Ammonia oxidation over copper investigated with in situ NEXAFS spectroscopy in the soft X-ray range

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1. Introduction

Ammonia containing exhaust gas is still a problem in many chemical processes, *e.g.* in the ammonia slipstream treatment after deNO$_x$-SCR [1] or in the purification of reformats for fuel-cell applications [2]. Besides the decomposition of ammonia to nitrogen and hydrogen the selective catalytic oxidation to nitrogen and water

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (1)$$

is consistent with a wide range of applications [3] and the subject of this investigation. In addition to reaction (1) the total oxidation

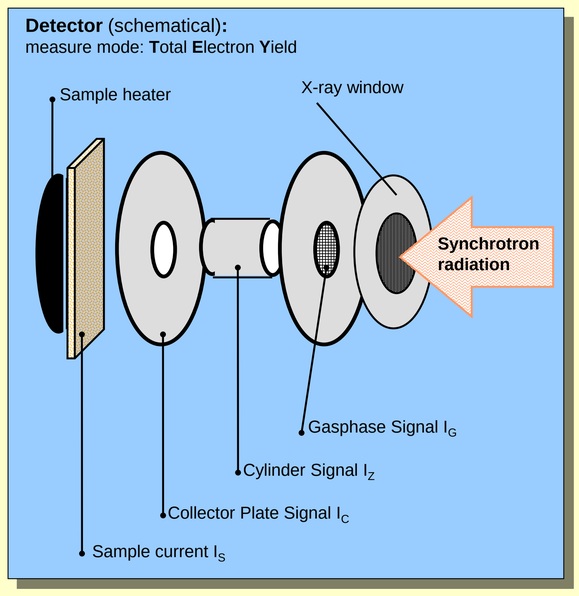
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (2)$$

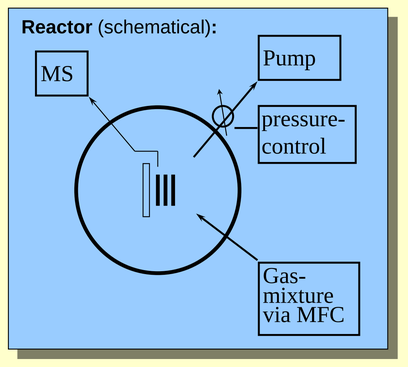
is possible in oxygen containing feed gas. Because of the production of hazardous nitric oxide this reaction path has to be totally suppressed. This is the most important selection criteria for a suitable catalyst.

2. Method

- **N**ear **E**dge **X**-Ray **A**bsorption **F**ine **S**tructure (NEXAFS) Spectroscopy in **soft energy range** ($h\upsilon$ = 350 - 550eV)
- provides **electronic structure** of involved species and by comparison with reference spectra **chemical state of the catalyst surface**
- **in situ:** reaction is observed via mass spectrometry
- **high pressure:** up to several mbars

➢ **aim: detect the catalytically active surface structure of the catalyst**



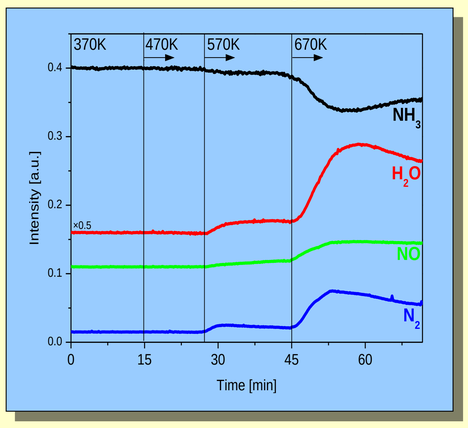


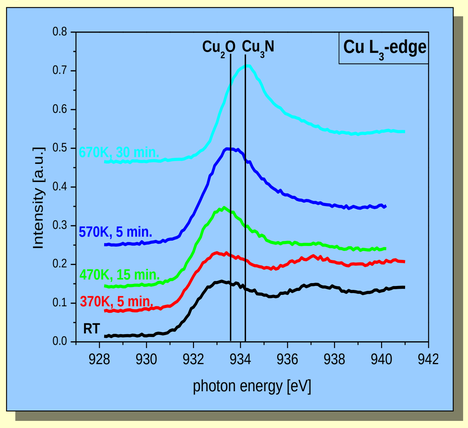
Beamlines at BESSY II:

- U49/1 and UE56/2 (Undulator)
- PM1 (bending magnet)

3a. Results @ p=1.2mbar and Cu^0

with NH_3:O_2 = 1:12 and increasing temperature





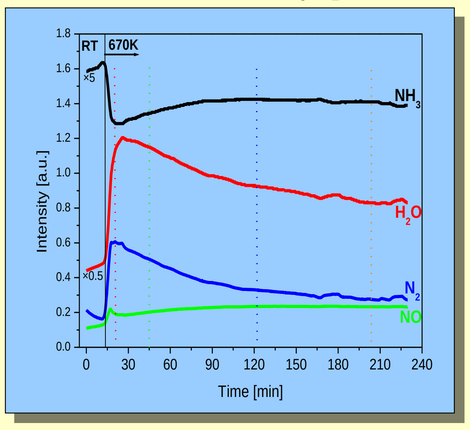
1. Oxidation of **copper metal** to **copper(I)oxide** 2. Reaction

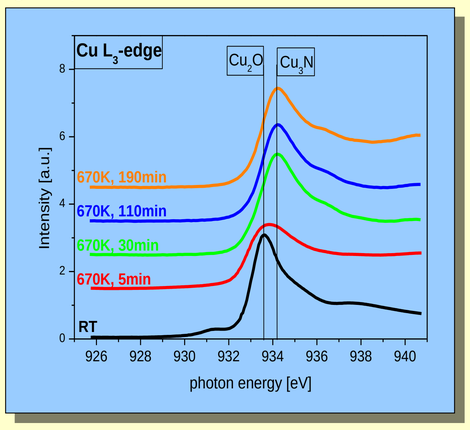
Deactivation due to **copper(I) nitride**

no NO production high N_2 amounts

3b. Results @ p=1.2mbar and Cu_2O

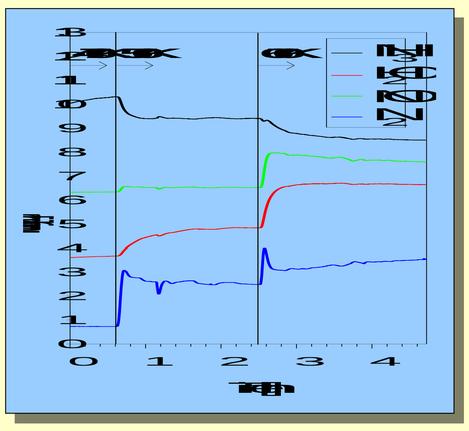
with NH_3:O_2 = 1:12 and increasing temperature

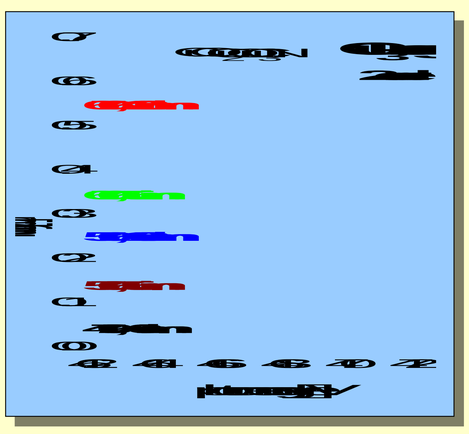




3c. Results @ p=1.2mbar and CuO

with NH_3:O_2 = 1:12 and increasing temperature

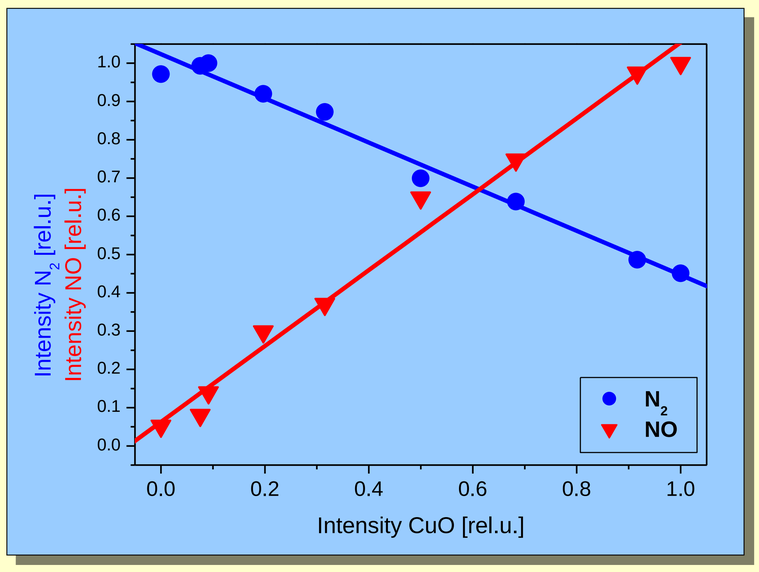




No deactivation **no** copper(I) nitride **less N_2 production high NO amounts**

4. Conclusions

Correlation of the products with CuO surface intensity:



➢ **copper(II)oxide catalyzes the total oxidation of ammonia to NO**

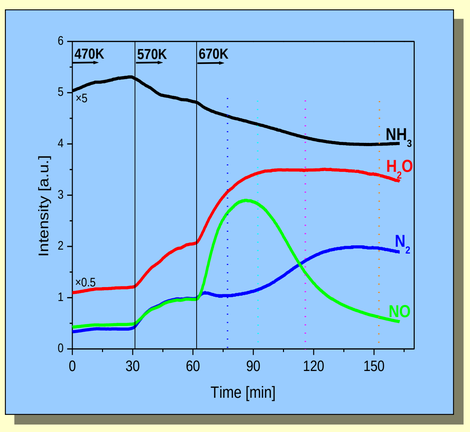
➢ **partial oxidation to nitrogen is catalyzed by copper(I)oxide**

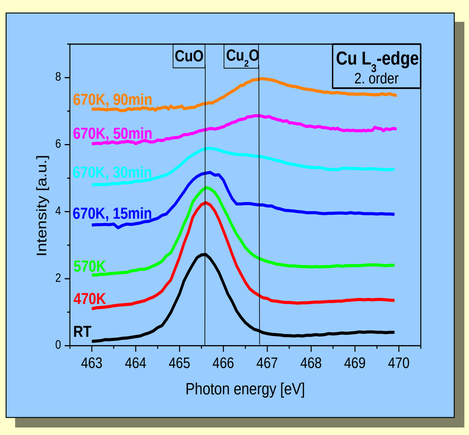
High **NO** production with **CuO**

High **N_2** production with **Cu_2O**

3d. Results @ p=0.8mbar and CuO

with NH_3:O_2 = 1:12 and increasing temperature





References

[1] H.Bosch and F.J.J.G. Janssen, Catal. Today **2** (1988) 369

[2] Lu Gang, J. van Grondelle, B.G. Anderson, and R.A. van Santen, J.Catal. **186** (1999) 100

[3] T. Curtin, F. O'Regan, C. Deconinck, N. Knüttle, and B.K. Hodnett, Catal. Today **55** (2000) 189

[4] R.W. Mayer, M.Hävecker, A. Knop-Gericke, and R. Schlögl, submitted to Catal. Lett.

Acknowledgement

The staff of BESSY II is gratefully acknowledged for their support in beamline operation.

5. Structure - Function relation

➢ A monoatomic nitrogen intermediate can either recombine to N_2 and desorb or react with the substrate to deactivate the copper

➢ Temperature and pressure (coverage) affect critically the pathways for oxidation or nitridation

➢ Copper metal is oxidized to Cu_2O or CuO