Microstructural investigations of ternary Cu / Zn / Al oxide catalysts for methanol steam reforming

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Introduction

Cu-catalysts supported on ZnO/Al_2O_3 mixed oxides are of considerable industrial interest for methanol synthesis, water-gas shift reaction as well as methanol steam reforming. The catalyst preparation is basically deciding for the electronic and structural properties of the final copper catalyst ("chemical memory" effect). In order to elucidate synthesis pathways to the active "real structure", a fundamental understanding of the relation between both surface and bulk structure and the catalytic performance is necessary ("structure-activity relationship"). Here, we compare structure activity correlations drawn for binary Cu/ZnO model catalyst [1-4] to microstructural properties of various ternary catalysts with alumina as an additional phase.

Binary Cu/ZnO (CZ)

Ternary $Cu/ZnO/Al_2O_3$ (CZA)

Temperature Pogrammed Reduction

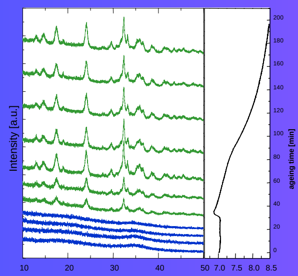

Fig.1: XRD powder patterns of the washed CZ precursor and pH evolution as function of aging

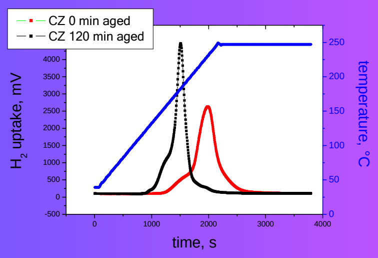

Fig.2: TPR of a non aged and a 2 h aged CZ catalyst

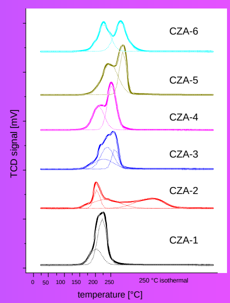

Fig. 7: Hydrogen consumption during TPR of the CZA catalysts.

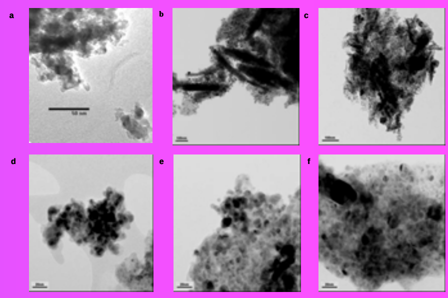

Fig. 8: Transmission electron micrographs of the activated $Cu/ZnO/Al_2O_3$ catalysts at different magnifications: (a) + (d) CZA-1, (b) + (e) CZA-2, (c) + (f) CZA-4

Bulk structure (in situ X-ray diffraction, in situ X-ray absorption spectroscopy)

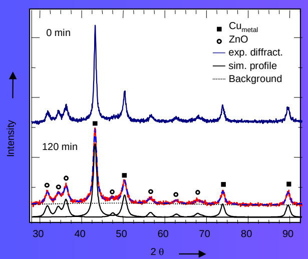

Fig. 3a In situ XRD pattern of non aged and aged Cu/ZnO catalysts (250°C in steam reforming gas mixture)

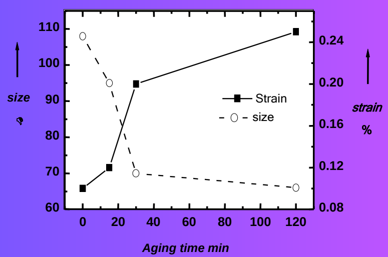

Fig. 3b Cu crystallite size and lattice strain as function of precipitate aging

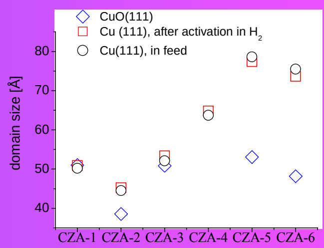

Fig. 9: Domain sizes determined from the XRD line broadening of the calcined precursor, the activated and the used catalyst respectively

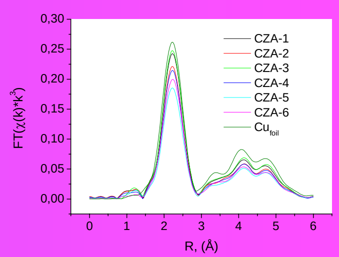

Fig. 10: Experimental Cu K-edge FT(χ(k)·k³) of the $Cu/ZnO/Al_2O_3$ catalysts under reaction conditions (250 °C)

Catalytic activity in methanol steam reforming

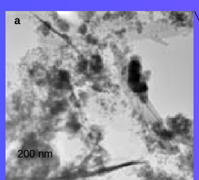

Fig. 5a TEM of a 0 min aged Cu/ZnO catalyst

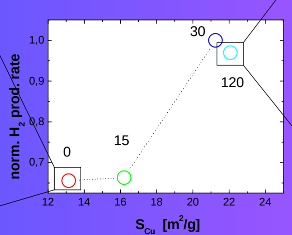

Fig. 6 Specific Cu surface area as function of aging time vs. catalytic activity in methanol steam reforming

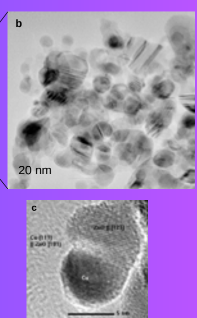

Fig. 5b and c: HRTEM of a 120 min aged Cu/ZnO catalyst

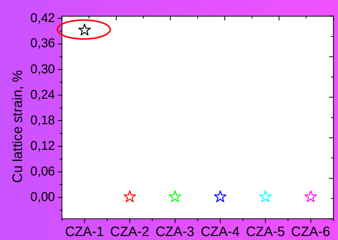

Fig. 11: Cu micro-strain determined by line profile analysis of the activated catalysts

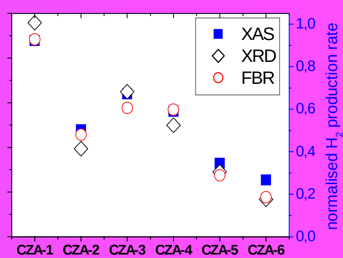

Fig. 12: Comparison of H_2 production rates obtained from *in situ* experiments (XRD, XAS) and measured in a fixed bed micro-reactor (FBR)

Summary

- Defect rich, disordered structure of Cu and ZnO (XRD, XAS)
- Homogeneous microstructure of small, highly dispersed and well intermixed Cu and ZnO particles required for superior $Cu/ZnO/Al_2O_3$ catalysts (TPR, TEM)

→ Enhanced thermal stability as well as activity in MSR

Correlations (Cu surface area, Cu lattice strain vs. activity) found for the binary Cu/ZnO model system [1-4] applicable for the $Cu/ZnO/Al_2O_3$ system

References

[1] Günther *et. al.*, Catal. Lett., 71, **2001**, 37

[2] Kniep *et. al.*, Angew. Chem., 43, **2004**, 112

[3] Ressler *et. al.*, Angew. Chem., 117, **2005**, 4704

[4] Kniep *et. al.*, J. Catat., 236, **2005**, 34

Acknowledgement:

The authors acknowledge DFG for financial support (SPP 1091, " Brückenschläge in der heterogenen Katalyse").