



MAX-PLANCK-GESELLSCHAFT



# In situ investigations of Cu/ZnO catalysts during calcination in different gas atmospheres



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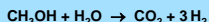
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## Motivation

Hydrogen based fuel cells that power electric motors are a desirable technology for future auto-mobile applications. However, the storage and handling of hydrogen for this purpose is quite problematic.

The *steam reforming of methanol* is a promising way to produce the required hydrogen on board from a more convenient fuel:



A catalyst for this reaction should have the following properties:

- 1) low operating temperature
- 2) low CO production (CO is a fuel cell poison)
- 3) good long term stability, even under rapidly changing operating conditions

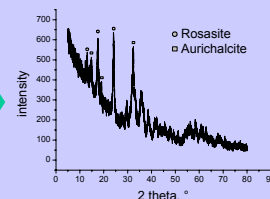
Unfortunately, industrially used steam reforming catalysts do not meet these requirements.

Methanol synthesis, the reverse reaction of methanol steam reforming, is produced industrially with copper based catalysts. These copper catalysts (such as Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) in principle meet requirement 1), but fail at point 2) and 3).

In order to find catalysts better suited for the on-board production of hydrogen, we investigated the influence of the gas phase composition during calcination of Cu/ZnO catalyst with a variety of methods, including in-situ XAS.

## Sample Preparation

A Cu/ZnO catalyst with a molar ratio of Cu:Zn = 70:30 was prepared by co-precipitation of (Cu,Zn) hydroxycarbonates from metal nitrate solution:



Calcination was conducted with an identical temperature program (total flow: 20 ml/min, heating rate: 5 K/min, 603 K for 3 hrs.) in: (a) 20 vol.-% O<sub>2</sub> in He, (b) 20 vol.-% CO<sub>2</sub> in He, and (c) He.

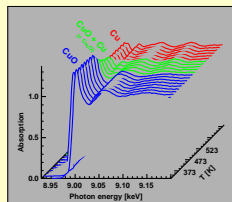
Afterwards, the oxide precursors were reduced in situ (5 vol.-% H<sub>2</sub> in He, flow: 40 ml/min, heating rate: 6 K/min, 523 K for 1 hr.).

## Information gained from in situ X-ray absorption spectroscopy

### XANES analysis

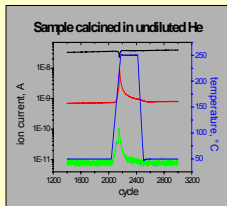
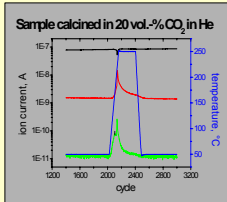
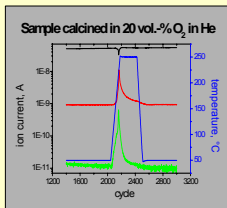
The near edge region (XANES) of the spectrum may be used as fingerprint for phase identification and quantification. X-ray diffraction (XRD) fails here because of a low time resolution and very small crystallites in our samples.

- A series of spectra taken in situ (e.g. from a temperature programmed reduction, TPR) can be subjected to a *principal component analysis* (PCA) to deduce the number of phases present.
- *Target transformation* based on the principle components obtained helps to identify suitable references to describe the series of spectra.
- The XANES may then be fitted with a linear combination of the chosen references to quantify the phase composition as a function of time and thus to describe the reaction kinetics.



In situ Cu K-edge XANES spectra of a temperature programmed reduction from CuO/ZnO to Cu/ZnO in 5 vol.-% H<sub>2</sub>

- Independent of the gas phase composition applied during calcination all samples exhibit a sequential reduction pathway of CuO to metallic Cu with Cu<sub>2</sub>O as an intermediate phase.



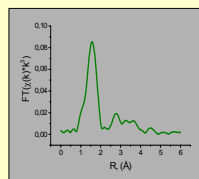
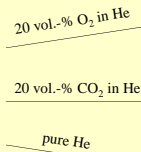
Mass spectra of a temperature programmed reduction from CuO/ZnO to Cu/ZnO in 5 vol.-% H<sub>2</sub> (black: H<sub>2</sub>; red: H<sub>2</sub>O; green: CO<sub>2</sub>; blue: temperature)

### EXAFS analysis

The extended fine structure (EXAFS) of the spectrum contains information about the geometric structure around the absorber atom (copper).

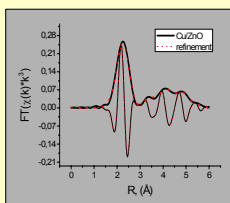
- For single phases, an EXAFS fit with a structural model can identify the phase more reliably than a XANES analysis. Temperature effects can be accounted for by fitting the Debye-Waller factor.
- For phase mixtures, phase identification based on EXAFS fitting is not very reliable, because the number of free parameters increases dramatically.
- However, constrained with the phase information from the XANES analysis, an EXAFS fit of a two phase mixture may yield more details on the phases such as deviations from the ideal structure.

### Calcination



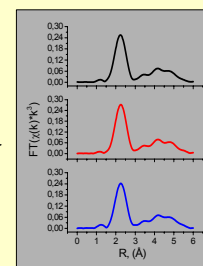
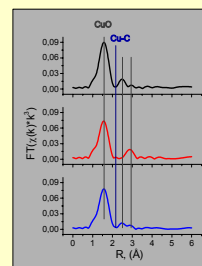
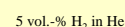
Fourier transform of (Cu,Zn) hydroxycarbonate measured at the Cu K-edge (at room temperature).

### Cu<sub>fcc</sub> structural model



EXAFS fit of a Cu<sub>fcc</sub> structural model to (dashed line) to the experimental Cu K-edge FT(k) (k3) (solid line).

### Reduction



Fourier transforms of differently calcined CuO/ZnO precursors measured at the Cu K-edge (at room temperature).

Fourier transforms of the reduced CuO/ZnO catalysts measured at the Cu K-edge (at room temperature).

Pair	CN	R [Å]			σ <sup>2</sup> [Å <sup>2</sup> ]		
		O <sub>2</sub>	CO <sub>2</sub>	He	O <sub>2</sub>	CO <sub>2</sub>	He
Cu - Cu	12	2.544	2.542	2.543	0.0102	0.0098	0.0109
Cu - Cu	6	3.626	3.621	3.627	0.0165	0.0162	0.0173
Cu - Cu	24	4.425	4.420	4.423	0.0164	0.0159	0.0170
Cu - Cu	12	5.071	5.068	5.074	0.0299	0.0313	0.0294
Cu - Cu	24	5.786	5.779	5.775	0.0274	0.0270	0.0266

Structural parameters obtained from refinement of theoretical fcc copper metal to the experimental Cu K-edge EXAFS function recorded after reduction at ambient temperature ( $k = 3$  to  $13 \text{ \AA}^{-1}$ ;  $R = 1.7$  to  $6 \text{ \AA}$ . Refinement includes 3 single and 9 multi scattering paths:  $N_{\text{sc}} = 27$ ;  $N_{\text{free}} = 11$ ). The high Debye-Waller factor (at room temperature) from this fit indicates a high degree of disorder and/or rather small crystallites. This is in line with results from in situ XRD

**A c k n o w l e d g e m e n t : The Hamburg Synchrotron Radiation Laboratory, HASYLAB, is acknowledged for providing beamtime for this work.**