



## Combined *in situ* XPS and *in situ* soft XAS study of Cu/ZnO catalysts for methanol steam reforming

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### Introduction

Copper-zinc oxide (alumina) catalysts have found industrial use for the low temperature methanol synthesis, for the low temperature water-gas shift reaction, and for the steam reforming of methanol following the reaction [1]:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ . An important application could be the onboard production of hydrogen for fuel cell application. It is the proposed synergistic effect in the binary copper/zinc oxide that makes this system interesting for investigation [2]. The knowledge of the relationship between the catalytic activity, surface structure, and bulk structure is necessary in order to elucidate synthesis pathways to new and improved catalysts. Obviously, the surface properties play a decisive role for the understanding of a catalyst. Here, we report on a combined *in situ* X-ray photoelectron spectroscopy (XPS) and *in situ* soft X-ray absorption spectroscopy (XAS) study of the surface of differently prepared Cu/ZnO catalysts under activation conditions ( $\text{H}_2$ , 250 °C) and under methanol steam reforming reaction conditions ( $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ , 250 °C), i.e. under the presence of a reactive environment. Using the unique properties of synchrotron radiation, the depth sensitivity of XPS was tuned from the outermost surface layer to deeper layers without destruction of the material. Furthermore, the dynamics of the surface were studied by taking fast, single scans, i.e. temperature programmed reduction/reaction (TPR)-XPS (see Fig. 3).

## Experimental

Cu/ZnO catalysts (molar ratio Cu:Zn = 70:30) were prepared by co-precipitation of mixed copper zinc hydroxy carbonates at constant pH = 7 (denoted CAT). Additionally, material was synthesized by separate precipitation of the hydroxy carbonates for comparison (denoted MIX). The precipitates were aged under constant stirring in their mother liquor for different times (0 min – 120 min). The resulting precursors were washed (80 °C, 80 ml H<sub>2</sub>O), dried (110 °C, 20 h) and calcined (330 °C, 3 h, static air) under the same conditions. Zn2p/3p, Cu2p/3p, O1s, C1s XP core level spectra were taken in a temperature range of 25 °C – 250 °C in the presence of 0.25 mbar H<sub>2</sub> and in the H<sub>2</sub>O/CH<sub>3</sub>OH reaction mixture (p<sub>tot</sub>=0.25 mbar), respectively. Cu L<sub>2,3</sub> - and Zn L<sub>2,3</sub> - near edge X-ray absorption fine structure (NEXAFS) spectra were taken under these conditions as well. Synchrotron radiation delivered by the undulator U49/2 at the storage ring BESSY was used. Changes in the gas phase composition were monitored by on-line mass spectrometry simultaneously to the spectroscopic characterization of the catalyst surface (compare to Fig. 3).

## Results

We found that the reduction process of the catalyst is crucial for its structure under methanol steam reforming conditions. A sequential two-step reduction process at the surface (CuO → Cu<sub>2</sub>O → Cu) was observed. The Zn3p/Cu3p core level intensity ratio altered strongly during the reduction in H<sub>2</sub>. In the first reduction step (CuO → Cu<sub>2</sub>O), an increase was observed. Further reduction caused a decrease of this intensity ratio. This observation stresses the dynamic behavior of the surface and the presence of strong surface modifications during the activation process.

Residual carbon species (carbonates and others) were observed on the surface even after prolonged calcination in air (Fig. 1). The Zn L<sub>3</sub>-NEXAFS indicates the presence of a zinc species different to ZnO by the occurrence of a resonance at the onset of the absorption edge (“A” in Fig. 2). This modification is likely caused by the residual carbonates. These carbonate species de-

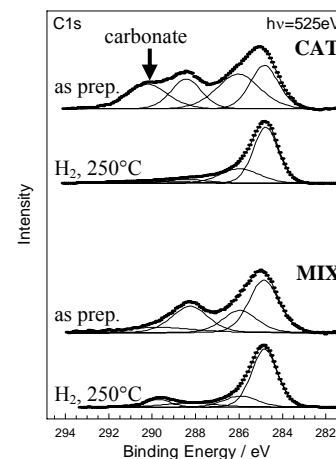


Fig. 1: C1s core level spectra of the co-precipitated material (CAT) and the separate precipitated material (MIX) before the activation in H<sub>2</sub> and after the treatment.

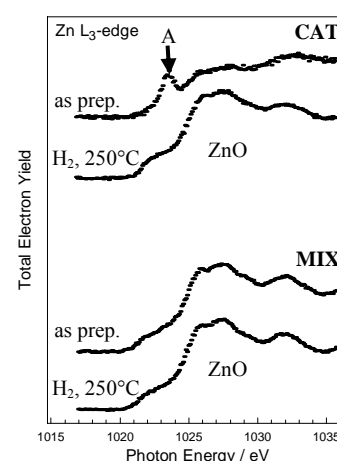
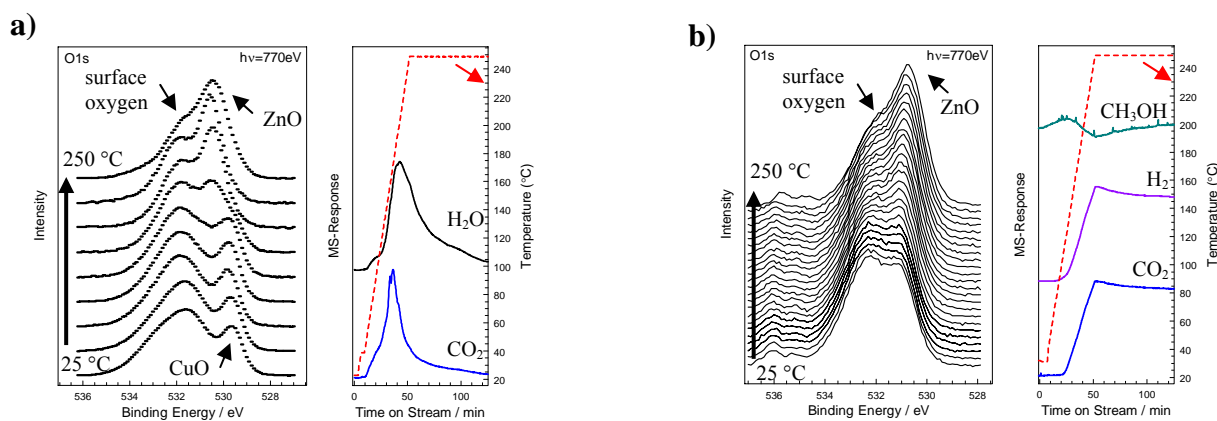


Fig. 2: Zn L<sub>3</sub>-NEXAFS of the co-precipitated material (CAT) and the separate precipitated material (MIX) before the activation in H<sub>2</sub> and after the treatment.

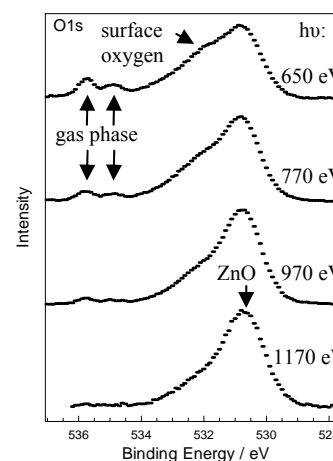


**Fig. 3:** *O1s* core level spectra of the co-precipitated catalyst (CAT) during the activation in 0.5 mbar  $H_2$  (a) and in the reaction mixture of  $CH_3OH$  and  $H_2O$  (b). XP spectra were taken while the temperature was ramped from 25 °C to 250 °C (TPR-XPS). Simultaneously, the gas phase composition was monitored by on-line mass spectrometry.

composed during the reduction of the catalyst in  $H_2$  and a NEXAFS typical for ZnO was obtained. The decomposition of the carbonates caused the  $CO_2$  trace in the mass spectrum (Fig. 3a) while the  $H_2O$  signal is the result of the reduction of CuO to Cu. Consequentially, the reduction process was accompanied by the disappearance of the CuO peak in the O1s XP spectra shown in Fig. 3a.

The material synthesized by separate precipitation (MIX) instead of co-precipitation of copper/zinc hydroxyl carbonates (CAT) did not show this carbonate species (Fig. 1). The Zn  $L_3$ -NEXAFS indicates solely ZnO (Fig. 2). This material was much less active in the methanol steam reforming reaction than the co-precipitated catalyst.

Furthermore, a surface oxygen species was found after activation and under methanol steam reforming reaction conditions that is primarily located in the outermost surface layers of the reduced catalyst (Fig. 3). This fact was verified by taking O1s XP spectra at different incident photon energies (Fig. 4). Comparison to reference compounds and literature data suggests the assignment to OH-species that are known to create a modified, defective surface on single phase ZnO [3]. The activity of the catalyst was proven by the detection of the reaction products  $H_2$  and  $CO_2$  in the gas phase and the consumption of methanol when the catalyst was heated in the reaction mixture. The methanol conversion was approx. 5% at 250 °C (Fig. 3b). Gas phase peaks of  $CH_3OH$  and  $H_2O$  were observed under methanol steam reforming reaction conditions in the O1s spectra at high binding energies (BE > 534 eV, Fig. 3b and 4).



**Fig. 4:** *O1s* core level spectra of the catalyst under methanol steam reforming reaction conditions. The photon energy was varied as indicated. Thus, the surface sensitivity increases from down to up.

This investigation highlights the potential of surface sensitive in situ methods like high pressure XPS and high pressure soft XAS in material science in general and catalysis research in particular.

## References

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