Structure and Activity of Copper/Zinc Oxide Catalysts studied using X-ray Diffraction and Absorption Spectroscopy

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ABSTRACT

This thesis reports on bulk structure-activity relationships of Cu/ZnO catalysts for methanol synthesis and methanol steam reforming using X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). XRD line profile analysis was applied to series of activated binary Cu/ZnO catalysts with varying molar ratios to determine the microstructure of Cu and ZnO. The procedure affords for both phases a considerable microstructural imperfection due to nanocrystallinity and microstrain as a function of the Cu/Zn ratio. Bulk defects are considered to be the origin of the observed structural disorder of Cu and ZnO which can originate from dissolution of Zn in Cu, incomplete reduction and epitaxial bonding of metal Cu clusters to the ZnO lattice. Additional EXAFS measurements at the Cu K and the Zn K edge show that about 5% ZnO are dissolved in the CuO matrix of the calcined precursors.

A sample set of binary Cu/ZnO catalysts with varying molar ratios (90/10 through 10/90) is studied under methanol synthesis conditions at 493 K and at atmospheric pressure. A positive correlation of the turnover frequency for methanol production with the observed microstrain of copper in the Cu/ZnO system is found. In addition, the bulk structure of various binary Cu/ZnO catalysts for methanol steam reforming is studied by in situ XRD and XAS under activation and working conditions. The evolution of bulk phases from CuO/ZnO precursors during activation with hydrogen is studied using temperature programmed reduction (TPR). Using time-resolved in situ XANES measurements at the Cu K edge during TPR experiments the degree of reduction was monitored. It is shown that Cu₂O forms prior to Cu. The extent of reduction to Cu exhibited a typical nucleation and growth behavior with an enhanced reaction rate for samples with a lower copper content. Reduction of CuO/ZnO in the presence of water vapor resulted in Cu crystallites with a higher selectivity in methanol steam reforming (optimum composition 60-70 mol-% Cu). Adding oxygen (20 vol-%) to the feed gas lead to the formation a mixture of Cu(II) and Cu(I) oxide accompanied by a complete loss of activity. After switching back to steam reforming conditions the activity is regained and the catalyst shows an increased Cu crystallite size (up to 40%). EXAFS measurements at the Cu K and the Zn K edge indicate a structural disorder of the Cu particles in the medium range order and the dissolution of Zn atoms (up to ~ 4 mol-%) in the copper matrix. Upon oxidation/reduction cycles the disorder in the copper particles increases while Zn segregates out of the copper bulk. A structural model is proposed which ascribes the enhanced activity to structurally disordered (strained) copper particles due to an improved interface interaction with ZnO.