Bridging the “pressure gap”: Investigation of the ammonia oxidation over copper with in situ NEXAFS in the soft X-ray range under mbar pressure conditions


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Introduction

For understanding the mechanism of catalytic reactions in situ methods are absolutely necessary [1]. Moreover, it is an improvement to use surface sensitive methods also under reaction conditions. For this reason an in situ NEXAFS technique was developed giving the possibility to investigate an active catalyst with the surface sensitive X-ray absorption spectroscopy in the soft X-ray range while the catalytic reaction takes place in the mbar pressure range in a flow reactor environment [2]. From the obtained NEXAFS spectra the electronic structure of all species involved can be determined, leading to the chemical structure of the catalyst surface and the intermediates thereon. Thus the description of the catalytically active surface structure for a specific reaction becomes possible. Complemented by mass spectrometry a correlation between different surface structures of the catalyst and catalytic performance becomes feasible.

For ammonia oxidation two main reaction paths are possible: on one hand the partial oxidation with nitrogen (and water) as main products and on the other hand the total oxidation to nitric oxide or nitrogen dioxide. The partial oxidation is the only useful path for industrial application, e.g. in ammonia slipstream treatment in SCR DeNOx process or purification of flue gases [3]. The total oxidation leads to nitrogen oxides, hence this reaction has to be totally suppressed.

Results

We investigated the ammonia oxidation with a copper foil (99.99+% as catalyst under several reaction conditions, i.e. various oxygen-ammonia-ratios, temperatures and particularly pressures. Two pressure regimes can be distinguished:

At 0.4 mbar absolute pressure the reaction to both, N\(_2\) and NO occurs at temperatures above 575K, but the formation of copper nitride causes a fast deactivation of the catalyst within 1h. This development shown in Fig. 1a for a 1:12 ammonia-to-oxygen ratio is also visible in even more oxygen-rich feeds up to a 1:50-ratio, with the only difference that it takes the more time to deactivate, the higher the oxygen content is. Increasing the pressure up to 1.2 mbar leads to a completely different behavior: though the reactions starts at temperatures around 575K, too, no nitride formation is detectable (Fig. 1b). Instead the production of N\(_2\) and NO remains steadily over several hours without deactivation.

Furthermore at 675K, 1.2 mbar and a ammonia-oxygen-ratio of 1:12 a slow change in selectivity to N\(_2\) occurs with time, i.e. the nitrogen yield increases and the nitric oxygen production decreases. Simultaneously, the structure of the catalyst surface changes from copper(II)oxide to copper(I)oxide,
allowing the conclusion that the partial oxidation of ammonia to nitrogen is mainly catalyzed by copper(I)oxide, whereas copper(II)oxide is required for the total oxidation. Additionally the lack of any resonances in the N K-edge NEXAFS spectra at 1.2 mbar (Fig. 1b) reveals that no nitrogen containing intermediate resides on the surface. This is different to results obtained from UHV experiments [4] where amide and imide species are found on the surface after ammonia exposure. This observation is, however, comparable to the case of methanol oxidation over copper, where on contrary to UHV results no surface CHx species was found in in situ NEXAFS investigations [5]. Such findings underline the relevance of high pressure surface sensitive in situ methods for the development of an experimentally founded understanding of heterogeneous surface reactions.

References