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

R.W. Mayer [a,*], M. Hävecker [b], A. Knop-Gericke [b] and R. Schlögl [b]

[a] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
E-mail: mayer@fhi-berlin.mpg.de
*[b] BESSY GmbH, Albert-Einstein-Allee 15, 12489 Berlin, Germany*

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 correlation of different reaction products to the current surface structure of the catalyst. It is shown that a change in total pressure from 0.4 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.

KEY WORDS: catalytic oxidation of ammonia over copper; partial oxidation; copper(I) nitride; copper oxides; *in situ* NEXAFS

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

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (1)$$
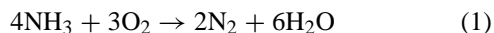
is relevant for a wide range of applications [3] and the subject of this investigation. In addition to reaction (1) the total oxidation

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (2)$$
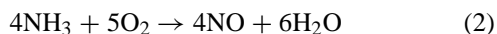
is preferred in oxygen-containing feed gas. Because of the production of hazardous nitric oxide this reaction path has to be totally suppressed. This is the most important challenge for the design of a suitable catalyst.

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 one 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 elucidation of 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].

2. Experimental

All experiments were carried out in a two-chamber UHV system, of which one chamber with a base pressure of $<5 \times 10^{-9}$ 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 ($\varnothing$ 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 [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 of 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
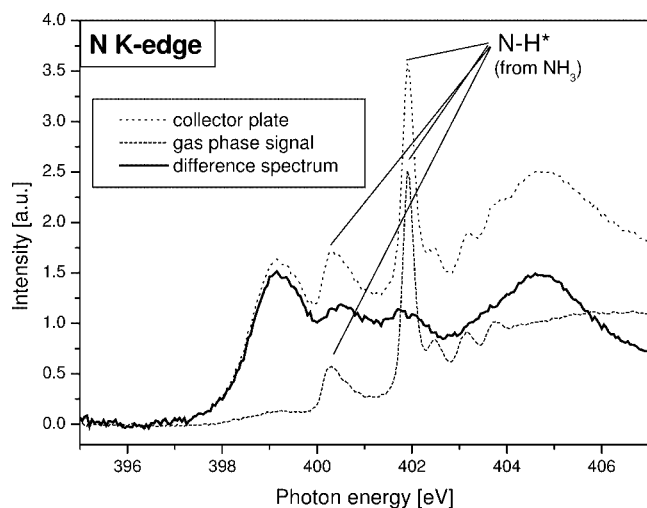
Figure 1. Example of data treatment at the N K-edge: the spectrum from the collector plate (· · ·) is adjusted to the gas phase signal (- - -) until the N–H* resonances disappear in the difference spectrum (—), which then contains resonances from the sample only.

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 (figure 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.

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 approximately 30 min, leading to a reproducible initial state of the catalyst of copper(II) oxide. The investigations were performed in the continuous-flow mode with ammonia (99.98%, Linde) and oxygen (99.9990%, Linde) flows of 0.38 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 an oil-free foreline pump and monitored with a Baratron pressure gauge, which measures independent of the composition of the gas phase. A quadrupole mass spectrometer is connected to the reaction chamber *via* a capillary (⌀ 3 mm) sucking off the gas phase just above the sample.

3. Results and discussion

3.1. $p_{abs} = 0.4$ mbar

The partial pressure profiles in figure 2 were obtained at an total pressure of $p_{abs} = 0.4$ mbar with a stepwise in-
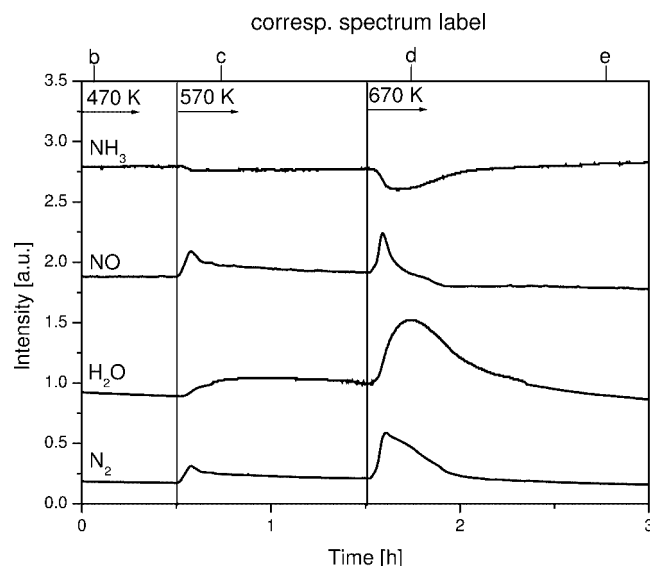

Figure 2. Mass spectra of NH_3, NO, H_2O and N_2 of the reaction at $p_{abs} = 0.4$ mbar, $NH_3 : O_2 = 1 : 12$, with increasing temperature.

Table 1
Ammonia conversion and selectivities to N_2 and NO for reaction at 0.4 mbar (figure 2) and 1.2 mbar (figure 4) at different temperatures.

	0.4 mbar[a]		1.2 mbar	
	570 K	670 K	570 K	670 K
X_{NH_3} (%)	4.1	20.1	24.7	49.3
S_{N_2} (%)	80.5	89.5	52.5	29.2
S_{NO} (%)	19.5	10.5	47.5	70.8

[a] The values for 0.4 mbar represent the maxima.

creased temperature from 300 to 670 K. Below 470 K no conversion was detectable and initial ammonia oxidation occurred at 570 K. The conversion and selectivity data are collected in table 1. Within 45 min the conversion dropped to 20% of its maximum value. At 670 K the activity, yield and deactivation are different with 90 min 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.

The N K-edge spectra in figure 3(A) show that nitrogen-containing species grow on the catalyst surface, indicated by the increasing resonance intensities. From comparison with figure 2 it occurs that this nitrogen species is blocking the surface. In figure 3(B) the resonances of the copper L_3-edge at 465.6 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 cannot 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 investiga-
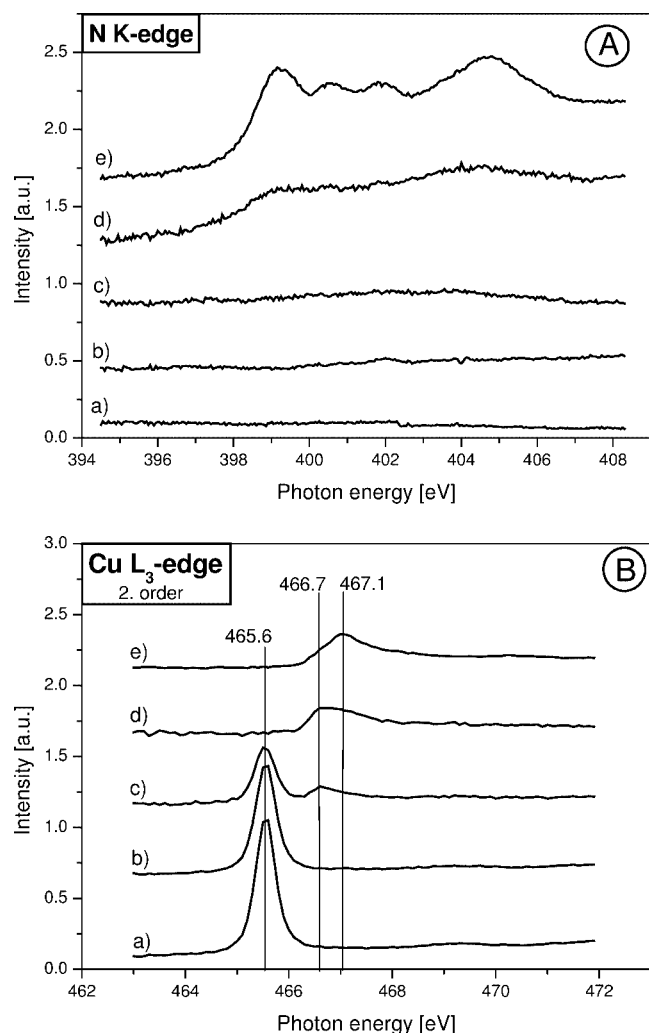
Figure 4. Mass spectra of NH_3, NO, H_2O and N_2 of the reaction at $p_{abs} = 1.2$ mbar, $NH_3 : O_2 = 1 : 12$, with increasing temperature.

Figure 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 spectrum takes *ca.* 10 min to record.

tions [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 figure 2.

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 to 150 min.

3.2. $p_{abs} = 1.2$ mbar

The mass spectrometer data for the reaction at $p_{abs} = 1.2$ mbar are presented in figure 4. It is easy to see, that the

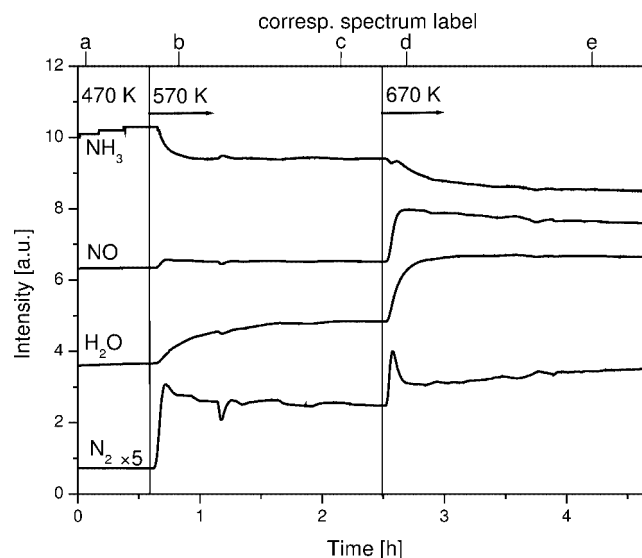reaction profile is completely different from that at $p_{abs} = 0.4$ mbar. The ammonia oxidation ignites at 570 K and remains in steady operation at this temperature. A rise in steady state conversion of ammonia and a change in selectivities (see table 1) are detected after increasing the temperature to 670 K. The corresponding NEXAFS spectra are presented in figure 5: At the N K-edge (figure 5(A)) 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 (figure 5(B)) exhibits at low temperature ($T \leqslant 570$ 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.

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 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].

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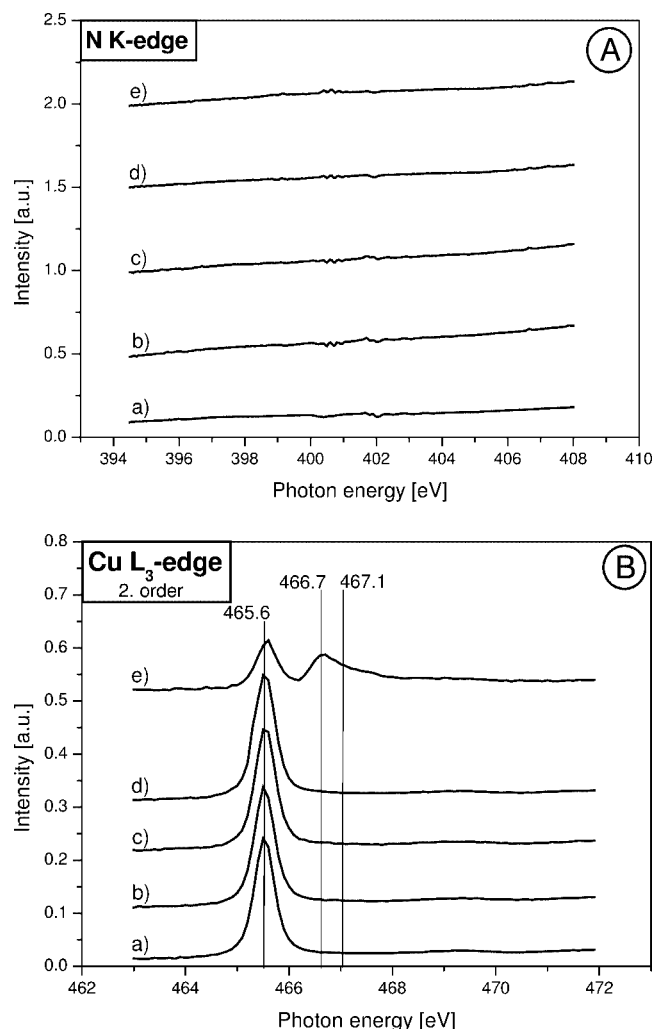
Figure 5. NEXAFS spectra (difference spectra) at the N K-edge (A) and the Cu L_3-edge (B) from the reaction at $p_{abs} = 1.2$ mbar, $NH_3 : O_2 = 1 : 12$ at (a) 45 min at 470 K, (b) 15 min at 570 K, (c) 90 min at 570 K, (d) 15 min at 670 K and (e) 100 min at 670 K. The N and Cu spectra were recorded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

much smaller variations is obvious from the present data. Second, the UHV experiments were performed in 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 oxy-dehydrogenation 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 $\sim$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 does not 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.

3.3. 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 (figures 3(B) and 5(B)) 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, is 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 figure 6. This correlation gives clear evidence that the partial oxidation of ammonia to nitrogen is catalyzed by Cu_2O, whereas CuO is the active phase in the total oxidation to NO.

4. 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 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
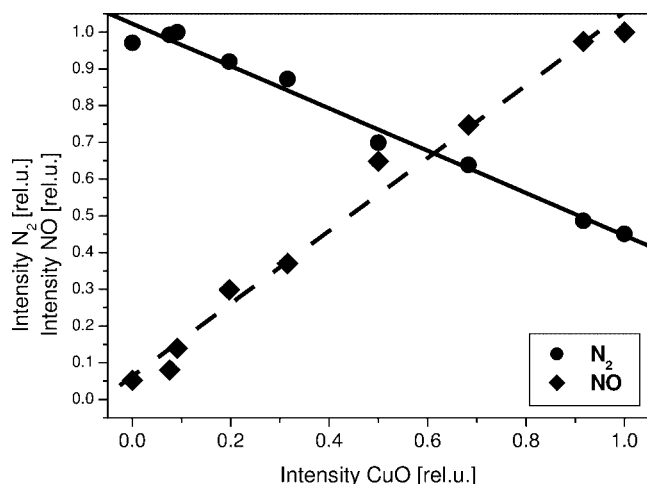
Figure 6. Correlation of the relative intensities of N_2 (—) and NO (- - -) with the intensity of CuO for the ammonia oxidation at 0.8 mbar, 670 K and $NH_3 : O_2 = 12$.

no decrease in activity is detectable and no copper nitride is formed within 2 h at 570 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 reveals 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 gases.

(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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