



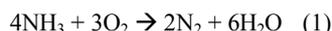
## The ammonia oxidation over copper: First experiments with copper clusters investigated by means of in situ NEXAFS

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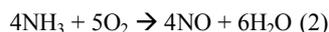
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### Introduction

The partial oxidation of ammonia to nitrogen and water according to



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



is also preferred in oxygen containing feed gas. Copper and its oxides were found to be potential catalysts for these reactions [1,2]. The aim of our investigation is to reveal the catalytically active surface species. We have found that copper(II)oxide (CuO) catalyzes the total oxidation to NO, whereas copper(I)oxide (Cu<sub>2</sub>O) is absolutely necessary for the desired partial oxidation to nitrogen [3]. These results were obtained using a copper foil as model catalyst. However, since real catalysts usually consist of oxide or zeolite supported small copper particles (like Cu-ZSM-5 or Cu/Al<sub>2</sub>O<sub>3</sub>), the question arises whether these results are transferable to real catalyst systems. To answer this question we have performed experiments using small copper particles that are deposited on a gold grid covered with amorphous carbon.

### Experiment

All experiments were carried out in a double chamber UHV system. The first chamber (base pressure  $3 \times 10^{-9}$  mbar) was connected to beamline UE 56/2 at BESSY II. The second chamber is used as reactor and is separated from the first by

a 100 nm thick silicon nitride window ( $\varnothing$  4 mm aperture), withstanding a pressure of at least 100 mbar in the reaction chamber. The detector system is described in detail elsewhere [4,5].

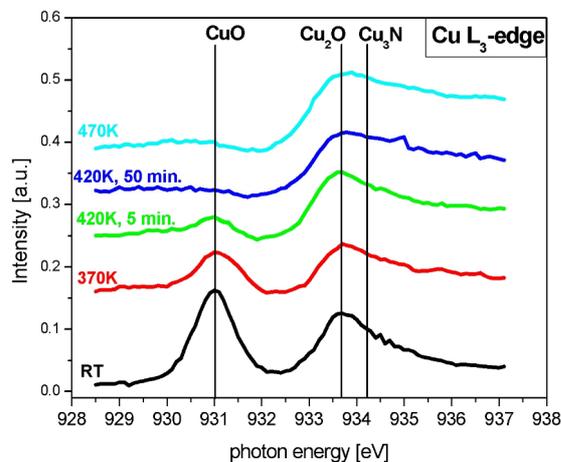
The sample was prepared using the inert gas aggregation method [6], where copper clusters with a mean particle size of 2.8 nm are produced by aggregation of supersaturated copper vapor [7]. For the experiments with the copper clusters we applied the same reaction conditions like in our previous studies with copper foil, i.e. 1.2 mbar absolute pressure, 0.38 ml/min NH<sub>3</sub>, and 4.5 ml/min O<sub>2</sub>. The pressure in the reaction chamber ( $p_{\text{abs}}$ ) was adjusted with a valve at the reactor outlet to a foreline pump, and the gas flows were provided by calibrated mass-flow-controllers. Since the clusters were expected to react at lower temperatures than the (bulk) copper foil and to prevent sintering, the clusters were heated from room temperature up to not more than 470K in steps of 50 degrees (in difference to the mentioned studies with copper foil). A quadrupole mass spectrometer is connected to the reaction chamber to analyze the product gas, which allows a correlation of the products with the state of the catalyst's surface.

### Results and discussion

Fig. 1 shows the NEXAFS spectra of the Cu L<sub>3</sub>-edge at different temperatures and time.

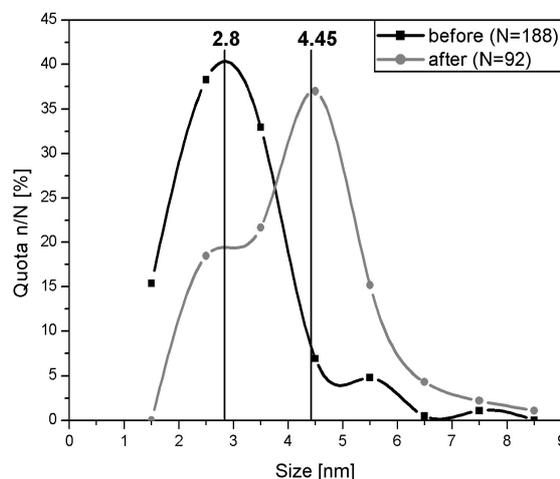
At room temperature the clusters consist mainly of CuO and Cu<sub>2</sub>O, as indicated by the two resonances at 931.0 eV and 933.6 eV. After heating to 370 K a slight reduction of the CuO is visible. This effect is intensified by further heating to 420 K. After 5 min at this temperature only small contributions of CuO are found, and after 50 min no CuO is detect-

able anymore. Instead, an additional resonance at 934.2 eV appears as shoulder of the  $\text{Cu}_2\text{O}$  resonance.



**Fig. 1:** NEXAFS spectra of the copper clusters at the  $\text{Cu L}_3$ -edge at different temperatures

This resonance can be identified as copper(I)nitride ( $\text{Cu}_3\text{N}$ ) which is present also after further heating to 470K. Therefore, it can be concluded that the formation of  $\text{Cu}_3\text{N}$ , which is well known from our former experiments with copper foil, also takes place with copper clusters, but – as expected – at lower temperatures. Unfortunately, no ammonia conversion could be detected by mass spectrometry, what is ascribed to the very low total copper content of about  $100 \mu\text{mol}$  in the sample. In addition to in situ NEXAFS, the sample was investigated by TEM before and after the reaction. The size distributions of the copper clusters determined by the TEM images are shown in Fig. 2.



**Fig. 2:** Size distributions of the copper clusters before and after the reaction

The increased mean size and reduced number of clusters after the reaction indicates a slight sintering of the clusters during the reaction. However, a film formation by spreading of the clusters can be excluded. Thus, the NEXAFS spectra (Fig. 1) are actually obtained from the copper clusters, which have reacted with the gas phase. Since the conversion of ammonia could not be determined by mass spectrometry, further experiments using different gas flows are necessary to provide a longer residence time of the reactants and therefore a higher conversion. We will also investigate if the clusters have reached their equilibrium size with 4.45 nm or if they will sinter even more to form bigger clusters.

## References

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