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Investigation of ammonia oxidation over copper with in situ NEXAFS in the soft X-ray range: Influence of pressure on the Catalyst performance

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Abstract

The oxidation of ammonia over polycrystalline copper was investigated by means of in situ NEXAFS (near edge X-ray absorption fine structure) spectroscopy in the soft X-ray range. The reaction, carried out in a 1:12 excess of oxygen, was observed by mass spectrometry. The simultaneous detection of the surface electronic structure and its catalytic performance allows to correlate different reaction products to the current surface structure of the catalyst. It is shown that a change in total pressure from 0.4 mbar to 1.2 mbar severely affects the reaction path. Copper (I) nitride was identified as poison and a copper oxide was found to be the active phase for the selective oxidation of ammonia to nitrogen.

Keywords: catalytic oxidation of ammonia over copper, partial oxidation, copper (I) nitride, copper oxides, *in situ* NEXAFS

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

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

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

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

is preferred 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 challenge for the design of a suitable catalyst.

Copper and its oxides were found to be potential catalysts for this reaction [1-3]. We studied the ammonia oxidation over copper by means of in situ NEXAFS in the energy range of the N K-edge, the copper L-edge and the O K-edge. This element-specific method allows to investigate the electronic structure of the copper surface in situ, *i.e.* while the reaction occurs in the mbar pressure range and a significant conversion of the feed can be observed by mass spectrometry. Comparison of the in situ spectral data with reference spectra allows to elucidate to the chemical state of the catalyst surface, which is correlated with the product yields. In this way the catalytically active phase was identified as well as the phase responsible for catalyst deactivation. This approach was successfully employed for the case of methanol oxidation over copper [4,5].

Experimental

All experiments were carried out in a two chamber UHV system, of which one chamber with a base pressure of $<5\times10^{-9}$ mbar was connected to the U49/1-SGM beamline [6] of BESSY II, the Berlin electron storage ring for synchrotron radiation. The second chamber used as reactor is separated from the first by a 300 nm polyimide window (Ø 8 mm aperture), providing a transmission of ca. 30% of

the synchrotron light in the desired energy range, but also withstanding a pressure of at least 100 mbar in the reaction chamber. The detector system, which is described in detail in refs. [7-10], mainly consists of an aluminum plate facing the sample ("collector") and a so shielded gold mesh, both working in total-electron-yield (TEY) mode. Due to their different shape and spatial arrangement, the collector signal is a mixture between electrons from the sample and the gas phase at the N K-edge, whereas the gold mesh provides an almost pure gas phase signal.

To obtain the desired sample spectra the recorded signals are first normalized to the beam intensity, that is obtained with a gold mesh in the refocusing chamber of the beamline and therefore independent from any gas in the reaction chamber. After subtraction of the pre-edge background the spectra were normalized to the N-H*-resonance at 401.9 eV [11]. Then the collector signal is increased by multiplication with a constant factor until the sharp N-H*-resonance (from gaseous NH_3) disappears in the difference spectrum, *i.e.* the gas phase-spectrum is subtracted from the collector spectrum (Fig.1). This resulting spectrum includes resonances only from the sample surface. The copper L-edge spectra were recorded with second order light to achieve a better resolution. The data analysis procedure is less difficult due to the absence of any resonances in the gas phase in this energy range, so that only a normalization to the beam intensity and a pre-edge background subtraction are required.

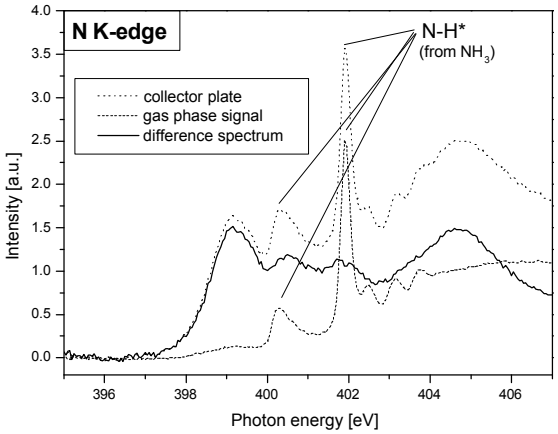

Fig. 1: Example of data treatment at the N K-edge: The spectrum from the collector plate (dotted line) is adjusted to the gas phase signal (dashed line) until the N-H* resonances disappear in the difference spectrum (solid line), which then contains resonances from the sample only.

The sample was a polycrystalline copper foil (99.99+%, Goodfellow). A platelet of ca. 25 mm × 12 mm was fixed to a chemical inert ceramic heater on a manipulator, providing heating of the foil without unwanted heat transfer to the sample manipulator metal device. The temperature was controlled by a Ni-CrNi-thermocouple. For all experiments the copper foil was pre-oxidized in 1 mbar O_2 at 770 K for approx. 30 min, leading to a reproducible initial state of the catalyst of copper (II) oxide. The investigations were performed in the continuos flow mode with ammonia (99.98%, Linde) and oxygen (99.9990%, Linde) flows of 0.38 ml/min and 4.5 ml/min, respectively, controlled by calibrated mass-flow-controllers. The pressure in the reaction chamber (p_{abs}) was adjusted with a valve at the reactor outlet to a oil-free foreline pump and monitored with a Baratron pressure gauge, which measures independent from the composition of the gas phase. A quadrupole mass spectrometer is connected to the reaction chamber via a capillary (Ø 3 mm) sucking off the gas phase just above the sample.

Results and discussion

p_{abs} = 0.4 mbar

The partial pressure profiles in Fig. 2 were obtained at an total pressure of p_{abs} = 0.4 mbar with a stepwise increased temperature from 300 K to 670 K. Below 470 K no conversion was detectable and initial ammonia oxidation occurred at 570K. The conversion and selectivity data are collected in Table 1. Within 45 minutes the conversion dropped to 20% of its maximum value. At 670K the activity, yield and deactivation are different with 90 minutes duration until complete deactivation. The NO yield profile is different from that of the N_2 profile indicating that two different processes occur on chemically different sites. No production of N_2O could be found in the mass spectra.

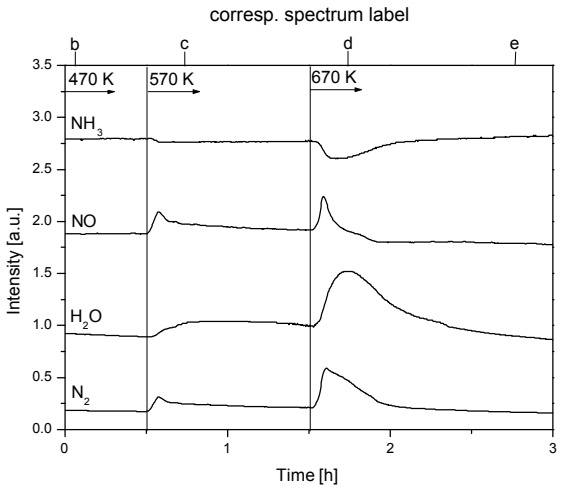

Fig. 2: Mass spectra of NH_3, NO, H_2O, and N_2 of the reaction at p_{abs} = 0.4 mbar, NH_3:O_2 = 1:12, with increasing temperature.

The N K-edge spectra in Fig. 3a show that nitrogen-containing species grow on the catalyst surface, indicated by the increasing resonance intensities. From comparison with Fig. 2 it occurs that this nitrogen species is blocking the surface. In Fig. 3b the resonances of the copper L_3-edge at 465.6 eV and 466.7 eV can be identified as CuO and Cu_2O [12], respectively. In contrast, the resonance at 467.1 eV appearing after 70 min. at 670 K can not be assigned to any copper oxide. The shift in the Cu L_3-edge

shows that copper must be part of the inhibiting species, excluding the possibility that the deactivation is caused by a nitrogen-containing adlayer on the surface. A possible reaction of copper oxide with ammonia is the formation of copper (I) nitride, found already in 1841 by Schrötter [13]. In addition, the formation of a nitride like surface structure was found in UHV investigations [14]. Reference spectra from a pressed pill of clean Cu_3N (99.5%, Alfa) are in good agreement with the spectra obtained in situ at the Cu L-edge as well as N K-edge and allow to assign the resonance in the Cu L_3-edge spectra at 467.1 eV to copper (I) nitride. The deactivation of the copper catalyst is ascribed to the formation of copper (I) nitride in the ammonia oxidation at p = 0.4 mbar seen in Fig. 2.

Table 1: Ammonia conversion and selectivities to N_2 and NO for reaction at 0.4 mbar (Fig. 2) and 1.2 mbar (Fig. 4) at different temperatures. Note: The values for 0.4 mbar are representing the maxima.

		0.4mbar		1.2mbar	
		570K	670K	570K	670K
X_{NH3}	[%]	4.1	20.1	24.7	49.3
S_{N2}	[%]	80.5	89.5	52.5	29.2
S_{NO}	[%]	19.5	10.5	47.5	70.8

To identify the relevance of the partial pressures we repeated the experiment with decreased NH_3-to-O_2-ratios of 1:20 and 1:50. Even with 50 times more oxygen than ammonia in the feed gas, the deactivation occurred in all cases by copper (I) nitride formation, but the time required to form the copper (I) nitride extended from 90 min. to 150 min.

p_{abs} = 1.2 mbar

The mass spectrometer data for the reaction at p_{abs} = 1.2 mbar are presented in Fig. 4. It is easy to see, that the reaction profile is completely different from that at p_{abs} = 0.4 mbar. The ammonia oxidation ignites at 570 K and remains in steady operation at this temperature. A rise in steady state conversion of ammonia and a change in selectivities (see Table 1) are detected after increasing the temperature to 670 K. The corresponding NEXAFS spectra are presented in Fig. 5: At the N K-edge (Fig. 5a) no resonances are detectable, thus no nitrogen-containing species are present on the copper oxide surface. Possible N-H species adsorbed on the catalyst can be excluded down to an abundance of 0.1 monolayer [11]. The copper L_3-edge (Fig. 5b) exhibits at low temperature (T ≤ 570 K) only one resonance at 465.6 eV. After 5 min. at 670 K this is still the only resonance, but 115 min. later an additional resonance appears at 466.7 eV. Both resonances can be assigned to copper (II) oxide and copper (I) oxide, respectively. The typical resonance for copper (I) nitride at 467.1 eV is missing which is in good agreement with the NEXAFS data at the N K-edge and the conversion data, indicating no copper (I) nitride formation and hence no deactivation.

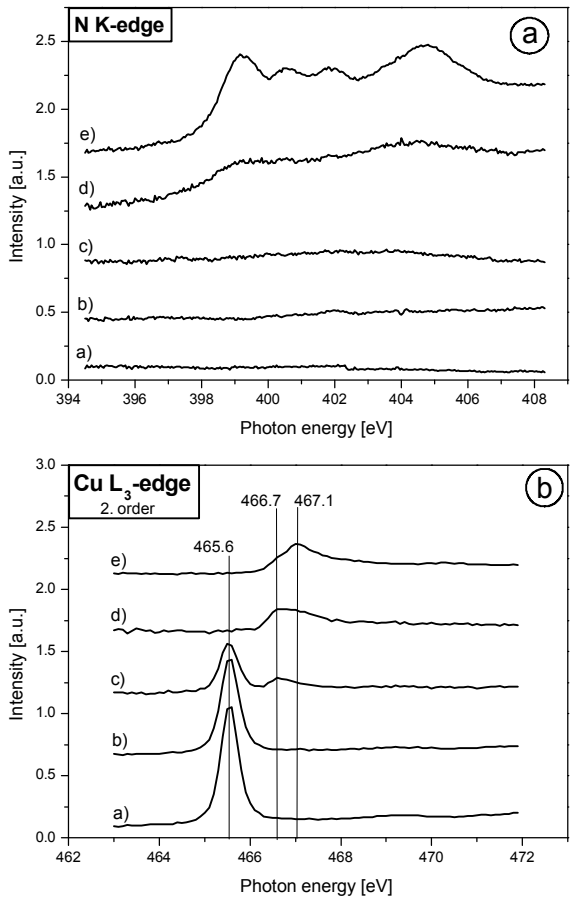

Fig. 3: NEXAFS spectra (difference spectra) at the N K-edge (a) and the Cu L_3-edge (b) from the reaction at p_{abs} = 0.4 mbar, NH_3:O_2 = 1:12 at a) room temperature, b) 470 K, c) 570 K, d) 15 min. at 670 K, and e) 70 min. at 670 K. The N and Cu spectra were recorded successively at each temperature / time; one specrum takes ca. 10 min. to record.

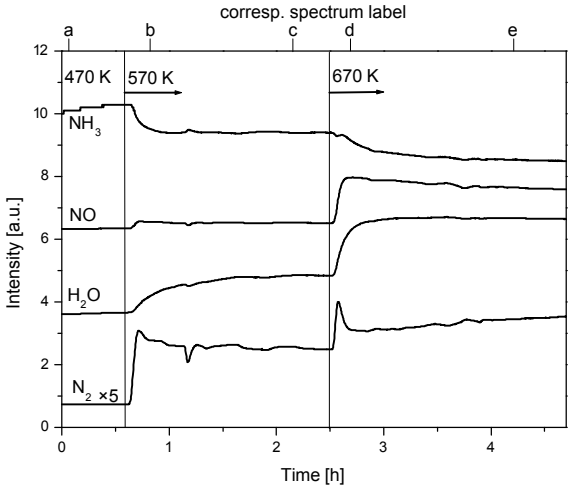

Fig. 4: Mass spectra of NH_3, NO, H_2O, and N_2 of the reaction at p_{abs} = 1.2 mbar, NH_3:O_2 = 1:12, with increasing temperature.

The lack of any detectable amount of nitrogen containing species on the surface is in contrast to UHV investigations of the ammonia adsorption on copper surfaces with preadsorbed oxygen [15,16] or simultaneous adsorption of a ammonia-rich NH_3-O_2-mixtures [17-20]. In all articles NH_x species, in particular imide-groups, were reported to be adsorbed or formed at the copper surface what should led to resonances in the N K-edge NEXAFS spectra. Furthermore, hydroxyl groups [17], H_2O_2 [18] or water [15,16,19,20] were the co-products from oxygen stemming either from Cu-O-rows [15,16] or "hot" transient oxygen [18-20].

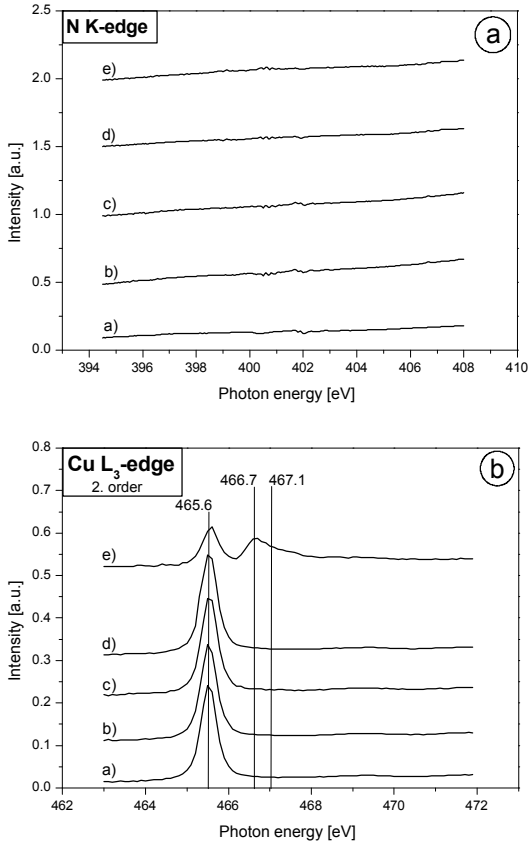

Fig. 5: NEXAFS spectra (difference spectra) at the N K-edge (a) and the Cu L_3-edge (b) from the reaction at p_{abs} = 1.2 mbar, NH_3:O_2 = 1:12 at a) 45 min. at 470 K, b) 15 min. at 570 K, c) 90 min. at 570 K, d) 15 min. at 670 K, and e) 100 min. at 670 K. The N and Cu spectra were recorded successively at each temperature / time; one specrum takes ca. 10 min. to record.

It is pointed out that the conditions of these studies differ significantly from these used here: First, the pressure in the UHV investigations was always below 10^{-6} mbar, whereas we are working in a pressure range six orders of magnitude higher. That the pressure plays an important role in even much smaller variations is obvious from the present data. Second, the UHV experiments were performed in an ammonia-rich gas mixtures with NH_3:O_2 of about 30:1 to 36:1. The third important difference is the temperature: The maximum temperature of the UHV measurements was 400 K (or below), where the high-pressure data indicates no conversion at all.

In addition, recent quantum-chemical studies of this reaction [21,22] provide enthalpies of the different reaction steps. A major result of these studies is the preference of an oxydehydrogenation of ammonia on a surface with pre-adsorbed oxygen over a clean copper surface. But it is also clearly shown that the reaction of adsorbed NH-groups with adsorbed atomic oxygen or OH-groups to adsorbed atomic nitrogen is exothermic. Therefore it is rather unlikely that on a copper metal surface and in excess oxygen the ammonia oxidation will stop at the level of imide and not react completely to either N_2 or NO_x. No imide species were identified at significant coverages under the present conditions which does, however, not rule out their relevance as transient intermediates with steady state coverages below ~0.05 monolayers.

The fast reduction of copper (II) oxide to copper (I) oxide and further formation of copper (I) nitride at p_{abs} = 0.4 mbar and its absence at p_{abs} = 1.2 mbar shows that this reaction is strongly pressure dependent. An explanation of this phenomenon by means of competitive adsorption is not sufficient, because the ammonia-to-oxygen ratio doesn't change, thus the ratio of the hits on the surface of both gases is the same and, in addition, the temperature is similar in both cases. A more likely explanation can be given if one considers the kinetics of the reduction of CuO and the re-oxidation of Cu_2O, respectively. The dependence of the reaction rates from the partial pressures of the gas phase components oxygen and ammonia may not to be the same for both reactions. The reaction order of the reoxidation can be stronger affected by the oxygen partial pressure than the reduction by the ammonia partial pressure. Consequently the catalytic reaction will be influenced by the partial pressures of each gas (and not of their ratio), and thus its chemical potential, what becomes visible in the results of our investigation.

The role of the oxide species

A comparison of the selectivities in Table 1 with the copper oxide detectable from the Cu L_3-edge NEXAFS spectra (Fig. 3b and 5b) reveals that a high N_2 selectivity like at p_{abs} = 0.4 mbar appears along with an intense copper (I) oxide signal (466.7 eV) whereas high NO selectivity is linked to a strong copper (II) oxide resonance (465.6 eV). This leads to the assumption that the production of N_2 and NO, respectively, are catalyzed by these different copper oxides. To substantiate this, an additional experiment was carried out under the same conditions except of an increase of the pressure to p_{abs} = 0.8 mbar. At this intermediate pressure, a steady but slow change of the catalyst surface composition from CuO to Cu_2O is detectable in the NEXAFS spectra (not shown here) together with a simultaneous transition in the reaction product mix from NO to N_2. A correlation of nitrogen and nitric oxide production with the surface abundance of copper (II) oxide is presented in Fig. 6. This correlation gives clear evidence that the partial oxidation of

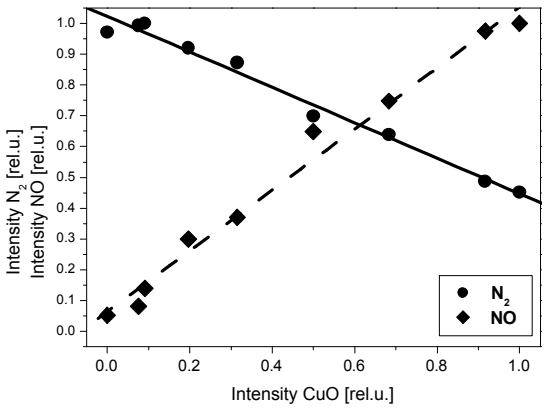

Fig. 6: Correlation of the relative intensities of N_2 (●, solid line) and NO (◆, dashed line) with the intensity of CuO for the ammonia oxidation at 0.8 mbar, 670K and NH_3:O_2 = 12.

ammonia to nitrogen is catalyzed by Cu_2O, whereas CuO is the active phase in the total oxidation to NO.

Conclusions

In the present work the important influence of the pressure at which a reaction takes place on the reaction path and the product distribution was shown. At a temperature of 570 K and 670 K and at a total pressure of p_{abs} = 0.4 mbar a fast deactivation of copper in the ammonia oxidation occurs due to nitride formation, whereas at p_{abs} = 1.2 mbar no decrease in activity is detectable and no copper nitride is formed within 2 hours at 570 K and 670 K, respectively. During reaction at 1.2 mbar no imide species could be detected on the catalyst surface as they were found in UHV investigations.

Furthermore, it was shown that the partial oxidation and the total oxidation of ammonia are catalyzed by different copper oxides: CuO was identified to be the active phase in the total oxidation to NO, whereas Cu_2O was found to catalyze the desired partial oxidation of ammonia to nitrogen.

The marked dependence of the reaction profile on very moderate pressure changes reveal the following points:

a) No reliable data about the oxidation state of copper can be obtained by ex-situ or reaction-quenched experiments.

b) The chemical potential of the gas phase regulates the abundance of Cu, Cu_2O and CuO sensitively at gas compositions relevant for tail gasses.

c) CuO is surface-reduced to Cu_2O at high total pressures as we found a significant N_2 selectivity in the absence of a detectable Cu_2O surface concentration (the surface sensitivity of our method decreases with total pressure).

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