Structure–activity relationships of ternary $Cu/ZrO_2/CeO_2$ catalysts for methanol steam reforming

A. Dennstedt [a], A. Mastalir [a,b], B. Frank [b], A. Szizybalski [a], H. Soerijanto [a,b], A. Deshpande [c], M. Niederberger [c], R. Schomäcker [b], R. Schlögl [a], T. Ressler [a,b]

[a] Fritz-Haber-Institut der MPG, Abteilung Anorganische Chemie, Faradayweg 4-6, 14195 Berlin, Germany
[b] Institut für Chemie, TU Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany
[c] Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Abteilung Kolloidchemie, MPI-KG, 14424 Potsdam, Germany

Contact: annedenn@fhi-berlin.mpg.de

Introduction

Steam Reforming: $CH_3OH + H_2O \rightleftharpoons 3\,H_2 + CO_2$ **T = 250 °C ; p = 1 bar**

Application: H_2 **production for fuel cell application (e.g. in cars) [1]**

Catalyst: $Cu/ZrO_2/CeO_2$

In order to eliminate the need for gas purification, more selective catalysts need to be developed.

Two different types of experiments were performed:

I) **Ex situ (25 °C):** **XAS** (Zr K edge + Ce L3 edge), **XRD**

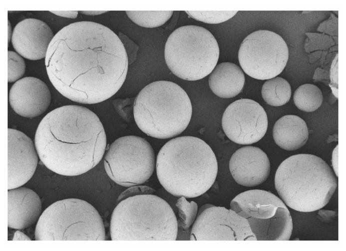
II) **In situ (25 °C – 250 °C, reduction in 2% H_2/He):** **XAS** (Cu K edge), **TG/DSC**, **XRD**

Furthermore, catalytic performance was investigated in a fixed bed reactor at atmospheric pressure.

Sample preparation

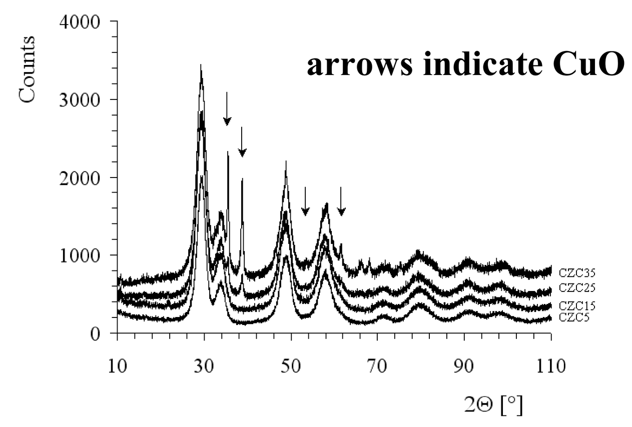
Step 1: $(NH_4)_2Ce(NO_3)_6$, $ZrO(NO_3)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$ **+ distilled water → coprecipitation**

Step 2: Templating: XAD-16 nonfunctional polystyrene beads



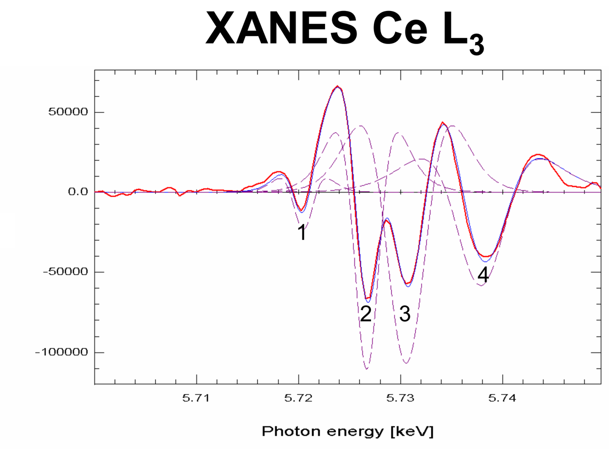
4 samples:

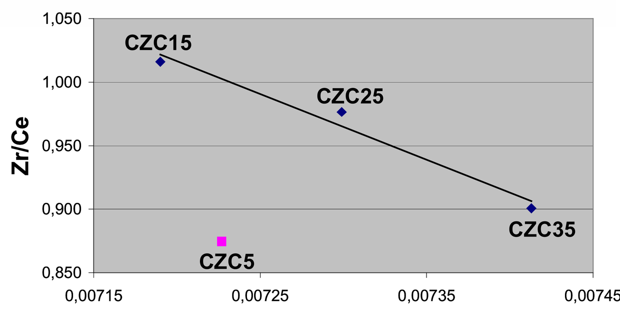
	BET area (m² g⁻¹) [2]	X-ray fluorescence analysis (%) [2]		
		Cu	Zr	Ce
CZC5	96	4.4	44.6	51.0
CZC15	102	12.1	44.3	43.6
CZC25	94	23.9	37.6	38.5
CZC35	83	31.0	32.7	36.3



Structural characterization (ex situ)

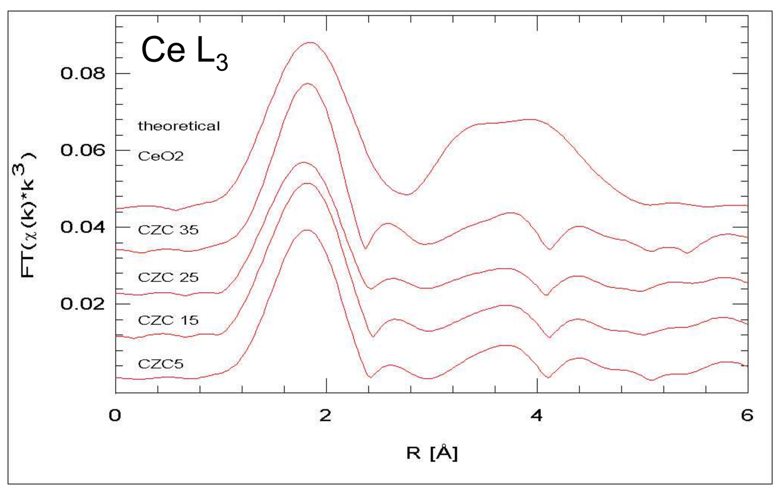
XANES Ce L_3



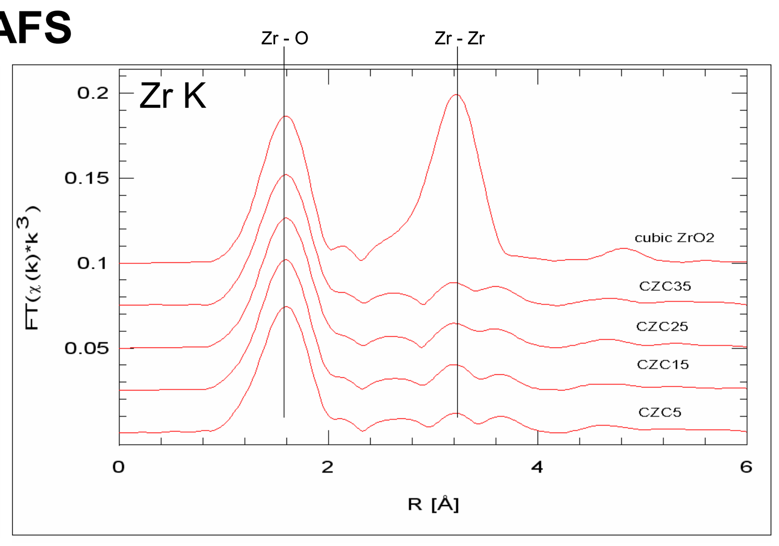


- difference between 3rd and 4th Lorentzian correlates with Ce-O distance [3]
  → with lower Zr/Ce ratio a larger Ce-O distance is observed
  → good agreement with Vegard´s law

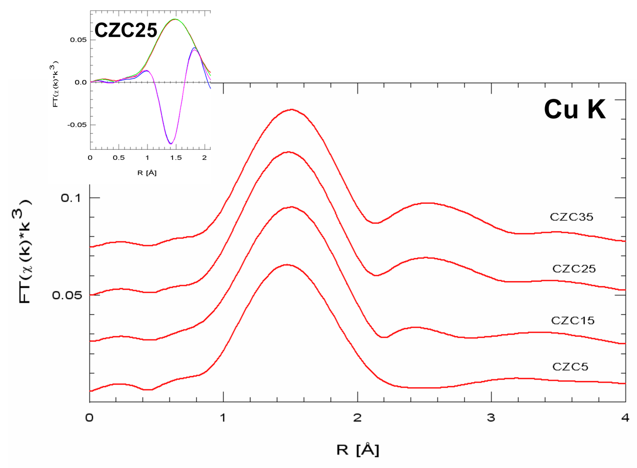
EXAFS



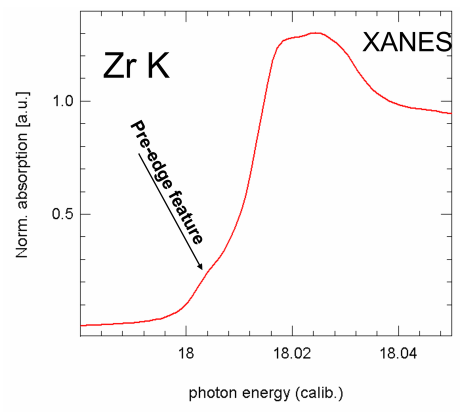
- different amplitudes in 1st shell



- only minor differences between the CZC samples

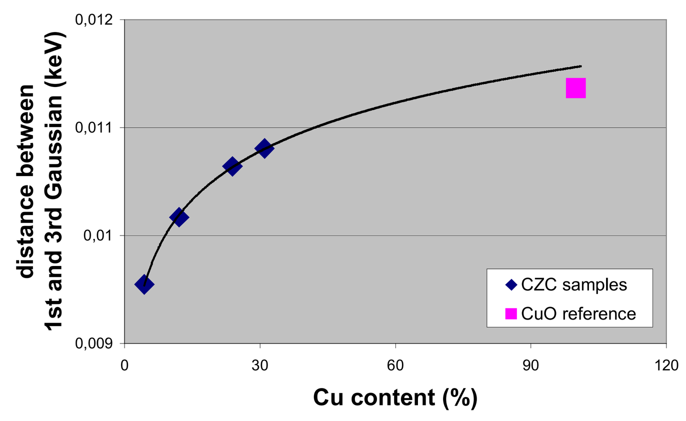


- fit of the 1st shell identified CuO



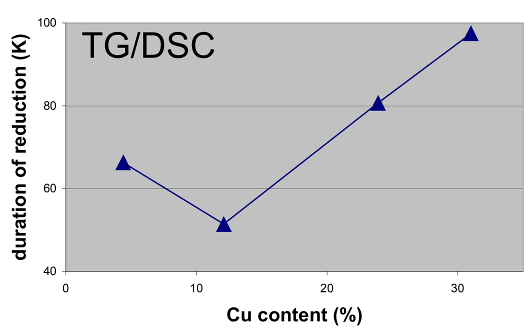
-pre-edge feature is typical for tetragonal structure in ZrO_2 [5]

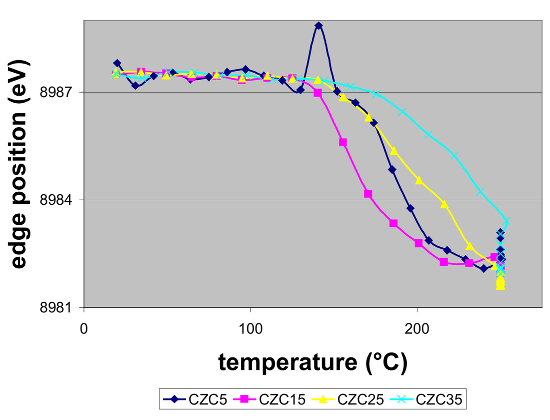
- shape of the RDF in the region of 3 – 4 Å does not correspond to that of CeO_2 or ZrO_2
→ indicates tetragonal solid solution



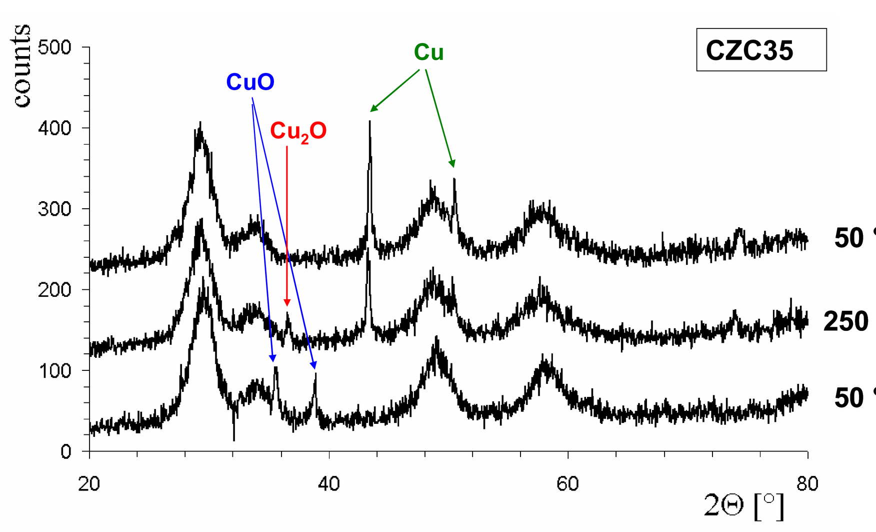
- XANES fit with 3 Gaussian functions
→ log dependence of distance from Cu content, may indicate continuous size variation

Structural characterization (in situ)

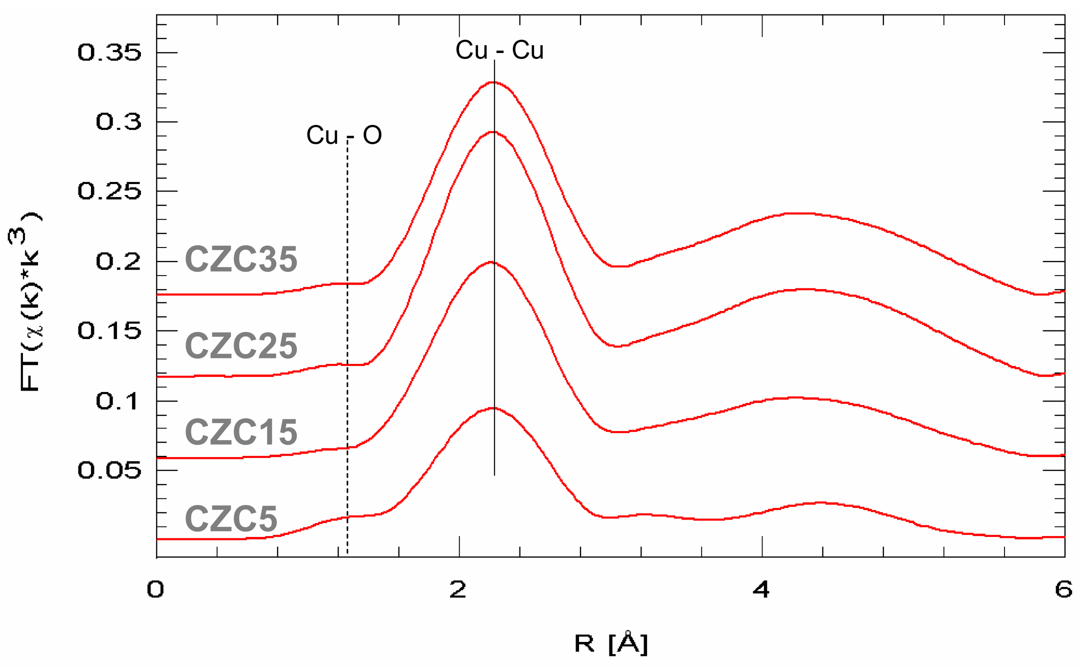




- TG/DSC and position of edge during XAS showed for samples with Cu >5%: Reduction needs more time and ends at higher temperatures with higher Cu content

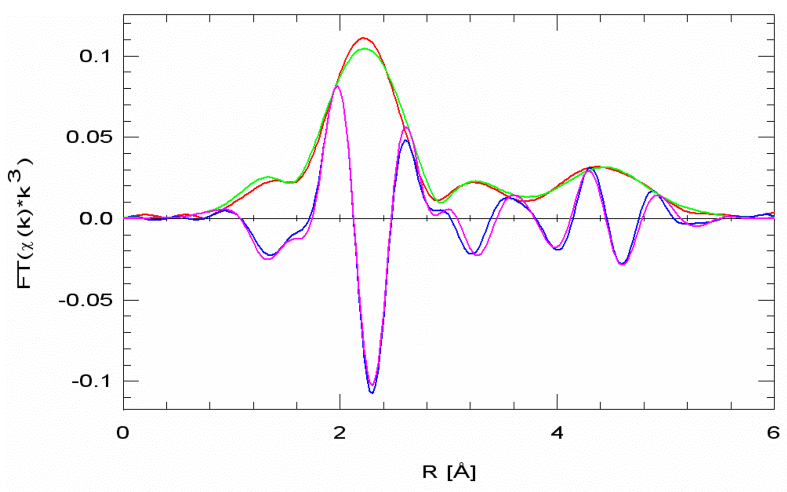


- Cu_2O detectable at high temperature during in situ XRD

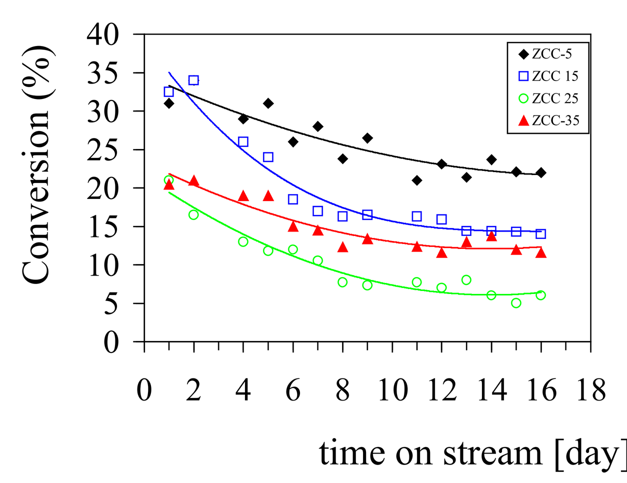


- **different amount of Cu-O in the reduced samples**
→ similar to Cu/ZrO_2 where an amount of oxygen in the copper particles was found [4]
- **highest oxygen content in CZC5 ←→ highest P_{CO}**

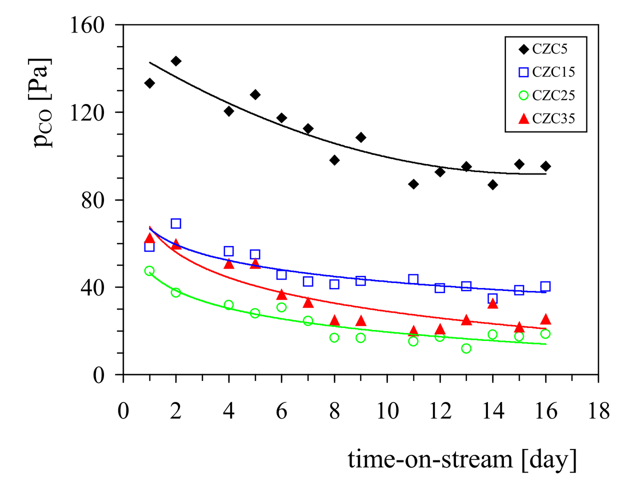
→ Possible to fit RDF of CZC5 with a combination of Cu and Cu_2O



Catalysis



- **no systematic variation with Cu content**
- **samples > 5 % Cu show good long-term stability**



- **samples > 5 % Cu: after 5 days CO levels were stabilized**

Conclusions

- *CZC5 shows different behaviour compared to the other CZC samples*
  - ✓ *more oxygen in the reduced sample*
  - ✓ *smaller Cu particles*
  - ✓ *stronger metal-support interaction*
- *XANES of Zr K edge and XRD indicate tetragonal structure*
- *low intensity of RDF at higher distances is indicative of a $(Zr,Ce)O_2$ solid solution*
- *for samples with >5% Cu, the Cu content influences the duration of reduction*
- *increase in Cu content from 5 % to 15 % has a beneficial effect on the catalytic performance of the CZC catalysts*

References:
[1] P. J. de Wild, M. J. F. M. Verhaak, Catal. Today 60 (2000) 3
[2] A. Mastalir, B. Frank, A. Szizybalski, H. Soerijanto, A.Desphande, M. Niederberger, R. Schomäcker, R. Schlögl, T. Ressler, J. Catal. 230 (2005) 464
[3] L. Douillard, M. Gautier, N. Thromat, J. P. Duraud, Nucl. Instrum. Methods Phys. Res. B 97 (1995) 133
[4] A. Szizybalski, F. Girgsdies, A. Rabis, Y. Wang, M. Niederberger, T. Ressler, J. Catal. 233 (2005) 297
[5] P. Li, I. W. Chen, J. E. Penner-Hahn, Phys. Rev. B 48 (1993) 10063

DFG SPP1091