Zirconium oxynitride as novel support for Cu in methanol steam reforming

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Introduction

Motivation:

- Hydrogen for fuel cells in mobile applications → could be provided by methanol [1]:

$$CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2$$

Previous studies:

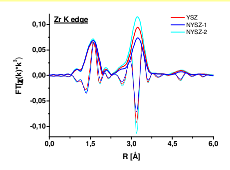
- Cu/ZrO_2 shows higher activity and lower selectivity to CO compared to commercial $Cu/ZnO/Al_2O_3$ catalysts [3]
- Activity of Cu/ZrO_2 was correlated to the amount of oxygen incorporated into the Cu phase [2]

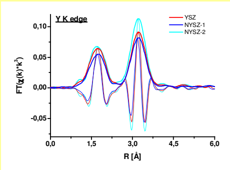
Aim:

- Preparation of new Cu based catalysts for methanol steam reforming by modifying the anion lattice of ZrO_2 by incorporation of nitrogen:

$$3O_O^x + N_2 \rightarrow 2N_O' + V_O^{\circ\circ} + 1{,}5O_2$$

Incorporation of nitrogen





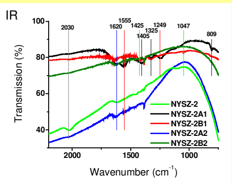
sample	N (wt%)	Zr-Zr (Å)	Y-Zr (Å)
YSZ	0	3,625	3,632
NYSZ-2	2,18	3,622	3,625
NYSZ-1	3,5	3,616	3,624

- N atoms are incorporated in vicinity of Y atoms
- Incorporation of nitrogen creates vacancies in the anion lattice next to Zr atoms

→ Such a replacement mechanism was also described by Li et al. [4] for the incorporation of Y into the ZrO_2 lattice.

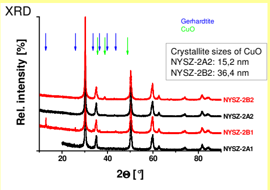
Calcination

Calcination at 250°C



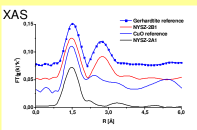
The catalyst prepared via the citrate route contains carboxylate groups at the surface (ν(COO) 1555 cm^{-1}, 1405 cm^{-1}) that are removed by calcination.

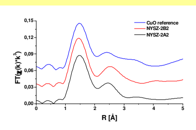
A loss of nitrogen is observed during calcination of the citrate derived catalyst.



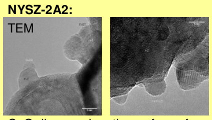
	Nitrogen content [wt%]	BET surface area [m²/g]
NYSZ-2	2,18	10,49
Expected after calcination	2,06	---
NYSZ-2A2	1,95	13,16
NYSZ-2B2	2,03	9,48

Evolution of nitrogen (m/e=14) was detected at 190-250°C during TG/DSC of NYSZ-2A1.



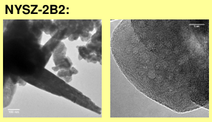


NYSZ-2A2:



CuO dispersed on the surface of the support

NYSZ-2B2:

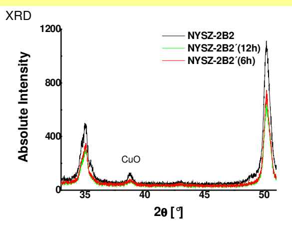


CuO needles

- X-ray absorption spectroscopy shows in coincidence with XRD the formation of Gerhardtite in the dried sample prepared by the nitrate route
- No information about the second coordination sphere of Cu is available from the X-ray absorption spectrum of the dried citrate derived catalyst
- In both calcined samples CuO was detected as the main Cu phase

→ Formation of Gerhardtite during nitrate route
→ Nitrate route results in larger CuO crystallites

Influence of calcination temperature



Results of XRD fit

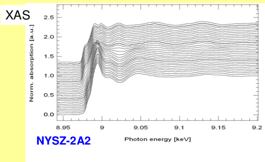
Sample	Crystallite size of CuO (nm)	CuO (wt%)
NYSZ-2B2	36,4	5,02
NYSZ-2B2`(12h)	27,8	4,97
NYSZ-2B2`(6h)	23,5	5,04

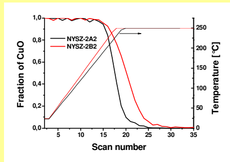
Calcination at lower temperatures leads to the formation of smaller CuO crystallites

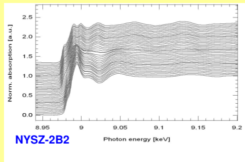
Preparation

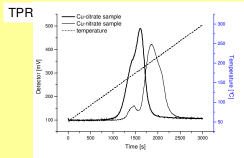
YSZ = yttrium-stabilized zirconia, 6 mol% Y_2O_3
NYSZ = nitrogen doped yttrium-stabilized zirconia

Reduction







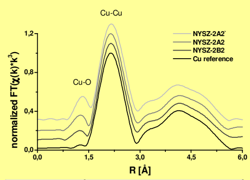


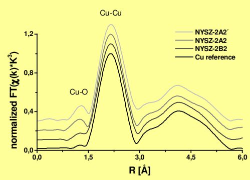
The copper in the citrate-based catalyst is reduced at lower temperature compared to Cu in the catalyst prepared by impregnation with nitrate

Steam reforming

Feed:	1,5 vol% CH_3OH + 1,5 vol% H_2O in He
Flow:	40 ml/min

EXAFS before and after steam reforming of methanol:



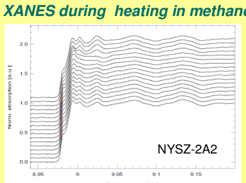


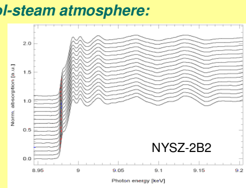
The reduced citrate derived catalyst (NYSZ-2A2) shows a higher amount of oxygen incorporated into the Cu lattice compared to the nitrate derived catalyst (NYSZ-2B2).

Sample	peak area			
	After reduction		After MSR	
	Cu - O	Cu - Cu	Cu - O	Cu - Cu
3400, calc. @ 190°C	0,0836	0,8621	0,044	0,8737
3454	0,0517	0,8427	0,0368	0,8369
3458	0,0279	0,8457	0,0142	0,8876

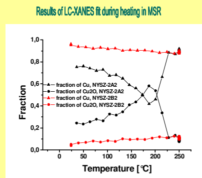
- Table shows results of fitting the normalized FTs
- The FTs were normalized to the first Cu-Cu distance

XANES during heating in methanol-steam atmosphere:





Results of LC-XANES fit during heating in MSR



Intermediate formation of Cu_2O observed during heating in the MSR feed

Summary

✓ **Ammonolysis of yttrium doped zirconia results in substitution of oxygen anions by nitrogen in the vicinity of yttrium lattice positions.**

✓ **Novel Cu based catalysts for methanol steam reforming have been prepared applying the nitrogen containing material as support. Impregnation has been performed using NH_3 containing aqueous solution of Cu citrate or aqueous solution of Cu nitrate.**

✓ **Crystalline Gerhardtite has been identified in the as-prepared nitrate based catalyst that decomposes during calcination in air leading to comparatively large CuO particles.**

✓ **Smaller CuO particles occur in the citrate derived catalyst. However, nitrogen was lost partially from the support during calcination.**

✓ **After reduction in hydrogen, the citrate based catalyst shows a higher degree of residual partial oxidation, indicated by the presence of Cu_2O, compared to the nitrate based catalyst. Under methanol steam reforming conditions, metallic copper prevails in both catalysts.**

References
[1] K.-O. Hinrichsen, and J. Strunk, Nachrichten aus der Chemie 54, 1080 (2006)
[2] A. Szizybalski, F. Girgsdies, A. Rabis, Y. Wang, M. Niederberger,and T. Ressler, J. Catal. 233, 297 (2005)
[3] H. Purnama, F. Girgsdies, T. Ressler, J.H. Schattka, R.A. Caruso, R. Schomäcker, and R. Schlögl, Catal. Lett. 94, 61 (2004)
[4] P. Li, I-W. Chen, and J. E. Penner-Hahn, Phys. Rev. B 48, 10074 (1993)

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