



**IN SITU STUDIES ON THE STRUCTURE AND ACTIVITY OF COPPER OXIDE /
ZINC OXIDE CATALYST IN STEAM REFORMING OF METHANOL USING
X-RAY DIFFRACTION AND ABSORPTION TECHNIQUES**

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Introduction and Motivation

The steam reforming reaction of methanol with high selectivity to hydrogen can be performed on copper/zinc oxide catalysts. In this work we intend to establish dependencies of the active copper phase on the structure of the oxidic precursor, and, hence on the according preparation parameters. Well-defined binary hydroxocarbonate precursors with different Cu/Zn ratios prepared according to the coprecipitation method at either decreasing or constant pH (pH = 7) were calcined to yield mixed oxides of copper and zinc [1]. By virtue of the complementary character of X-ray diffraction and X-ray absorption spectroscopy long-range and short-range structural information of the calcined and activated state of the catalyst is revealed. Structural evolution of the active copper phase under reductive and catalytic conditions is elucidated by in situ X-ray diffraction. Furthermore this investigation is devoted to the clarification of the role ZnO plays in affecting the copper phase microstructure (“synergism” in the Cu/Zn system [2,3]).

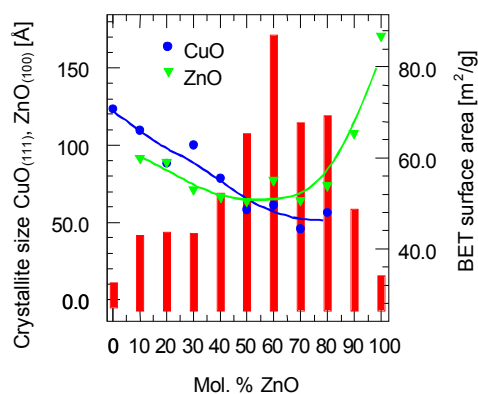
Experimental and Results:

Structural characterization of the Cu/Zn oxides with varying Cu/Zn ratios by XRD shows a minimum in crystallite size for both CuO and ZnO at a Cu/Zn ratio of about 0.4, (see Fig. 1). XAFS analysis substantiates these findings and elucidates a non linear dependence of the local order on the Cu/Zn ratio. In order to investigate the influence of water partial pressure on the copper reducibility and crystallite size the Cu/Zn oxides were subjected to different activation conditions: dry hydrogen (2.6 vol. % H₂ in He) and wet hydrogen (3 vol.% H₂O, 3 vol% H₂ in He). Line profile analysis of ex situ XRD patterns reveals a defect ZnO structure (size and strain) that is more prone to structural relaxation at higher temperatures than the copper crystallites. A clear dependence of both the onset of the reduction of copper and the copper particle size on the zinc oxide content could be detected by time-averaged in situ XRD. In addition, in situ XAFS was employed to monitor the formation of copper clusters. With decreasing copper content the onset of reduction is shifted from 200 °C (pure CuO) to 170 °C (40 at.% CuO) with a copper crystallite size of 150 Å and 40 Å, respectively. The catalytic activity of the Cu/ZnO samples was tested in an in situ XRD cell with a flow of 100 ml/min (MeOH/H₂O ratio = 4) and recorded by on-line mass spectroscopy. A quantitative description yields a constant selectivity to hydrogen whereas the conversion seems to be a function of the Cu content. Only minor changes in the Cu (111) FWHM were detected during time on stream measurements for Cu/ZnO samples. The Cu (111) line width under reaction conditions shows a decrease for pure copper samples that seems to be correlated with a declining hydrogen production rate (see Fig. 2).

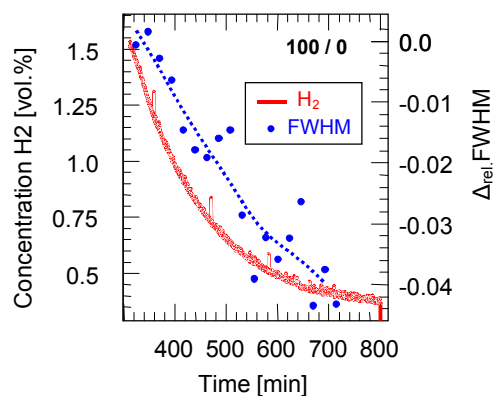


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Poster Weimar 21.-23. März 2001



1.2. Fig. 1: Composition dependent variation of crystallite size of CuO and ZnO



1.1. Fig. 2: Correlation of effluent $c(\text{H}_2)$ with rel. changes of the FWHM of Cu (111), (Cu/Zn = 100/0) during reaction at 523 K.

Conclusion:

This work provides evidence that the microstructural role of ZnO exerted on the reduced copper phase can merely be ascribed to a structural promotion alone. A chemical promotion can be imagined to account for the observed enhanced reducibility and activity for diluted Cu/Zn compositions. However, the origin of this promotion can emerge from the defect bulk structure and the way these defects, terminating at the surface, may influence the catalytic reaction (“structure sensitivity”) [4].

Literature:

- [1] see contribution of B. Bems *et al.* for this conference
- [2] H. Kobayashi, N. Takezawa, C. Minochi, *J. Catal.* 69 (1981) 487; *Faraday Disc.* 105 (1997) 395
- [3] M. S. Spencer, *Topics in Catal.*, 8, (1999), 259
- [4] M.M. Günter, T. Ressler, B. Bems, R. Schlögl, in preparation