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Comparison of oxidized polycrystalline copper foil with small deposited copper clusters in their behavior in ammonia oxidation: an investigation by means of *in situ* NEXAFS spectroscopy in the soft X-ray range

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The oxidation of ammonia to nitrogen or nitric oxide was investigated using on the one hand a polycrystalline copper foil and on the other hand deposited copper clusters prepared with the inert gas aggregation technique. The behavior in the oxidation of ammonia of both model catalysts was studied using *in situ* near-edge X-ray absorption fine structure (NEXAFS) spectroscopy in the soft X-ray range and mass spectrometry. It is shown that the copper foil reacts in a similar way to the copper clusters. Differences appear only with respect to the reaction temperature required, which is lower for the cluster sample. It can be concluded that the results obtained in experiments with polycrystalline copper foil are exemplary for and can be transferred to a supported copper catalyst consisting of small copper particles.

KEY WORDS: catalytic oxidation; ammonia; polycrystalline copper foil; copper cluster; *in situ* NEXAFS; copper(I) nitride.

1. Introduction

The partial oxidation of ammonia to nitrogen and water is a widely used process for ammonia slipstream treatment after DeNOx-SCR [1] or for purification of reformates in fuel cell applications [2]. Recent investigations showed that copper can be used as a catalyst for this oxidation [1–3]. We studied ammonia oxidation over copper with *in situ* near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and were able to show that the catalytically active surface for the partial oxidation to nitrogen is copper(I) oxide whereas copper(II) oxide catalyzes the total oxidation to nitric oxide [4]. In contrast to our investigations with polycrystalline copper foil as model catalyst, the catalysts used in industrial applications are oxide- or zeolite-supported copper particles and clusters, respectively. Therefore, the question arises as to whether the results obtained with copper foil are exemplary also for supported catalysts. With regard to many studies of the reaction behavior of clusters or small particles in general, the clusters are expected to react at some lower temperature. Furthermore, it remains to be shown that small copper particles react in the same way as and to give the same products as extended copper surfaces.

To answer these questions, we prepared small copper cluster with an average diameter of 2.8 nm by means of the inert gas aggregation technique on a gold grid covered with an amorphous carbon film, which is typically used in TEM. These copper clusters had to undergo the same reaction conditions as the copper foil that we investigated before, except for the temperature, which was increased very carefully from room temperature to 470 K while the NEXAFS spectra were recorded in a flow-through reactor. Before and after the reaction TEM images were taken to verify the morphology of the clusters.

2. Experimental

All experiments were carried out in a system consisting of two UHV chambers. One was used as the reaction chamber and was separated from the second by a 100 nm silicon nitride X-ray window providing a 4 mm aperture and withstanding a pressure difference of at least 100 mbar. The second chamber with a base pressure of $p < 5 \times 10^{-9}$ mbar was connected to the undulator beamline UE56/2-PGM1 [5], at BESSY II, the Berlin electron storage ring for synchrotron radiation. The mixture of the reaction gases was controlled by calibrated mass flow controllers, and the pressure was regulated with a valve in the outlet stream. The gas phase right above the sample was sucked off via a capillary (1 mm i.d.) and analyzed in a mass spectrometer. Thus, continuous monitoring of the gas phase was provided and gave the possibility to associate the actual gas-phase composition with the NEXAFS spectra. Therefore, a correlation of the reaction products and the conversion with the surface state of the catalyst was feasible.

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The NEXAFS spectra were recorded with a detector device operating in total electron yield mode (TEY) that has been described in detail [6–9]. The main feature of this detector device is the simultaneous but independent recording of the electrons emitted only from the gas phase and a mixed signal representing electrons from both the surface and the gas phase. After subtracting the pure gas phase from the mixed spectrum, one obtains the desired NEXAFS spectra, which show resonances only from the sample [4].

The cluster sample was prepared using the gas aggregation technique [10,11], which allows one to produce metal clusters in both the large size range (10–30 nm) and the intermediate size range (1–10 nm). The experimental setup that was used here has been described in detail elsewhere [12,13]. In this case the copper clusters were generated with a mean diameter of 2.8 nm. Copper (Alfa, 99.99%) was evaporated from a Knudsen cell by direct heating into an argon gas atmosphere. The copper vapor was efficiently cooled by collisions with gas atoms by means of a liquid nitrogen cooling trap. In regions of sufficiently high supersaturation a homogeneous nucleation occurred. This aggregation process was interrupted by a helium-cooled cryo-pump where most of the argon gas was condensed. An aperture on the axis of this pump allowed the production of a collimated cluster beam. The clusters were then deposited on an Au grid covered with an amorphous carbon film usually used in electron microscopy. After the deposition of the clusters the particles were exposed to air for 2 h and subsequently their distribution was investigated with an electron microscope (Philips CM200 FEG, maximum resolution 0.18 nm). In order to monitor if the reaction conditions had caused morphological changes such as sintering, the sample was reinvestigated by means of TEM after the reaction.

The copper foil (99.99+%, Goodfellow), which has a size of *ca.* 25 × 13 mm, was prepared with a Cu_2O surface by complete oxidation to CuO at 670 K in 1.0 mbar O_2 and subsequent UHV annealing to 720 K. After this procedure, the NEXAFS spectrum at the Cu L_3 edge showed only resonances of copper(I) oxide [14].

The reaction conditions used for both the copper foil and cluster experiments was a mixture of ammonia (99.98%, Linde, flow rate 0.38 Sml/min) with 4.5 Sml/min of oxygen (99.9990%, Linde), providing an $NH_3:O_2$ ratio of 1:12. The overall pressure used in these investigations was $p_{abs} = 1.2$ mbar, and the temperature was increased stepwise from 300 to 670 K (foil) or 470 K (cluster).

3. Results

3.1. Copper foil

We recently published results on the pressure dependence of the ammonia oxidation reaction obtained with copper foil as model catalyst which was preoxidized to copper(II) oxide as initial state [4]. It was shown that a temperature of at least 570 K is needed to ignite the reaction and an increase to 670 K doubles the ammonia conversion. However, at an absolute pressure of $p_{abs} = 0.4$ mbar an immediate reduction to Cu_2O occurred, followed by deactivation within 1 h due to the formation of copper(I) nitride. In contrast, at $p_{abs} = 1.2$ mbar the reaction remained steady for at least 2 h, but a very slow shift in the distribution of the products toward less nitric oxide and increased nitrogen occurred. Simultaneously, the catalyst surface was reduced from pure CuO to a mixture of CuO and Cu_2O. At an intermediate pressure of $p_{abs} = 0.8$ mbar a slow but steady change in the main product gas from nitric oxide to nitrogen was visible with a simultaneous modification of the catalyst surface from CuO to Cu_2O. Thus, a structure–function relation was established, indicating that copper(I) oxide catalyzes the desired partial oxidation of ammonia to nitrogen, whereas the total oxidation to nitric oxide is catalyzed by copper(II) oxide.

To support this, an additional experiment was carried out at an absolute pressure of $p_{abs} = 1.2$ mbar, starting with copper(I) oxide as the initial state of the copper foil. The mass spectrometric data for this reaction are presented in figure 1. After increasing the temperature to 670 K, the ammonia oxidation occurs with a maximum conversion of $X_{NH_3} = 41.9\%$ after 5 min time on-stream, which is in good agreement with the results obtained earlier [4]. As expected from the previous results, the selectivity toward nitrogen is high ($S_{N_2} = 76.9\%$) at the beginning of the reaction. Within 3 h the conversion of ammonia drops to $X_{NH_3} = 18.6\%$ and the selectivity toward nitrogen is decreased to almost 50%. The NEXAFS spectra of the copper L_3 edge (shown in figure 2) reveal the reason for this deactivation: the

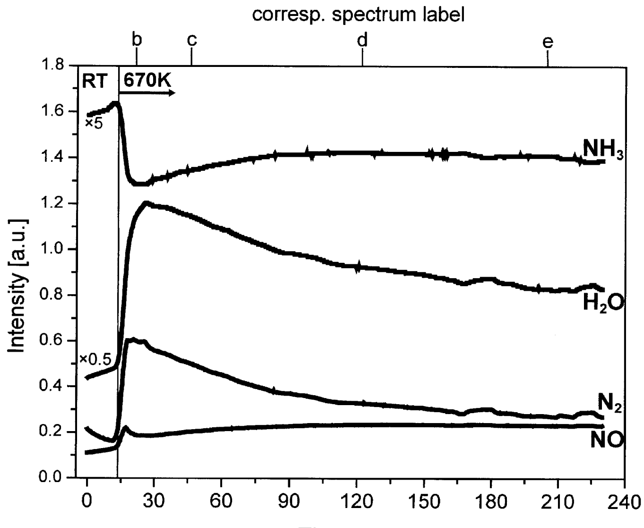

Figure 1. Mass spectra of NH_3, NO, H_2O and N_2 of the reaction at $p_{abs} = 1.2$ mbar, $NH_3:O_2 = 1:12$, copper foil.

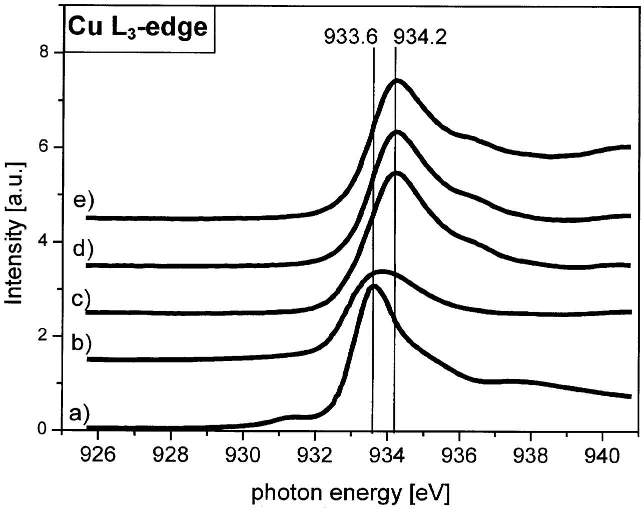

Figure 2. NEXAFS spectra at the Cu L_3 edge from the reaction of the copper foil at $p_{\mathrm{abs}} = 1.2\,\mathrm{mbar}$, $NH_3 : O_2 = 1:12$, at (a) room temperature, (b) after 5 min at 670 K, (c) after 30 min at 670 K, (d) after 110 min at 670 K and (e) after 190 min at 670 K.

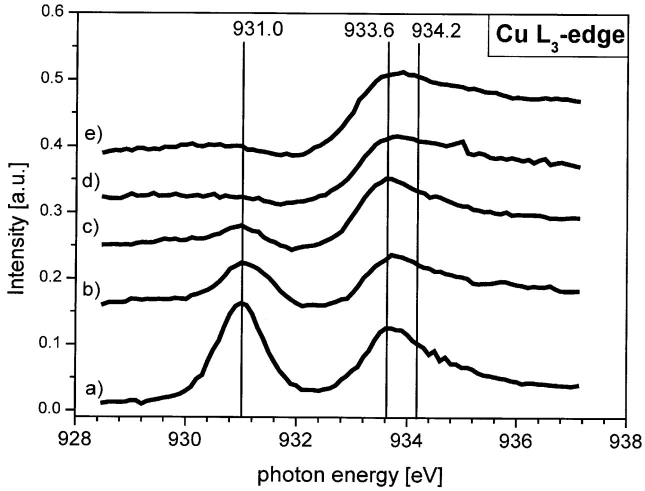

Figure 3. NEXAFS spectra at the Cu L_3 edge from the reaction of the copper cluster at $p_{\mathrm{abs}} = 1.2\,\mathrm{mbar}$, $NH_3 : O_2 = 1:12$, at (a) room temperature, (b) after 5 min at 370 K, (c) after 5 min at 420 K, (d) after 30 min at 420 K and (e) after 5 min at 470 K.

formation of copper(I) nitride, which is identified by the resonance at 934.2 eV in contrast to the initial copper(I) oxide with its resonance at 933.6 eV [14]. The reason for the remaining activity is the co-existence of copper oxide patches with the nitrided surface, as indicated by the broadened resonance structure for the nitride, which is not induced by the spectral resolution of the experiment.

In contrast to a pressure of $p_{\mathrm{abs}} = 0.4\,\mathrm{mbar}$ [4], it takes several hours and thus very much longer to form the copper(I) nitride. Moreover, only partial deactivation ending in a reduced steady-state activity of the copper catalyst takes place at an absolute pressure of $p_{\mathrm{abs}} = 1.2\,\mathrm{mbar}$, providing a larger excess of active oxygen required to prevent irreversible, complete nitridation.

3.2. Copper clusters

The NEXAFS spectra of the copper L_3 edge from the cluster sample in figure 3 show that the initial state of the cluster was a mixture of copper(I) oxide (933.6 eV) and copper(II) oxide (931.0 eV). Since a freshly mounted copper foil never exhibited any CuO but only Cu_2O, this gives evidence for the high reactivity of these small particles even at room temperature. The cluster sample was heated only up to 470 K in the reaction atmosphere. This temperature is high enough to cause a reduction of the copper(II) oxide to Cu_2O, as can easily be seen from the disappearance of the CuO resonance at 931.0 eV. The formation of copper(I) nitride is visible from the obvious broadening of the resonance if compared with spectrum (a), which is caused by the superposition of a large contribution from Cu_2O with a small contribution from Cu_3N, resulting in the reverse situation as discussed with figure 2. The spectral resolution is reduced here compared with the experiments with copper foil owing to the extremely small amount of the sample (about 100 nmol of copper). The spectral behavior qualitatively similar to that discussed with the copper foil gives evidence that a reaction with the ammonia–oxygen mixture occurred, and the well known formation of copper(I) nitride took place. The mass spectrometric data give an additional hint on the catalytic activity of copper clusters in the ammonia oxidation as shown in figure 4. Small changes occur in the volume flow from the reaction cell into the differentially pumped mass spectrometer due to varying gas temperature and condensation problems that might induce ion current changes, although no reaction took place. The ion current signals were normalized on the signal of $m/z = 15$. The masses $m/z = 14$, 15 and 17 represent fragments of ammonia, and therefore the normalized $m/z = 17$ signal is a straight line. The resulting signal for $m/z = 14$ clearly shows distinguishable peaks at 44 min (370 K) and at 81 min (420 K) that can be caused only by nitrogen-containing species other than ammonia. Since a peak for $m/z = 28$ coincides with the peak in the signal for $m/z = 14$, it can be concluded that this signal is not an artifact (ensured by the normalization procedure) and can be attributed unambiguously to the production of N_2. A peak in the ion current of NO (24 min) is observed additionally to the peak for N_2 at 420 K. The yield of NO and N_2 shows peaks which occur not immediately after the increase in temperature. The unsatisfactory thermal contact between the TEM grids with the deposited cluster on it and the heating stage might be the reason for the delay.

The TEM image of the copper cluster sample before the reaction is presented in figure 5. The clusters with a mean size of 2.8 nm are distributed randomly over the support. The TEM image after the reaction (figure 6) and the comparison of size distribution of the clusters

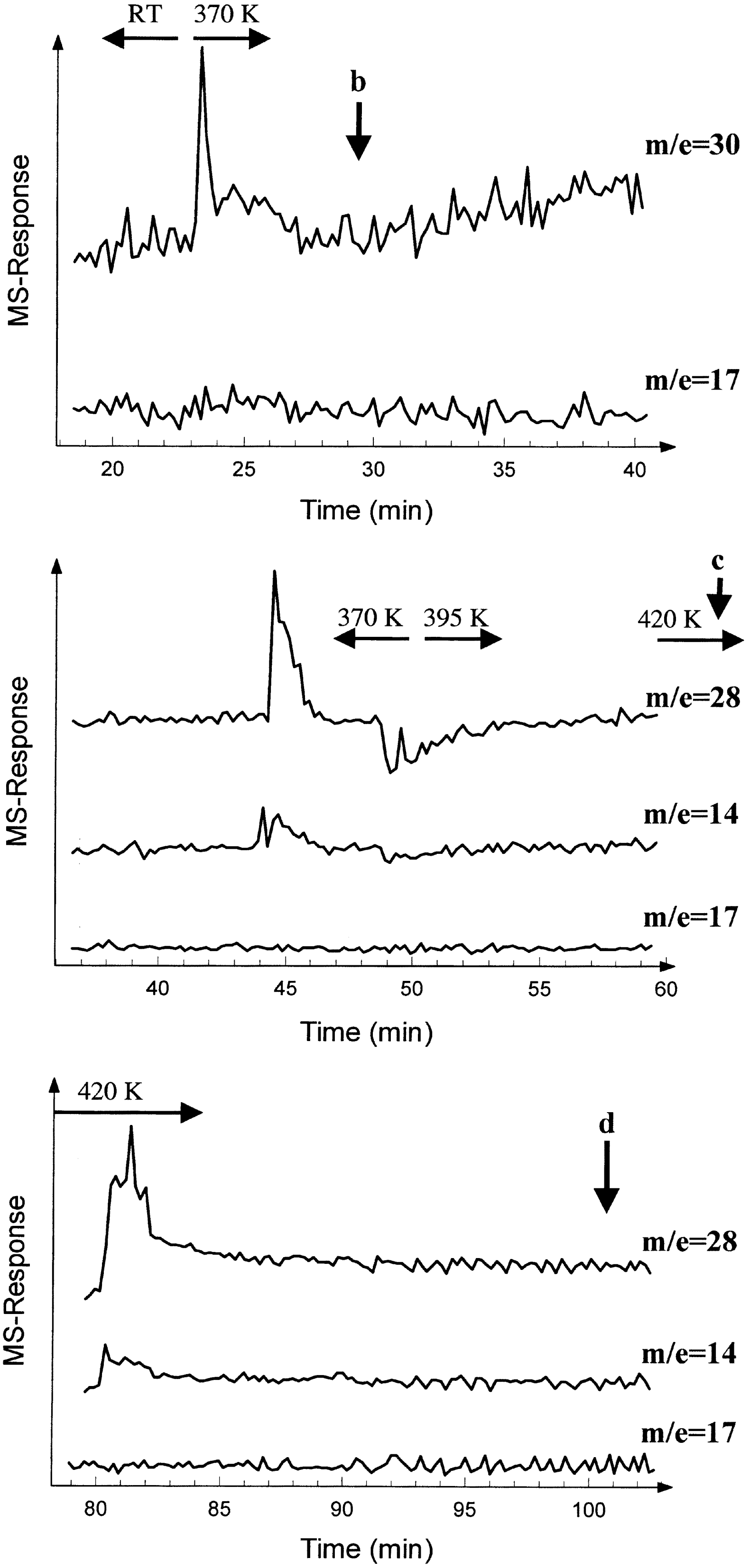

Figure 4. Mass spectrometer signal of NO ($m/z = 30$) and N_2 ($m/z = 28.14$) normalized on the ion current of ammonia ($m/z = 15$) are plotted as a function of time. The masses $m/z = 14$, 15 and 17 represent fragments of ammonia. The straight line of $m/z = 17$ after normalization demonstrates the successful removal of artifacts. Since the peaks of $m/z = 14$ at 44 min (370 K) and 81 min (420 K) coincide with peaks in $m/z = 28$, it can be concluded that the signal is due to the formation of nitrogen. The temperature of the catalyst is indicated. The time scale is given relative to the detection moment of NEXAFS spectrum (a) in figure 3. The detection moment of NEXAFS spectra b, c and d (figure 3) is indicated by arrows in the plot.

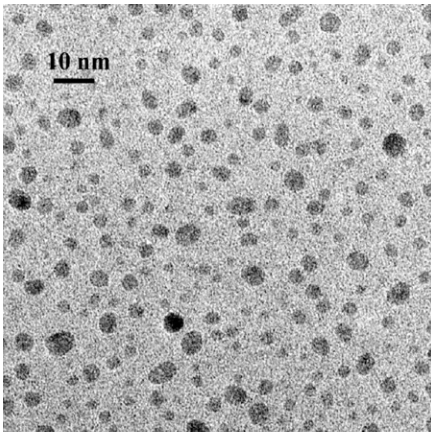

Figure 5. TEM image (*ca.* 110 × 110 nm) of the copper cluster sample before the reaction. Average particle diameter: 2.8 nm.

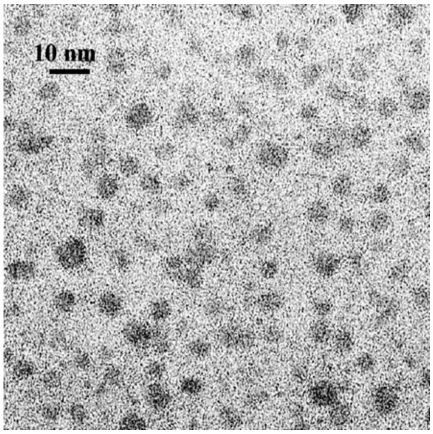

Figure 6. TEM image (*ca.* 110 × 110 nm) of the copper cluster sample after the reaction. Average particle diameter: 4.45 nm.

before and after reaction in figure 7 reveal that the average diameter of a large fraction of the clusters had increased, indicating partial sintering of the weakly supported clusters. However, owing to the fact that no film formation due to spreading of the clusters occurred, it can be concluded that evidently the clusters have reacted. Moreover, the contrast of the clusters after reaction is slurred, indicating a loss of internal ordering as a consequence of the spectroscopically observed chemical transformation.

4. Discussion

The results obtained with a copper foil as model catalyst, which are presented here and in an earlier paper [4], show that deactivation of the partial oxidation activity due to formation of copper(I) nitride cannot be avoided at all pressures from 0.4 to 1.2 mbar after the sample has reached a maximum abundance of Cu_2O. The nitride formation as a possible reaction of copper oxides with ammonia was found first by Schroetter in 1841 [15], but could also be seen in recent UHV studies of copper single crystals [16,17]. It can be concluded that the clusters also reacted with the ammonia because of the increasing formation of Cu_3N which is visible in the NEXAFS spectra of the copper cluster sample (figure 3, spectra c → e). The formation of copper(I) nitride gives evidence that the ammonia oxidation occurred at these clusters since there is no other possibility of forming Cu_3N in this atmosphere. Additionally, the production of NO and N_2 and therefore the catalytic activity of the copper clusters could be demonstrated by the normalization of the related ion current on the ion current of ammonia ($m/z = 15$). Peaks in the ion current of $m/z = 30$ and 28 indicate at least the temporary

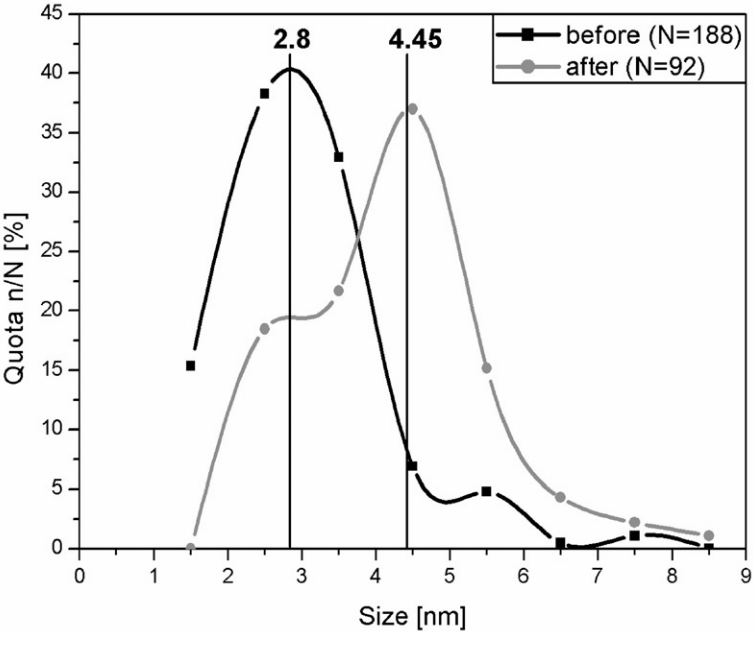

Figure 7. Size distribution of the copper clusters before (■) and after (●) the reaction.

formation of NO and N_2 by the catalytic oxidation of ammonia over copper clusters. The formation of N_2 in the gas phase coincides with the formation of Cu_3N on the catalyst surface. The decreasing abundance of CuO on the surface (figure 4, spectra a and b) coincides with the formation of NO. Therefore, the same structure–function relation as established for the copper foil can be assumed for the interaction of the ammonia–oxygen mixture with the copper clusters. Even if the TEM images show that the clusters had slightly sintered, the particular cluster topology remained and no spreading and film formation occurred. Therefore, the NEXAFS spectra in figure 3 were evidently obtained from the clusters, which reacted with the ammonia.

5. Conclusions

We have presented results obtained with copper foil as a model catalyst and compared them with those obtained with deposited copper clusters. Since copper(I) nitride formation occurred in both cases, it can be concluded that the foil reacts in a similar way and to give the same products as small particles or clusters, except for the reaction temperature, which is much lower in the latter case. The observed peaks in the ion current of NO and N_2 give a hint on the catalytic activity of copper clusters in the ammonia oxidation. It can be assumed that the experiments and results obtained with copper foil as a model catalyst in ammonia oxidation are exemplary for the reaction behavior of copper clusters or small particles. The results of an *in situ* investigation of so-called nanoparticles under the mentioned reaction conditions (1.2 mbar, 470 K) presented here can be regarded as an important step in the investigation of small particles and their reaction behavior, both scientifically and methodically.

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