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Bulk structural investigations of Cu/ZnO catalysts for methanol steam reforming

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Abstract:

Cu/ZnO catalyst can be used to produce hydrogen by steam reforming of methanol with high selectivity and activity. Therefore, methanol is considered as an alternative ”automotive” fuel and could serve as a hydrogen source for fuel cell applications. Although the Cu/ZnO system has been studied in great depth, both after reduction and under working conditions for methanol synthesis, the active Cu phase for methanol reforming has not yet been fully elucidated. In this study we used two complementary bulk techniques, in situ X-ray diffraction and X-ray absorption spectroscopy to elucidate bulk structural changes of Cu in Cu/ZnO systems during activation and under methanol steam reforming conditions while the gas phase is analyzed on-line with a calibrated mass spectrometer.

The evolution of bulk phases from CuO/ZnO precursors during temperature-programmed reduction (TPR) with hydrogen was studied. 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 Cu_2O forms prior to Cu. Adding oxygen (20 vol-%) to the feed gas leads to the formation of a mixture of Cu^{2+} and Cu^{+} phases accompanied by a complete loss of activity. After switching back to steam reforming conditions a higher activity is attained while 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. [1] 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 [2]) copper particles due to an improved interface interaction with ZnO.

[1] M.M. Günter, T. Ressler, R.E. Jentoft, B. Bems, Journal of Catalysis 203 (2001) 133 - 149.
[2] M.M Günter, T. Ressler, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl, Catalysis Letters 71(1-2) (2001) 37-44.