Zirconium oxynitride as new support for Cu in methanol steam reforming

A. Dennstedt, A. Trunschke, R. Schlögl

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

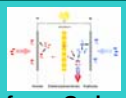
N. Frenzel, M. Lerch, T. Ressler

Institut für Chemie, TU-Berlin, Sekr. C2, Straße des 17. Juni 135, 10623 Berlin, Germany

Introduction

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

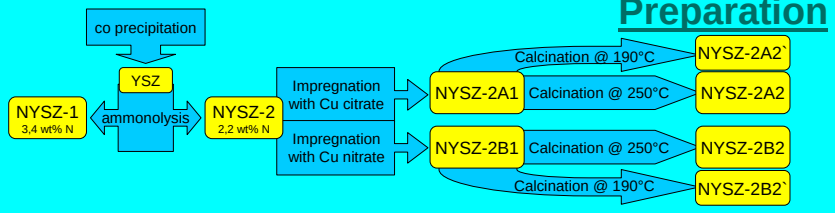
$CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2$

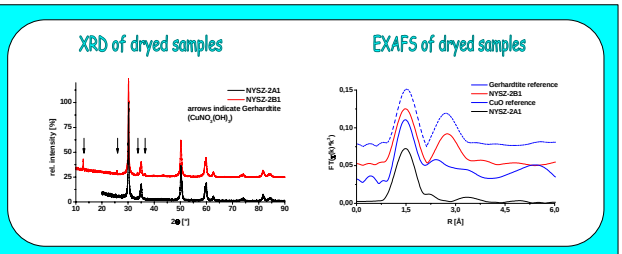


Aim: Preparation of new Cu based catalysts for methanol steam reforming

Methods:
XRD
ex situ XAS @ Cu K, Zr K and Y K edge
in situ XAS @ Cu K edge

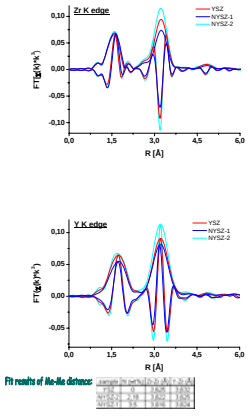
Preparation





Results

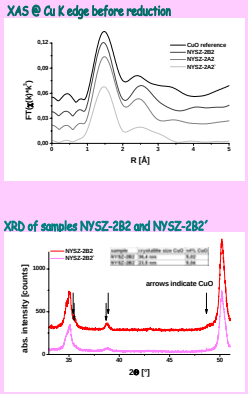
Influence of nitrogen incorporation



N atoms incorporated in vicinity of Y atoms
Vacancies created around Zr atoms
→ Such a replacement mechanism was also described by Li et al. [3] for the incorporation of Y into the ZrO_2 lattice.

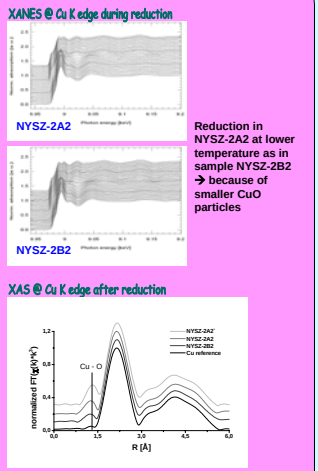
NYSZ-1 has the highest amount of cubic phase

Influence of calcination temperature



Lower calcination temperature
→ smaller crystallites

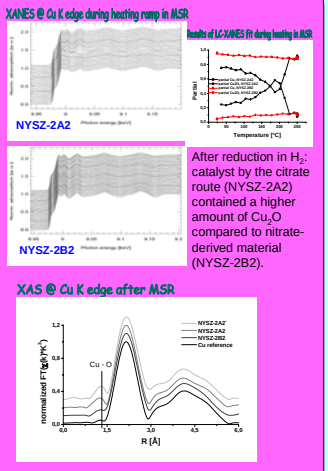
Influence of reduction



Reduction in NYSZ-2A2 at lower temperature as in sample NYSZ-2B2 → because of smaller CuO particles

Cu-O distance detected in reduced samples as desribed by A. Szizybalski [2] → higher intensity in the case of citrate route and lower temperature

Influence of MSR conditions



After reduction in H_2: catalyst by the citrate route (NYSZ-2A2) contained a higher amount of Cu_2O compared to nitrate-derived material (NYSZ-2B2).

The intensity of the Cu-O distance decreases during MSR, most significantly in the case of the sample calcined at 190°C (NYSZ-2A2`).

Conclusions

- N incorporated around Y atoms
- Gerhardtite as intermediate after drying of the nitrate-based catalyst
- higher intensity of Cu-O distance in reduced samples and higher decrease of intensity of Cu-O distance during MSR in the case of lower calcination temperature

HASYLAB is acknowledged for providing beamtime.

Contact: annedenn@fhi-berlin.mpg.de

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] P. Li, I-W. Chen, and J. E. Penner-Hahn, Phys. Rev. B 48, 10074 (1993)