Cu/ZrO_2 Catalysts for Methanol Steam Reforming: Structure - Activity Correlations

A. Szizybalski, F. Girgsdies, R. Schlögl, T. Ressler

Fritz-Haber-Institute of the Max-Planck-Society, Department of Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin, Germany

J.H. Schattka, Y. Wang, R.A. Caruso, M. Antonietti, M. Niederberger

Max-Planck-Institute of Colloids and Interfaces, Colloid Department, Am Mühlenberg, Haus 2, 14476 Golm, Germany

MAX-PLANCK-GESELLSCHAFT

ZEIT-Stiftung Ebelin und Gerd Bucerius

AC FHI

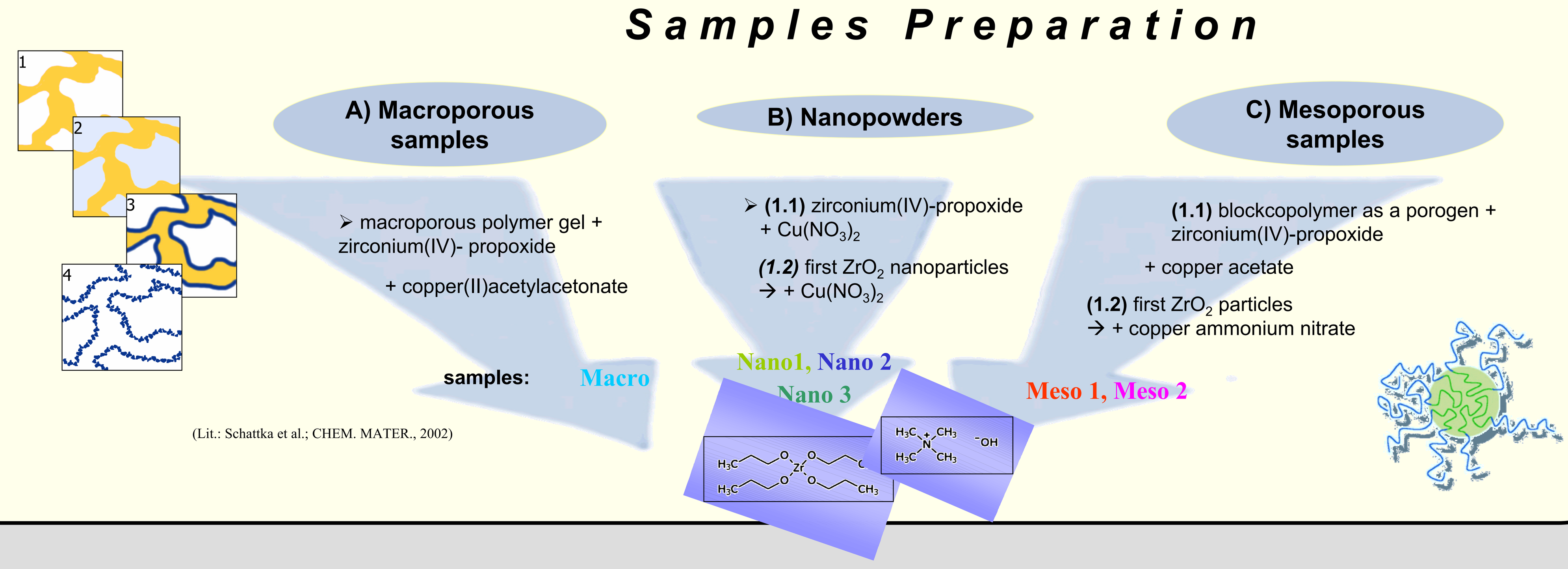
MPI K+C

Motivation

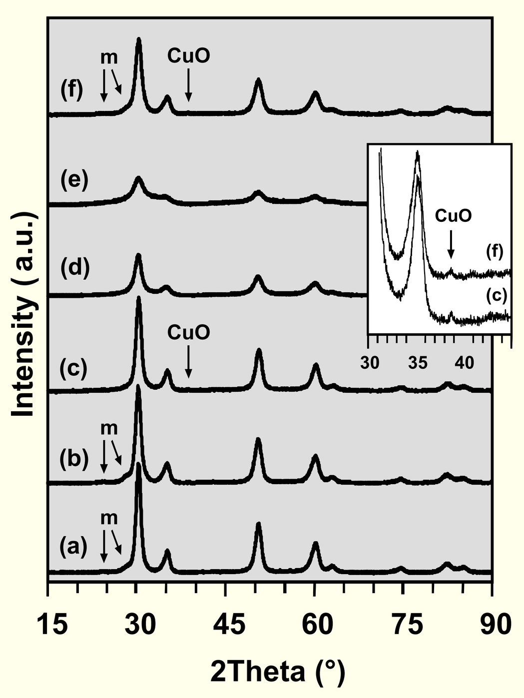
$CH_3OH + H_2O$ ® $CO_2 + 3\ H_2$

- **on-board** production of H_2 for mobile **fuel cell** applications based on our knowledge about Cu/ZnO systems [1,2,3]
- preparation of improved catalysts [4] (Rational Catalyst Design)
- Investigation of structural changes in correlation with catalytic activity and stability under reaction conditions with **in-situ XAS** (X-ray absorption spectroscopy), **in-situ XRD** (X-ray diffraction)

Samples Preparation



Catalyst Precursors



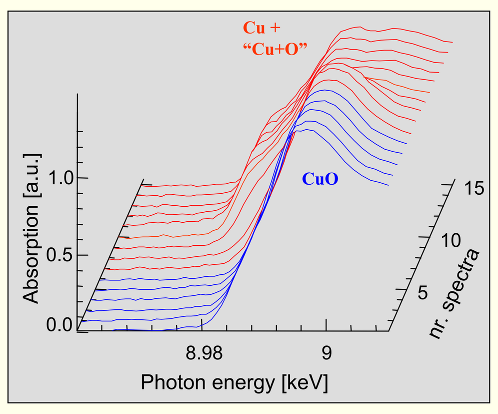
X-ray diffraction patterns

- with X-ray diffraction (XRD) difficult to detect copper phases because of the low copper concentration and very small crystallites
- copper phase detectable only in *Nano 3* and *Macro*
- ZrO_2 mostly tetragonal (high temperature modification)
- well crystallised in nanopowders, and macroporous samples but less crystallised in mesoporous materials

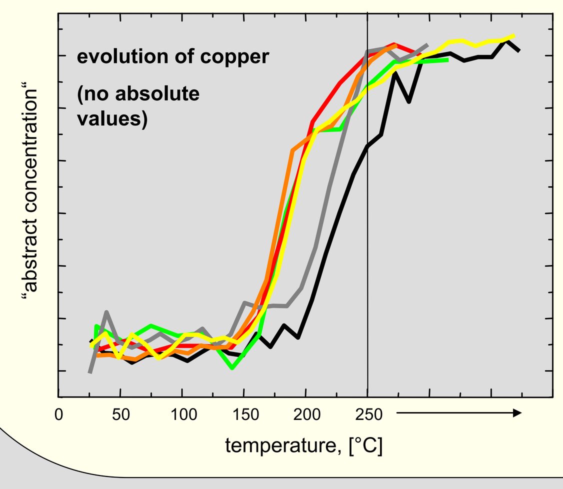
XRD patterns of "as prepared" CuO/ZrO_2 samples. Arrows mark small peaks of monoclinic zirconia (m) and CuO a) Nano 1, b) Nano 2, c) Nano 3, d) Meso 2, e) Meso 1, f) Macro

Reduction Kinetics

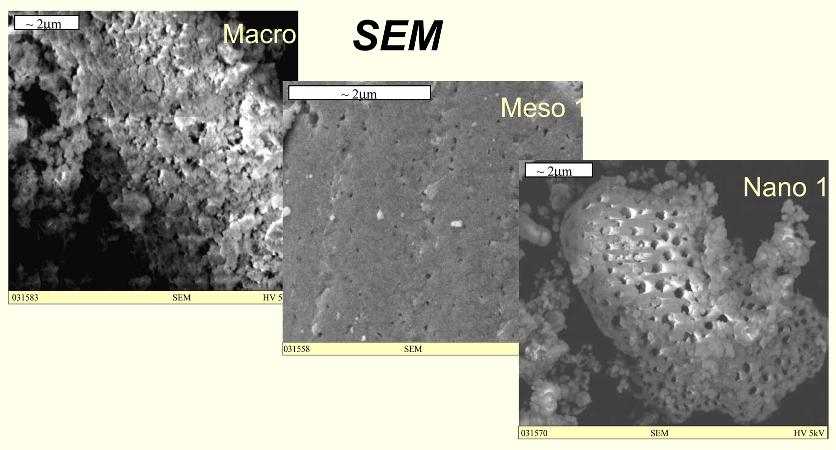
XANES



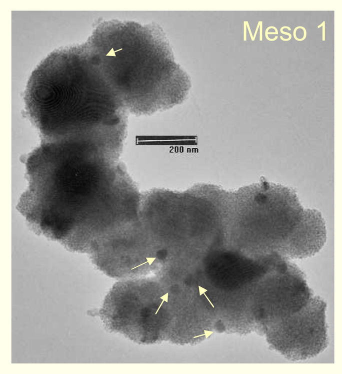
In situ Cu K edge XANES spectra from CuO/ZrO_2 to partially oxidised Cu/ZrO_2 during a TPR in 2 % H_2/He



SEM



TEM

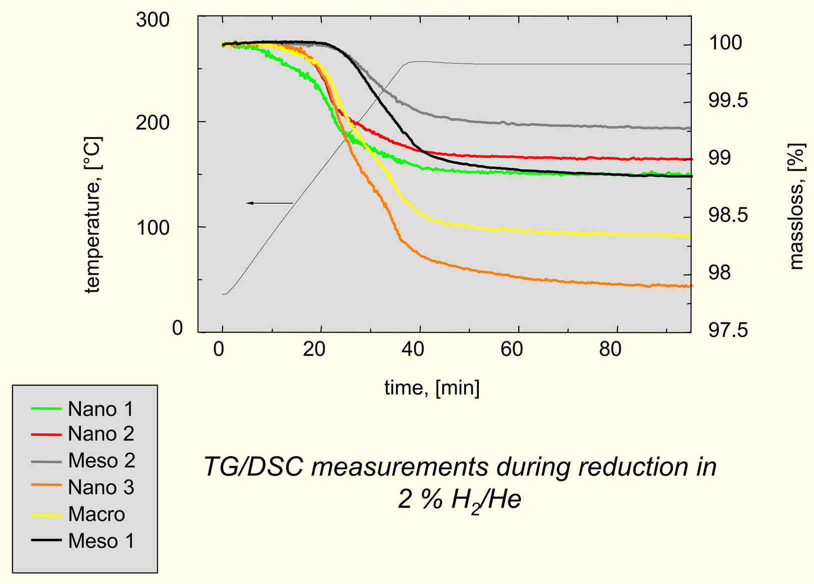


Mesoporous samples:

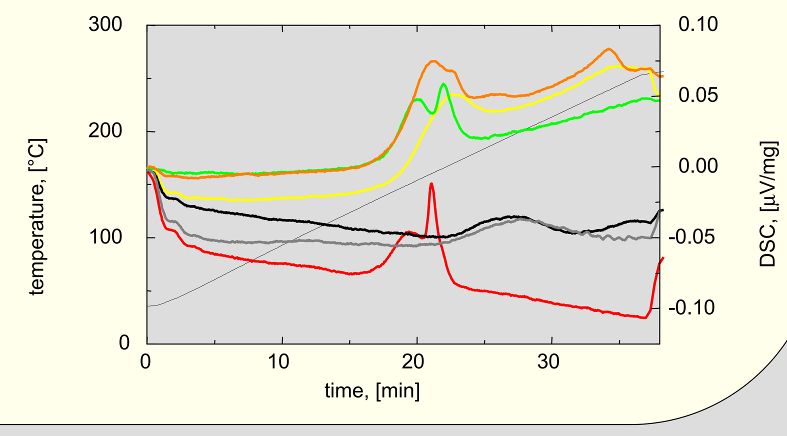
- compacter materials
- larger copper particles → reduction is retarded

TG and XANES analysis results support observation of incomplete reduction from EXAFS

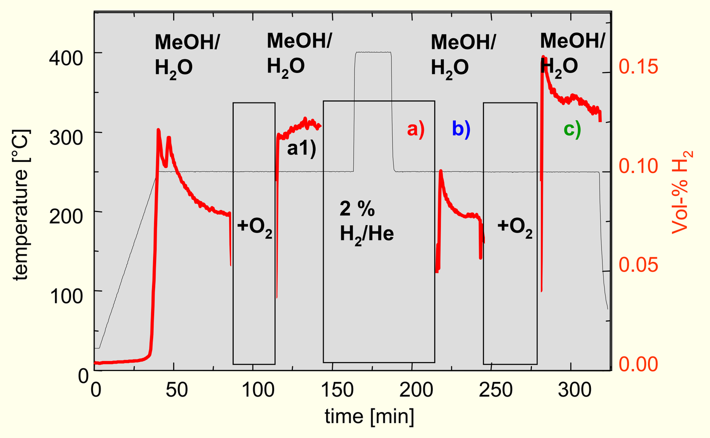
TG / DSC



TG/DSC measurements during reduction in 2 % H_2/He

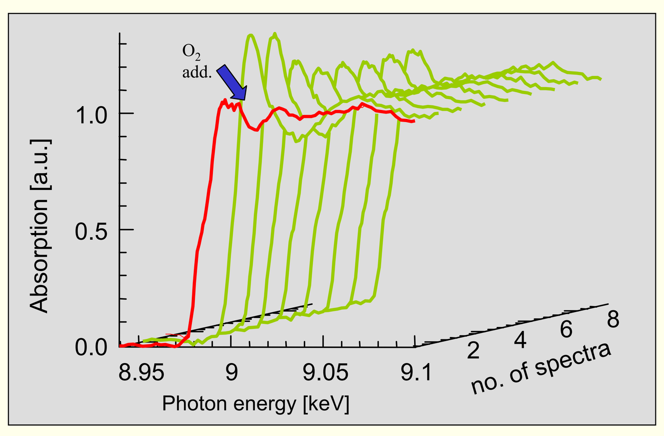


Structure-Activity Correlations

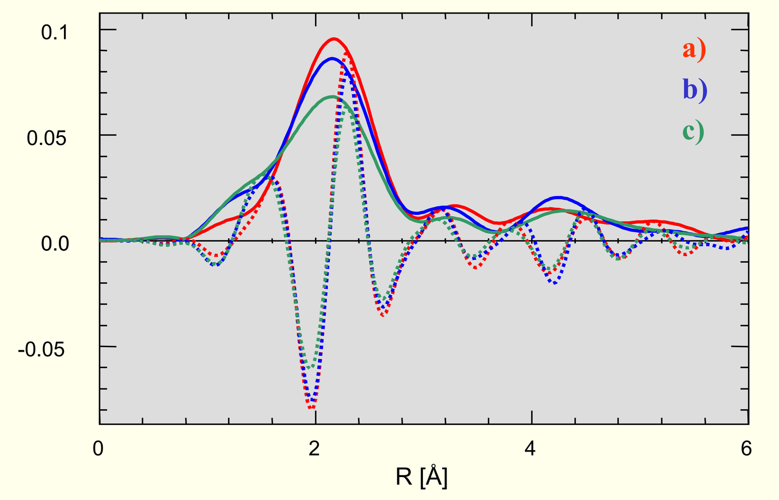


Evolution of H_2 production during MSR ***(incl. heating to 400°C in 2 % H_2)***

→ increase in hydrogen production after O_2 add. and prove of thermal stability

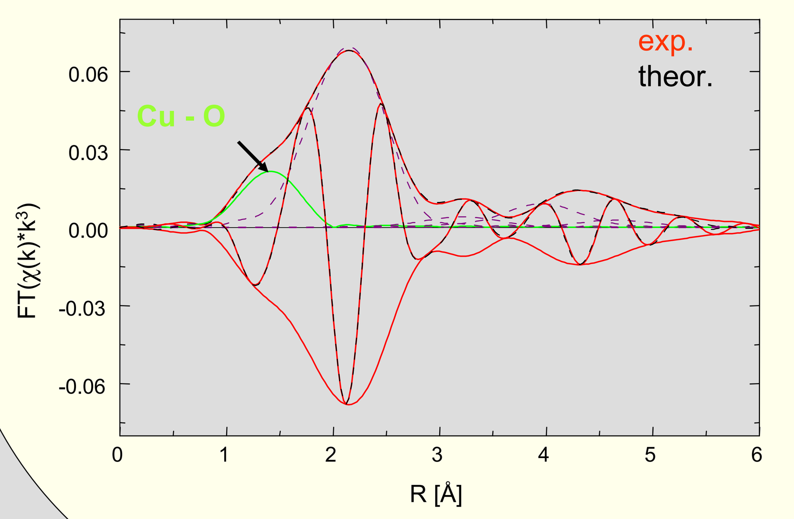


In situ Cu K edge XANES spectra after reduction in feed (red) and during incomplete rereduction after temp. addition of O_2 (green)



RDF of Cu/ZrO_2 catalyst after 400°C in 2% H_2 in a) 2 % H_2, b) feed, c) feed, after O_2 pulse

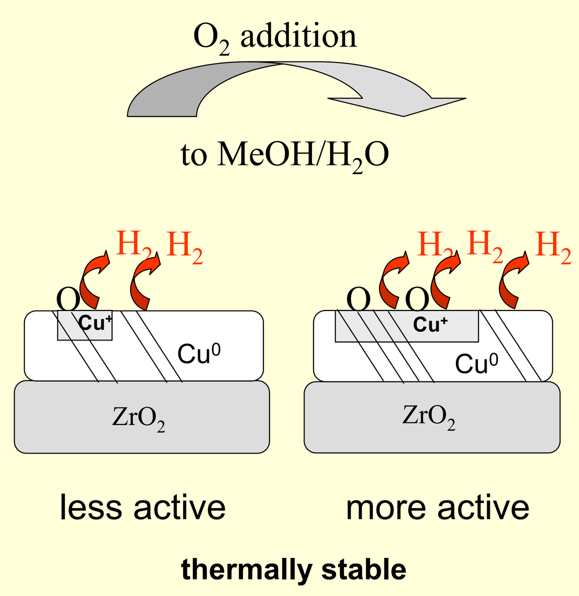
→ increasing O_2 contribution correlates to higher amplitude in the 1st and lower in the 2nd shell



EXAFS fit of mixture of Cu/Cu-O model to data after oxygen addition

Conclusions

Structural Model



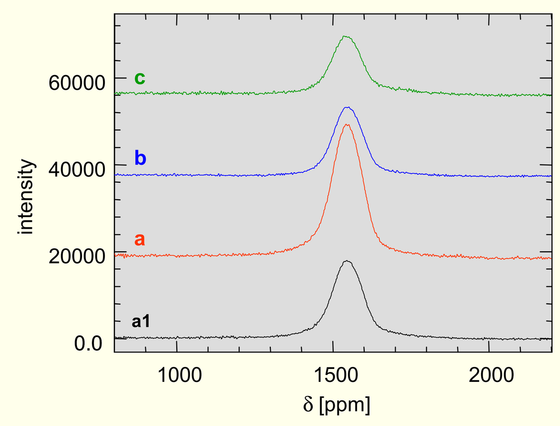
- composition of catalyst precursors: CuO + ZrO_2 (mainly tetragonal)
- reduction with methanol/ water results in copper metal + copper oxide phase
- temporary O_2 addition into the feed increases microstrain and oxygen contribution

➡ increase in hydrogen production

→ partially oxidised Cu nano particles on ZrO_2 are active for MSR

- catalysts are thermally stable (400°C)
  → no severe sintering
  no loss of activity after reactivation

^{63}Cu NMR



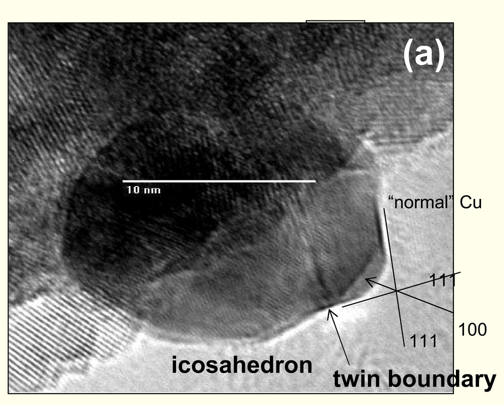
Sample Nano 1	left FWHM	right FWHM	ratio low/high
a1	97	111	**0.87**
a	106	104.6	0.99
b	92.6	105.2	0.88
c	93.5	120.2	**0.78**

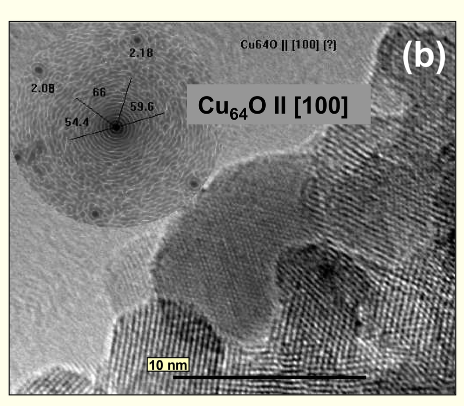
asymmetric line profiles indicate strain/disorder

→ strain/disorder is highest after O_2 addition

sample name	feed red. oxygen contrib.	feed red. vol-% H_2	post O_2 add. oxygen contrib.	post O_2 add. vol-% H_2
Nano 1	30	0.08	47	0.12
Nano 3	27	0.11	43	0.05
Meso 1	39	0.017	39	0.026
Meso 2	60	0.28	51	0.34
Macro	38	0.196	58	0.213

Oxygen contributions calculated from EXAFS spectra after reduction in feed and after oxygen addition, and hydrogen production





TEM analysis

Cu/ZrO_2 catalysts show a large variety of copper and copper oxide particles, e.g multiple twins *(a)* (icosahedral and dodecahedral), distorted Cu or suboxides, higher oxides, and some cases of interface formation with the ZrO_2 support. The TEM micrograph and powerspectrum shown can be interpreted as a $Cu_{64}O$ suboxide particle or, alternatively, as strongly distorted (strained) copper *(b)*. This may influence the electronic structure and the reactivity.

Acknowledgement :

This project is supported by the ZEIT-Stiftung.

References:

(1) M.M. Günter et al., *J. Cat.* **203**, 2001
(2) H. Purnama et al., *Appl. Cat.*, 2003 accepted
(3) B. Kniep et al., *Angew. Chem.* **116**., 2004
(4) Y. Wang et al., *J. Mater. Chem.* **12**, 2002