



In situ XAFS Studies on the Structure of Copper Oxide / Zinc Oxide Catalysts

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Abstract:

Cu/ZnO supported on alumina is a well-known catalyst for the hydrogenation of CO and CO₂. In this work a combination of inorganic synthesis and physicochemical characterization is attempted to assess the influence of various preparation parameters on the resulting active copper phase. XAFS measurements of calcined precursors were carried out at the Cu K edge and the Zn K edge. Corresponding RDF show that both copper oxide and zinc oxide exhibit considerable deviations from a linear dependence of their structure on the composition. In agreement with XRD measurements those deviations coincide with the formation of different hydroxycarbonate precursors with different Cu/Zn ratios. From time-resolved in situ experiments at the Cu K edge the degree of reduction can be monitored using a combination of factor analysis (PCA) and least-squares XANES fitting with suitable reference spectra (e.g. Cu metal, Cu₂O, and CuO). The intermediate presence of Cu(I) species (i.e. Cu₂O) was confirmed. Repeated cycles of reduction and reoxidation revealed a reversible change between copper oxide and reduced copper clusters. However, the increased magnitude of the Cu-Cu shell and the appearance of higher shells in the re-reduced state indicate an increased crystallinity and/or particle size. The Zn RDF also reveals an increased intensity of higher Zn-O shells after reduction, while ZnO remains unreduced under the conditions employed.