<sub>2</sub> hydrogenation.

During activation in hydrogen a 2-step process was observed which involves the segregation of CuO NPs from the high-temperature (Cu,Zn) carbonate phase and the subsequent reduction and sintering of these NPs from evolves gradually from Cu<sup>2+</sup> over Cu<sup>+</sup> to Cu<sup>0</sup>. The ZnO<sub>x</sub> overlayer, is sporadically observed after reductive activation at elevated temperatures. Interestingly, cooling the sample reveals a high degree of ZnO<sub>x</sub> coverage of the Cu NPs. Temperature cycling indicates the dynamic and reversible nature of the ZnO<sub>x</sub> overlayer which is not stable at high temperatures. This is compounded by results obtained under hydrogen-rich (H<sub>2</sub>:CO<sub>2</sub>:He = 3:1:0.5, methanol synthesis) and hydrogen-lean feed compositions (H<sub>2</sub>:CO<sub>2</sub>:He = 1:1:0.5, reverse water gas shift conditions). The dynamics of the overlayer is corroborated by integral *in situ/operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Increasing the temperature to 400°C showed a sudden increase of the Cu lattice parameter, which then leveled off to the expected one for metallic Cu over 30 minutes, demonstrating the potential of *operando* selected area electron diffraction (SAED) for tracking alloying and reoxidation phenomena in real time and revealing the time constant of these phenomena.

The study sheds novel insights into how Cu wetting by  $\text{ZnO}_x$  is mediated by temperature as well as  $\text{H}_2$  and  $\text{CO}_2$  partial pressures through a delicate balance between transient Cu-Zn alloy formation and the reoxidation of Zn species to generate access to the Cu-ZnO perimeter [6].

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