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Structural Change of a Cu/ZnO Catalyst under Methanol Observed by ETEM

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Cu/ZnO-based catalysts have been used in methanol synthesis and methanol oxidation for decades [1, 2]. In order to improve the stability of these catalysts and catalytic performance, much effort has been invested to understand the impact of copper loading and metal promoters [3]. However, the structural evolution of the Cu/ZnO catalyst under industrially relevant conditions and interplay of the morphological-reactivity are still under debate [4, 5]. More *in situ* studies at reaction conditions are necessary for the elucidation of reaction mechanism and eventual optimization of next-generation Cu/ZnO catalysts. We synthesized a 30% wt Cu/ZnO by co-precipitation methodology. The particle size change under heat and methanol exposure was investigated using *in* and *ex situ* transmission electron microscopy (TEM) techniques.

The Cu/ZnO nanoparticles (NP) were prepared from an aqueous zinc and copper nitrate solution by addition of sodium carbonate solution. The resulting precipitate was dried and calcined in air at 400 °C for 3 h. The dry catalyst powder was then dispersed in ethanol and drop-cast onto a 10 nm thick Si_3N_4 membrane TEM grid. Using a Hitachi double-tilt heating holder inserted in a Hitachi H9500 environmental TEM, the sample was annealed at 250 °C and then exposed to methanol vapor inside the microscope. NP size distributions were generated from the acquired TEM images after each reaction step. The chemical compositions of before and after the reaction were determined using an energy X-ray dispersive spectrometer (EDS) attached to a FEI Talos operated at 200 kV. Subsequently, the elemental and quantitative distributions of Cu and Zn within the nanostructure were determined from the acquired STEM-EDS maps.

The TEM image and NP size distribution of the as-synthesized 30% wt Cu/ZnO NP, after annealing, and after methanol exposure are shown in Figure 1. The resulting size distribution of the NPs indicated aggregation after exposure to methanol vapor. EDS maps (Figure 2) revealed that Cu nanoparticles were aggregating while the structure and size of the ZnO NPs were maintained. The observed Cu NP aggregation was attributed to electron beam effect. Concurrent kinetic study on partial oxidation of methanol catalyzed by Cu/ZnO indicates that different methanol to O_2 feed ratios could change Cu oxidation state and reaction product distribution. Additional *in-situ* TEM studies with the co-feeding of methanol and O_2 gases at similar conditions to kinetic measurements are underway to further investigate the change of Cu/ZnO structure and Cu oxidation state [6].

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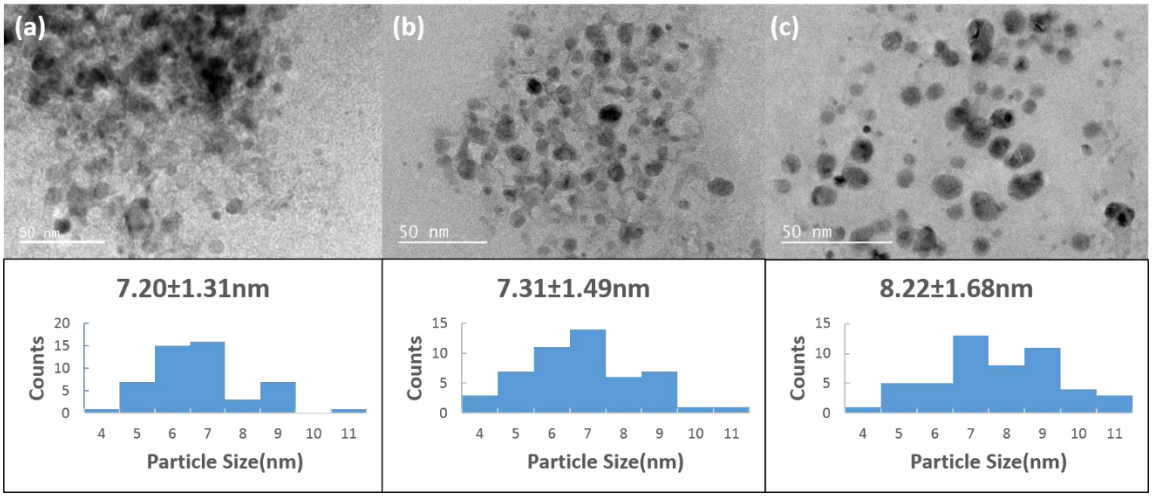

Figure 1. TEM image and size distribution of the CuO/ZnO nanoparticles. (**a**) As synthesized, (**b**) *in situ* TEM heating (250 °C) for 4 h and to (**c**) methanol vapor for 30 min (1x10^{-2} Pa).

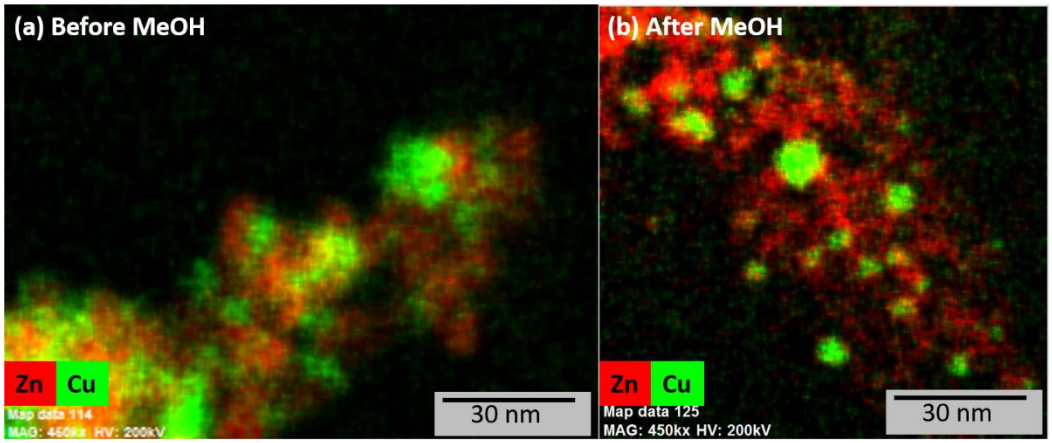

Figure 2. STEM-EDS elemental maps of Cu/ZnO nanoparticles before (**a**) and after (**b**) exposing to methanol (1x10^{-2} Pa) at 250 °C.