

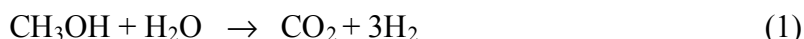
## IN SITU STUDIES ON THE STRUCTURE AND ACTIVITY OF COPPER OXIDE / ZINC OXIDE CATALYST IN STEAM REFORMING OF METHANOL USING X-RAY DIFFRACTION AND ABSORPTION TECHNIQUES

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### *Introduction and Motivation:*

Methanol is considered as an alternative “automotive” fuel because it contains hydrogen in a storable form which can be released by steam reforming (see *eq. 1*) [1]. The reaction can be performed with high selectivity to hydrogen on copper/zinc oxide catalysts. Whereas this catalytic system has been investigated in depth for the methanol synthesis reaction [2] the active Cu phase for the steam reforming reaction is not fully elucidated and, hence, controversial reaction mechanisms have been proposed [3]. Current effort is dedicated to the minimization of CO concentration which acts as a poison in fuel cell applications. In this work we intend to establish dependencies of the active copper phase on the activation (*i.e.* reduction) procedure, the catalyst composition (Cu/Zn ratio), and in addition preparation parameters of the precursor.

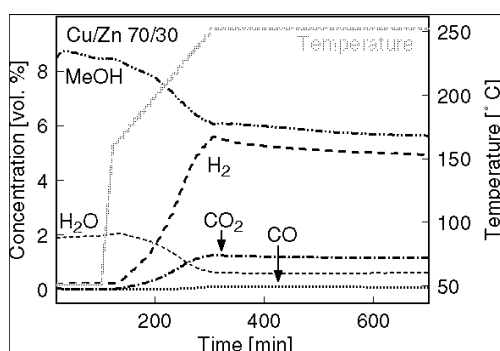


Well-defined binary hydroxocarbonate precursors with different Cu/Zn ratios prepared according to the coprecipitation method at either decreasing or constant pH (pH = 7) were calcined to yield mixed oxides of copper and zinc. By virtue of the complementary character of X-ray diffraction and X-ray absorption spectroscopy long-range and short-range structural information of the activated state of the catalyst is obtained. Structural evolution of the active copper phase under reductive and catalytic conditions is elucidated by in situ X-ray diffraction and absorption.

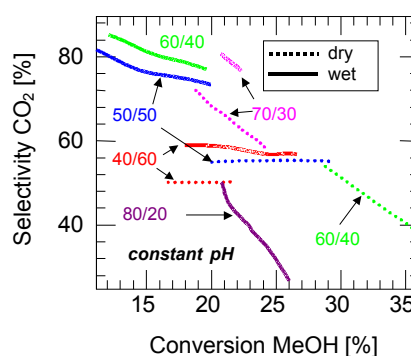
### *Experimental and Results:*

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. % H<sub>2</sub> in He) and wet hydrogen (3 vol.% H<sub>2</sub>O, 3 vol% H<sub>2</sub> in He). 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 in situ XRD. 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. In addition, in situ XAFS was employed to monitor the formation of copper clusters. From time-resolved in situ experiments at the Cu K edge the degree of reduction can be monitored using a combination of factor analysis (PCA) and least-squares XANES fitting with suitable reference spectra (*e. g.* Cu metal, Cu<sub>2</sub>O, CuO). The intermediate presence of a Cu(I) species (*i. e.* Cu<sub>2</sub>O) was confirmed. The catalytic activity of the Cu/ZnO samples was tested both in an in situ XRD- and an in situ XAS cell with the gas phase monitored by on-line mass spectroscopy (total flow of 100 ml/min and 25 ml/min, respectively, with a MeOH/H<sub>2</sub>O ratio = 4 (see Fig. 1). The experimental set-up

permits to quantify activity in steam reforming reaction in terms conversion and selectivity. It was found that the reduction conditions, i. e. “wet” or “dry” conditions, have a major impact on the selectivity as the wet reduction leads to an increased selectivity towards the desired steam reforming reaction (see Fig. 2). Furthermore, the Cu/Zn ratio seems to affect the activity as well. It was observed that with increasing ZnO-content the activity increases and an optimum composition is attained for a composition of Cu/Zn of 70/30 ~ 60/40. Higher ZnO-contents appear to favor other methanol decomposition products (e. g. CO) instead of the desired hydrogen and CO<sub>2</sub>. These observations hold for both preparation batches and indicate that the elemental composition of the catalyst determines the catalytic performance more than the pH during the coprecipitation [4].



1.1. Fig. 1: Typical time on stream behavior for a sample with Cu/Zn = 70/30 measured in XRD in situ cell. (MeOH/H<sub>2</sub>O ~



1.2. Fig. 2: Selectivity to CO<sub>2</sub> as a function of the conversion of MeOH obtained in the in situ XRD set-up at 250 °C for sample batch constant pH (MeOH/H<sub>2</sub>O ratio of > 4 at a total flow in 120

### Conclusion:

On the basis of both in situ techniques, this work provides evidence that the completely reduced Cu constitutes the active bulk phase for methanol steam reforming. Furthermore, the existence of oxidized copper species under working conditions can be ruled out. However, minor structural changes upon repeated oxidation and re-reduction cycles are found to increase the catalysts selectivity. The wet reduction conditions which results in a milder reduction of the copper phase and affords catalysts exhibiting a higher selectivity further corroborates these results. An optimum Cu/Zn ratio is found to be in the compositional range between 70/30 ~ 60/40 at.% Cu/Zn.

### Literature:

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