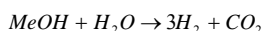


## Introduction

Cu-catalysts supported on ZnO-Al<sub>2</sub>O<sub>3</sub> 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”). Recently, we could show that for binary Cu/ZnO model catalysts additional to the copper surface area, defects in the bulk structure (e.g. structural disorder, impurities, lattice strain) correlate with the activity in methanol steam reforming (MSR) [1-4]. Here, ternary CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts (CZA-2 – CZA-6) prepared according to various patents have been analysed in a comparative study under MSR conditions. A commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst (CZA-1) was employed for comparison.



## Temperature Programmed Reduction

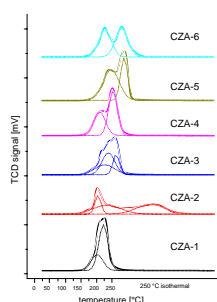
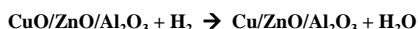


Fig. 1: Hydrogen consumption during temperature programmed reduction (TPR) of the CZA catalysts. Solid lines are experimental curves and broken lines are deconvoluted curves.



- only CuO is reduced to metallic Cu
- broad double peaks (TPR) indicate bimodal CuO particle size distribution visible by TEM (CZA-2 to 6)
- homogeneous microstructure of small and well intermixed Cu and ZnO particles for sample CZA-1

reducibility (reduction temperature and reduction profile) is an important factor in pre-determining the catalytic performance of the final catalyst

## Electron Microscopy (TEM)

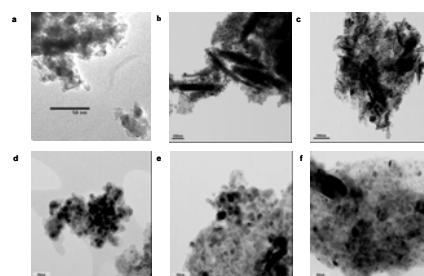


Fig. 2: Transmission electron micrographs of the activated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts at different magnifications: (a) + (d) CZA-1, (b) + (e) CZA-2, (c) + (f) CZA-4

## In situ X-ray diffraction (XRD)

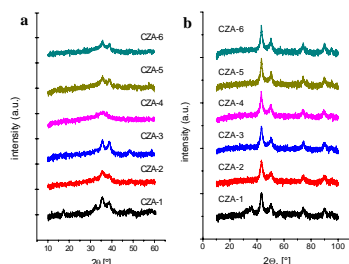


Fig. 3: *In situ* powder X-ray diffraction pattern recorded at ambient temperature of the calcined precursors (a) and of the reduced catalysts,  $T_R = 523$  K (b).

### Thermal Stability

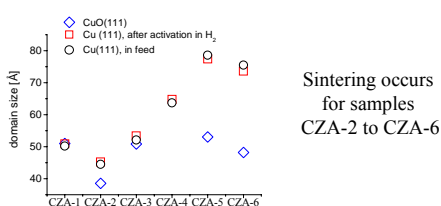


Fig. 4: Domain sizes determined from the XRD line broadening of the calcined precursor, the activated and the used catalyst respectively

## In situ X-ray absorption spectroscopy (XAS)

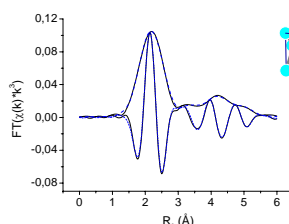


Fig. 5: Refinement of theoretical Cu EXAFS function (dashed line to the experimental Cu K-edge  $\text{FT}(\chi(k) \cdot k^3)$  (solid line) of CZA-1 catalyst under reduction conditions at 523 K.

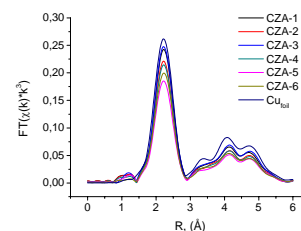


Fig. 6: Experimental Cu K-edge  $\text{FT}(\chi(k) \cdot k^3)$  of the activated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts in 2 vol.-% H<sub>2</sub> (He) at ambient temperature

## Catalytic activity in Methanol steam reforming (in situ XRD, in situ XAS, micro-reactor)

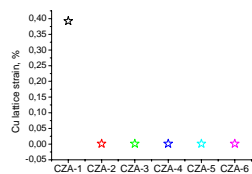


Fig. 7: Cu micro-strain determined by line profile analysis of the activated catalysts

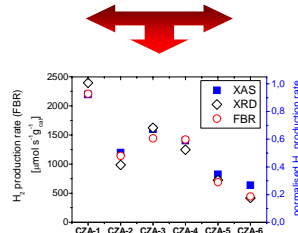


Fig. 8: Comparison H<sub>2</sub> production rates obtained from *in situ* experiments (XRD, XAS) and measured in a fixed bed micro-reactor (FBR) at 523 K, WHSV=2.4-2.8 h<sup>-1</sup>

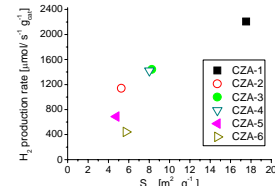


Fig. 9: H<sub>2</sub> production rate as a function of the Copper surface area determined by RFC

## 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/Zn/Al<sub>2</sub>O<sub>3</sub> 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 CuZnOAl<sub>2</sub>O<sub>3</sub> system

microstructural modification (microstrain) in Cu phase only for the most active catalyst (CZA-1) detectable

Significant differences in catalytic performance

non-linear correlation between Cu surface area and catalytic activity

- Activity not only dependent on the Cu surface area
- Defects in the bulk structure (e.g. microstrain) influence the catalytic performance

## References

- [1] Günther *et al.*, Catal. Lett., 71, 2001, 37
- [2] Knief *et al.*, Angew. Chem., 43, 2004, 112
- [3] Ressler *et al.*, Angew. Chem., 117, 2005, 4704
- [4] Knief *et al.*, J. Catal., 236, 2005, 34