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Oxidation of NH_3 on polycrystalline copper and Cu(1 1 0): a combined FT-IRAS and kinetics investigation

Isabelle Louis-Rose, Christophe Méthivier, Claire-Marie Pradier*

Laboratoire de Physico-Chimie des Surfaces, Ecole Nationale Supérieure de Chimie de Paris,
11 rue P. et M. Curie, 75005-Paris, France

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Abstract

The kinetics of the reaction of oxidation of ammonia on polycrystalline copper, has been investigated, in a re-circulating reactor, and correlated to a characterisation of the catalyst surface at different extent of conversions.

The rapid formation of a nitride or oxynitride phase and its reactivity have been demonstrated. Under oxidising conditions, $P_{NH_3} = P_{O_2}$, and up to 650 K, dinitrogen is the only product of the reaction; N_2O being formed when T or P_{O_2} increases further. The correlation of these kinetics results to an in situ characterisation of the same reaction at RT by Fourier-transformed infrared reflection-absorption spectroscopy (FT-IRAS), on a well defined Cu(1 1 0) surface, led to the following conclusion: two reaction pathways contribute to the conversion of ammonia: (i) its decomposition on copper; (ii) the reaction between ammonia molecules and oxygen adsorbed from the gas phase. The major adsorbed species is oxygen; intermediate species are NH_2, NH and possibly HNO formed when the oxygen surface concentration is sufficient. Increasing the pressure of oxygen induces, at high T, the formation of nitrous oxide; N_2O results from an oxidation of the surface copper nitride or from the interaction of two surface HNO intermediates.

Keywords: Ammonia catalytic oxy-dehydrogenation; Cu(1 1 0); N_2O; FT-IRAS; XPS

1. Introduction

Reactivity of ammonia has been extensively studied for the selective catalytic reduction (SCR) of NO ($4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$). Noble metals, transition metal oxides and zeolites-based catalysts are reported to be good catalysts for the SCR with high conversion at low temperature (470–770 K) [1,2]. Beside that, many papers have reported on the selective catalytic oxidation (SCO) of ammonia in connection with SCR process of NO_x. Most of the oxide catalysts for the SCR of NO_x are also effective for the SCO of ammonia [3–6].

The SCO of ammonia occurs following Eq. (1) at low temperature (<670 K):

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{1}$$

Nitrous oxide, an undesired by-product, may also be formed following Eq. (2):

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \tag{2}$$

Since N_2O is a greenhouse gas and contributes to the destruction of the ozone in the stratosphere, an effective catalyst should have a high selectivity towards

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* Corresponding author.
E-mail address: pradier@ext.jussieu.fr (C.-M. Pradier).

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nitrogen [5,7–9]. It is of primary importance to better understand the conditions of its formation [10].

According to Il'Chenko and Golodets [8], the oxidation of ammonia in the absence of catalyst starts at 650–670 K and leads to N_2 and H_2O. The catalytic oxidation of ammonia occurs at temperatures below 670 K on oxide catalysts such as Co_3O_4, FeO_3, MnO_2, V_2O_5, CuO [5,7,9,11–13] but in most cases, nitrous oxide is formed. Oxides such as CoO_3 and MnO_2, are the most active but also less selective towards N_2, whereas the less active, WO_3 and MoO_3, have the better selectivity towards N_2. CuO is an intermediate catalyst with rather good catalytic activity and selectivity towards N_2 [7].

Some authors have focused their attention on the mechanism of the reaction by studying the kinetics of the oxidation of NH_3 by O_2 [5,6,8] or characterising the interaction of NH_3 in the presence or absence of O_2 on several SCO or SCR catalysts [14–16]. In a previous paper, the interaction of ammonia and oxygen was investigated at room temperature on Cu(1 1 0), and the formation of dinitrogen had been made clear [17]. In the present paper, we aim at understanding the reaction mechanism of the oxidation of NH_3 by O_2 on copper by combining a kinetics study of the reaction of ammonia oxidation and an in situ characterisation of NH_3 and O_2 on a well defined copper surface. These studies, tentatively bridge the gap between high vacuum surface studies and real catalysis. They should enable to determine the surfaces species formed in situ in the presence of the reactants and bring new insights into the mechanism of the reaction, and the conditions in which N_2O can be formed.

2. Experimental

2.1. Copper substrates

Two different copper samples were used for the catalytic tests and the Fourier-transformed infrared reflection-absorption spectroscopy (FT-IRAS) characterisation, a polycrystalline plane copper sample and a Cu(1 1 0) crystal, respectively. The reason for that is that a large enough active area was necessary to get significant conversion figures, whereas a sample with a controlled structure was preferable for the UHV LEED and FT-IRAS characterisations. The copper polycrystalline sample was mechanically polished to the 1 μm grain; before all catalytic tests, it was reduced under a flow of hydrogen at $T = 870\,K$ for 1.5 h and cooled to room temperature under the hydrogen flow. The Cu(1 1 0) crystal was oriented to within 1° of its crystallographic orientation using X-ray back-reflection diffraction, mechanically and electrochemically polished before being mounted in the UHV chamber. The surface was then cleaned by successive Ar^+ ion sputtering ($P = 10^{-2}$ Pa, 500 V), heating up to 900 K to restore the surface crystallinity. Auger spectra were recorded with a CMA Riber spectrometer.

All XPS experiments were performed with a VG Escalab MK II spectrometer. An Al Kα anode (1486.6 eV) was used. The spectrometer was calibrated against Cu $2p_{3/2}$ at 932.7 ± 0.1 eV and Au $4f_{7/2}$ at 83.8 ± 0.1 eV. With this calibration, the C 1s line of carbon contamination appears at 284.7 eV on metallic copper. A pass energy of 20 eV was used. Data were acquired with 0.1 eV steps. The atomic fractions were obtained for each element by correcting the peak intensities with the Scofield factors [18].

When needed, oxygen was pre-adsorbed by heating the sample to 575 K under 1.3×10^{-3} Pa of oxygen during 30 min. This procedure led to a $I_{O(507\,eV)}/I_{Cu(48\,eV)}$ peak-to-peak Auger ratio equal to 0.16. The corresponding LEED pattern will be given in the following. Another procedure, $P_{O_2} = 0.1$ Pa, $T = 570$ K for 5 min led to the formation of Cu_2O in the superficial layers as checked by a punctual XPS analysis.

2.2. Catalytic reactor and reaction procedure

Catalytic experiments were performed in a re-circulation mode 800 cm^3 reactor. A mass spectrometer (MS) and a small cell, with KBr windows and a 14.5 cm^3 volume, enabling IR transmission analyses, were used to monitor the gas phase compositions during the reaction process. The reactants were introduced at partial pressures around a few 10^2 Pa in argon to reach 10^5 Pa as a total pressure. The reactor was heated to the desired temperature by an external oven and the temperature controlled by a thermocouple inserted in the oven. The rate of gas circulation was set to 2 l/h.

2.3. IRAS chamber and adsorption procedure

All absorption tests were performed in a UHV chamber that enables in situ IR measurements at grazing incidence (6°) using a FT-infrared spectrometer (NICOLET, Magna 550) equipped with a MCT wide-band detector, and two ZnSe windows transmitting infrared light between air and vacuum. The noise peak-to-peak intensity was, under these conditions, equal to 5×10^{-5}. A typical spectrum was obtained by averaging the signal over 600 scans at a resolution of $4\,\mathrm{cm}^{-1}$. Some spectra were recorded at $8\,\mathrm{cm}^{-1}$ or after only 300 or 100 scans when kinetics data were searched. These conditions enabled to record a spectrum every 3 or every min. A spectrum was recorded first before gas admission and used as a reference. Ammonia, and oxygen adsorption experiments were performed at room temperature, under dynamic conditions.

3. Results

3.1. Catalytic activity

The interaction of pure ammonia, $P = 2 \times 10^2$ Pa in argon, was first tested at 650 K on a pure metallic copper surface. Almost one-third of ammonia was converted after 110 min of reaction and surprisingly, the amount of nitrogen formed in the gas phase was extremely low. No other product was detected. The copper surface was, at the end, dull and like covered with a brown film.

Fig. 1 shows the conversion of ammonia, in the presence of oxygen, on the initially reduced copper samples, at various temperatures. All reactions were run in the presence of an equimolecular ratio, $P_{\mathrm{NH_3}}/P_{\mathrm{O_2}}$, corresponding to slightly oxidising conditions with respect to the stoichiometry of reaction (1). After a period of 10 min, during which the conversion is slow, the slope of all curves increases and only varies slightly for 30–70 min, a period that we called “stationary”; then, it decreases again showing a slower conversion of NH_3; the conversion tends to reach a maximum value that strongly depends on the temperature.

The rate of conversion indeed increases with temperature. An apparent activation energy was calculated from the rate values in the stationary stage: a value of $50\,\mathrm{kJ\,mol}^{-1}$ was found in agreement with other works [19]. The only products of the reaction, at 550 and 620 K were dinitrogen and water.

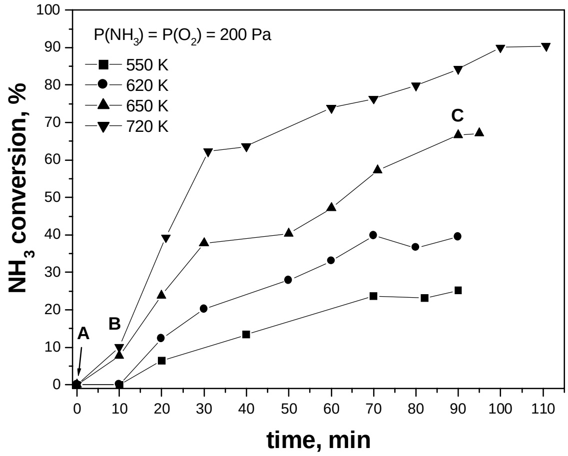


Fig. 1. Conversion of NH_3 as a function of time and at various temperatures, on copper, $P_{\mathrm{NH_3}} = P_{\mathrm{O_2}} = 200$ Pa. A, B and C marks indicate the times at which XPS analyses have been performed.

At higher temperature, N_2O was formed as a by-product of the reaction. The selectivity to N_2O increases with temperature and with time while that to N_2 decreases. The changes in the selectivity, measured 70 min after gas admission, i.e. when the conversion has almost reached a plateau, are presented in Fig. 2.

The reactant pressures were varied in order to calculate the partial orders of the reaction at 650 K.

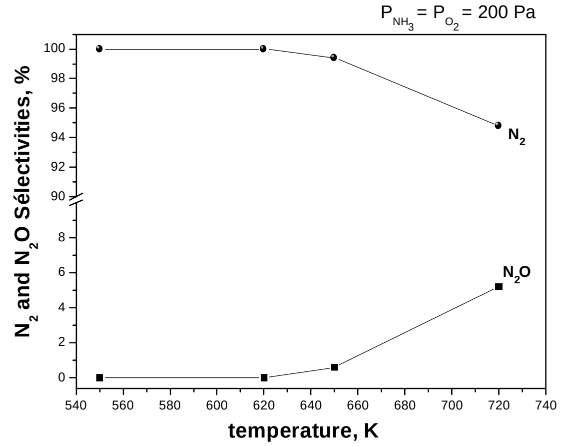


Fig. 2. Selectivity to N_2 and N_2O, at various temperatures, on polycrystalline copper after 70 min of reaction, $P_{\mathrm{NH_3}} = P_{\mathrm{O_2}} = 200$ Pa.

Table 1
Activity and selectivity of the reaction $NH_3 + O_2$ on copper for various pressures of oxygen

P_{O_2} (Pa)	Conversion of NH_3 after 20 min (%)[a]	Yield of N_2O after 20 min (%)[a]	Yield to N_2 after 20 min (%)	Conversion of NH_3 after 90 min (%)	Yield of N_2O after 90 min (%)	Yield to N_2 after 90 min (%)
100	11	0	4	26	0	17
200	24	0.1	6	67	0.2	27
1000	34	1	19	89	7	70
2800	59	3	17	94	16	62

[a] These values were calculated at the stationary stage of the reaction.

The reaction was investigated in the ranges described below and we measured the following partial orders:

- $P_{O_2} = 2 \times 10^2$ Pa and $0.6 \times 10^2\,\text{Pa} \leq P_{NH_3} \leq 2 \times 10^2$ Pa which implies $\alpha/NH_3 = 1$.
- $P_{NH_3} = 2 \times 10^2$ Pa and $1 \times 10^2\,\text{Pa} \leq P_{O_2} \leq 2 \times 10^2$ Pa which implies $\beta/O_2 = 1.2$ and $2 \times 10^2\,\text{Pa} \leq P_{O_2} \leq 28 \times 10^2$ Pa which implies $\beta/O_2 = 0.3$.

No changes in the selectivity were observed when the pressure of NH_3 varied between 0.6 and 2 mbar, whereas, passing to strongly oxidising conditions resulted in a net increase in the N_2O yield (see Table 1).

It is worth noting that, for all the values of P_{O_2} that have been tested, the conversion curve presents the same shape (see Fig. 3): little slope during the first 10 min followed by a higher rate and slow rate again after 30–40 min; for comparison, the curve showing the decomposition of ammonia alone, at 650 K, on copper is also reported in Fig. 3. In the absence of oxygen, the rate of conversion of ammonia was only reduced by a factor close to 2, compared with the result obtained in the presence of equal pressures of NH_3 and O_2, whatever the time of reaction.

Having in mind that numerous studies in the literature report the results of the reaction of selective oxidation of ammonia on oxide surfaces, the ammonia conversion was also investigated on a pre-oxidised copper surface: the copper sample was submitted to oxygen, $P = 10^3$ Pa for 10 min at $T = 650$ K, resulting in a sample covered with a layer of Cu_2O as checked by XPS. The conversion curve is presented in Fig. 4, together with that obtained on a reduced sample for comparison. The initial parts of the curves are very similar, showing a very limited influence of oxygen in an oxide lattice upon the surface reactivity. The rate and the final conversion are only 10–20% higher on the pre-oxidised surface than on the initially

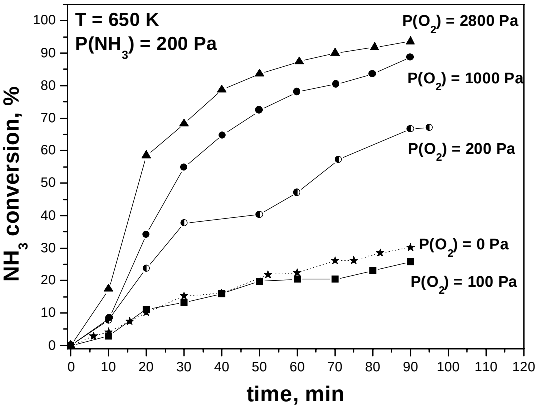


Fig. 3. Conversion of NH_3 as a function of time and for various pressures of oxygen, on polycrystalline copper, $P_{NH_3} = 200$ Pa.

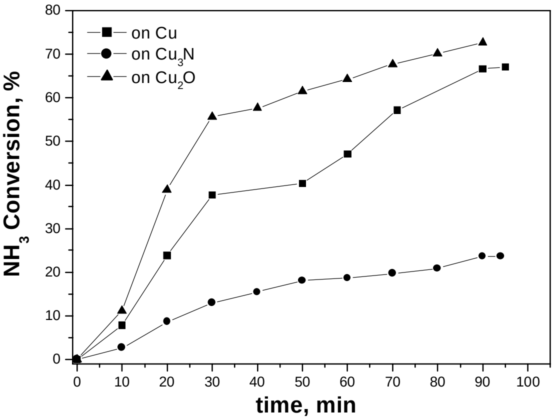


Fig. 4. Conversion of NH_3 as a function of time and at $T = 650$ K, on polycrystalline copper, copper nitride, Cu_3N, or copper oxide surfaces, $P_{NH_3} = P_{O_2} = 200$ Pa.

reduced sample. The selectivity is hardly affected by this pre-treatment of the surface (selectivity to $N_2O <$ 2% after 90 min of reaction whatever the initial state of the copper surface).

The reaction was also performed on a NH_3-pre-treated surface ($P_{NH_3} = 1.3 \times 10^2$ Pa for 90 min at 650 K). The XPS analysis of the surface after that treatment revealed that a thick (>50 Å) layer of Cu_3N was formed as demonstrated here below. The conversion of NH_3 on such a Cu_3N surface is reported in Fig. 4. One observes that the reaction is slower, by a factor 2–3, compared to the initially clean metallic surface; the conversion rate only slightly increases after 10 min of reaction: the change in the slope is less marked than in the preceding cases.

Note that on the initially metallic copper surface, at 650 K, the mass balance indicates that the amount of dinitrogen appearing in the gas phase corresponds to 40% of the converted amount of NH_3, whereas, on the initially copper nitride surface, the total amount of NH_3 is converted into N_2 which supports our statement that Cu_3N is first formed on metallic Cu surface. No N_2O was formed during the reaction initiated on a copper nitride surface.

3.2. FT-IRAS characterisation of NH_3 adsorption and reactivity on Cu(1 1 0)

Adsorbed ammonia may react, at room temperature, with oxygen leading to new molecular adsorbed compounds. Investigating this reaction at RT, rather than at 650 K, was expected to slower the reaction and hence to provide information about the possible reaction intermediates. Infrared spectra were recorded in the presence of reacting gases to avoid desorption of weakly bound intermediates. The FT-IRAS spectra of the species adsorbed when the Cu(1 1 0) surface was first submitted to pure ammonia, $P = 1.3 \times 10^{-3}$ Pa, and then to oxygen, $P = 1.3 \times 10^{-3}$ Pa, are reported in Fig. 5a. The intense band at 1200 cm^{-1} shows the adsorption of ammonia, via its N atom and the three H atoms in a C_{3v} symmetric position [20]. In agreement with other works, the signal growing at 2180 cm^{-1} was attributed to a polarised dinitrogen species resulting from a dehydrogenation of NH_3 [3,4,21]. When the admission of oxygen was stopped, a new band grew at 1430 cm^{-1} that we attribute to the deformation vibration of adsorbed NH imide species [4]. These intermediates are detected when oxygen is missing to complete the reaction of ammonia dehydrogenation. Fig. 5b, showing the areas of the bands at 1200 and 2180 cm^{-1}, along with the various gas conditions, confirms the role of oxygen in the formation of dinitrogen from ammonia. The amount of dinitrogen on the surface increases as soon as oxygen is present in the gas phase and, decreases when the admission is stopped. A very low amount remains on the surface after gas evacuation.

The reaction of dehydrogenation of NH_3 was still too rapid to detect surface intermediates. Thus, the interaction of a NH_3/O_2 mixture was tentatively investigated at lower pressure, 4×10^{-5} Pa, with the objective

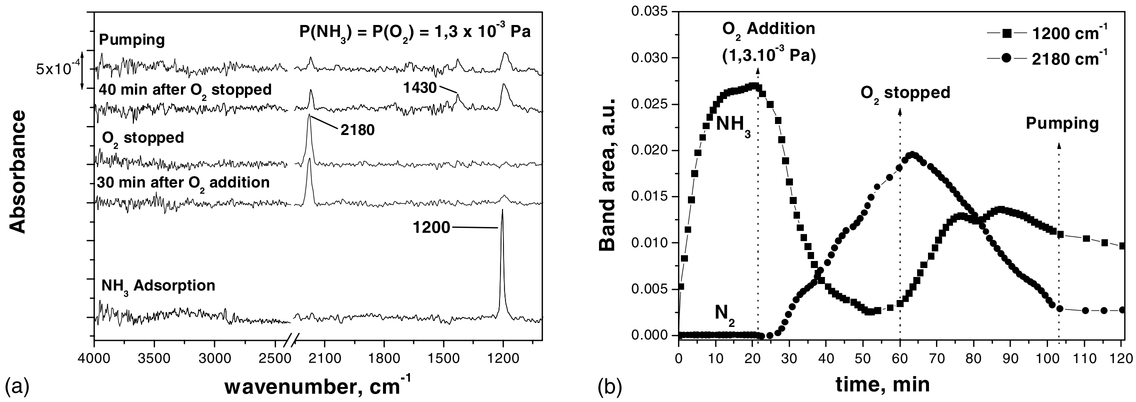


Fig. 5. (a) IRAS spectra recorded on Cu(1 1 0) in the presence of NH_3, $NH_3 + O_2$, and in vacuum, at RT; (b) the corresponding variations of the IRAS signals, respectively, ascribed to adsorbed NH_3 and N_2.

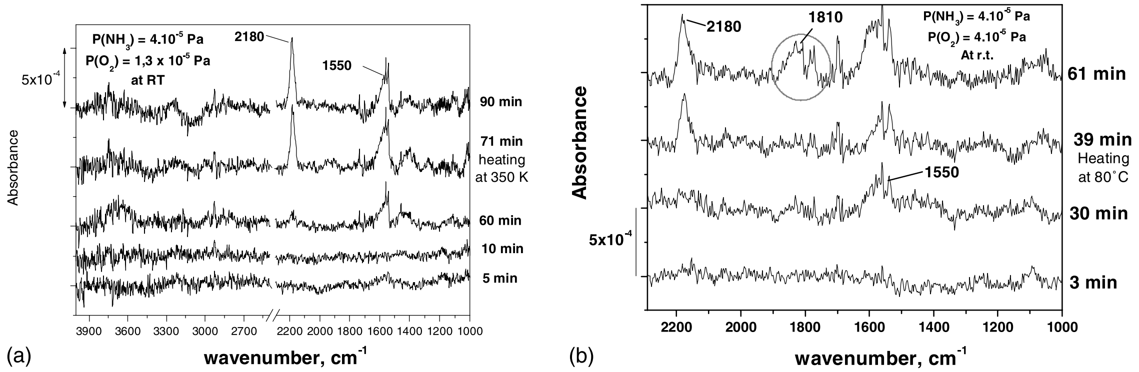


Fig. 6. IRAS spectra recorded on Cu(1 1 0) in the presence of $NH_3 + O_2$: (a) $P_{NH_3} = 4 \times 10^{-5}$ Pa, $P_{O_2} = 1.3 \times 10^{-5}$ Pa; (b) $P_{NH_3} = P_{O_2} = 4 \times 10^{-5}$ Pa.

of decreasing the rate of the surface reaction (assuming the orders, towards NH_3 and O_2 reactants positive, like under "catalytic" conditions) to try to detect intermediates. Fig. 6 reports the IRAS spectra recorded (a) in the presence of an excess of NH_3, (b) in the presence of an equimolar mixture. One sees that, at lower pressure, 4×10^{-5} Pa, the formation of dinitrogen did not occur at RT; it started once the sample was heated to 350 K, and an amide species, NH_2(a), was detected from the presence of an absorption band at 1550 cm^{-1} [3]. An interesting difference was observed when equal pressures of NH_3 and O_2 were used: in that case, NH_2 was not the only intermediate species but also a compound having absorption bands at 1780–1810 cm^{-1}. We can ascribe the latter to adsorbed NO [21–23], or to O–NH molecular species [24]. Note that all these species were identified on metallic cations except in Ref. [24] performed on Cu(1 1 0). The possible formation of H_2NO as an intermediate to the formation of N_2O will be discussed later in this paper.

Instead of admitting oxygen after, or at the same time as ammonia, oxygen was first adsorbed on the Cu(1 1 0) surface, an ordered c(6 × 2) structure was then observed by LEED, see Fig. 7, indicating a coverage near half a monolayer [25]. Ammonia was then admitted on this oxygen-modified surface and the corresponding IRAS spectra make clear the formation of three molecular compounds coexisting on the surface: dinitrogen (2180 cm^{-1}) as well as amide and imide intermediates (1540 and 1430 cm^{-1}, respectively) [4,14,20,21]. After 45 min of interaction, ammonia was evacuated and the LEED pattern showed the re-appearance of the p(1 × 1) substrate structure.

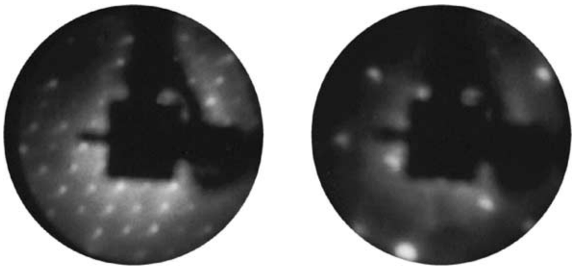

Cu(110) c(6x2)-O
(a)
Cu(110)-p(1x1)
(b)

Fig. 7. LEED patterns observed after (a) oxygen adsorption on Cu(1 1 0) and (b) interaction of NH_3 at RT.

This experiment was repeated but with evacuation of ammonia every 15 min for Auger analysis and re-admission. The Auger peak-to-peak ratios are given in Table 2. They show a progressive consumption of adsorbed oxygen and simultaneous increase of the nitrogen coverage.

Table 2
Auger peak-to-peak ratios at $t = 0$ and after 15, 30 and 45 min of interaction of NH_3 on O-pre-treated Cu(1 1 0)

	Auger ratios			
	$t = 0$	After 15 min	After 30 min	After 45 min
$O_{507\,eV}/Cu_{48\,eV}$	0.16	0.14	0.09	0.0
$N_{380\,eV}/Cu_{48\,eV}$	0	0.04	0.05	0.24

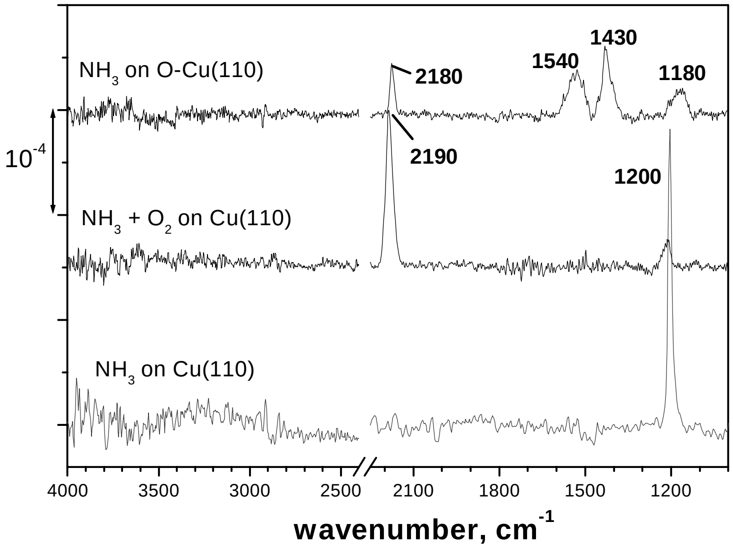


Fig. 8. IRAS spectra recorded on Cu(1 1 0) after 50 min of interaction of NH_3 ($P_{NH_3} = 10^{-3}$ Pa), $NH_3 + O_2$ ($P_{NH_3} = P_{O_2} = 10^{-3}$ Pa) and, on Cu(1 1 0)c(6 × 2)–O in the presence of NH_3 ($P_{NH_3} = 10^{-3}$ Pa).

The active role of oxygen from the gas phase or pre-adsorbed oxygen is clear in Fig. 8 which presents IRAS spectra recorded, after 50 min of interaction of ammonia alone, ammonia with oxygen on metallic copper, and ammonia alone on O-adsorbed Cu(1 1 0).

Note finally that when the copper surface was pre-oxidised into a Cu_2O thin layer, neither adsorption, nor formation of any molecular species could be evidenced upon admission of ammonia (spectra not shown).

3.3. Surface characterisation by XPS

The catalytic copper surface was analysed by XPS at three important stages of the reaction run at 650 K, before admission of the reactants, after 10 and 90 min, respectively (noted A, B and C in Fig. 1).

The Cu_{LMM}, O 1s and N 1s regions of the XPS spectra, at various times are shown in Fig. 9. At $t = 0$ min, the oxygen peak was hardly detectable (spectrum not shown). The Cu 2p region was also recorded; a copper peak was observed at BE = 932.8 eV. No satellite was ever detected as it would be expected if CuO was formed. The position of the copper Auger line, Cu_{LMM}, at 918.3 eV at $t = 0$ and 916.1 eV at $t = 10$, 90 min, suggests that the reaction was initiated on a metallic copper surface and that, already after 10 min, the copper surface was oxidised into a Cu^+ state. This change in the level of oxidation of copper was accompanied by the appearance of an intense nitrogen peak and a relatively weak oxygen peak. The former was symmetric, centred at 398.0 eV, a BE characteristic of adsorbed nitrogen or NH species. The latter was asymmetric and best fitted with two contributions, one at 530.8 eV attributed to oxygen adsorbed or in an oxide lattice, and a second one at 532.0 eV attributed to oxygen from adsorbed hydroxyl groups. The latter may be due to contamination during the transfer in the air or result from the oxy-dehydrogenation of NH_3. After 90 min of reaction (point C), the XPS spectra were very similar to those recorded after 10 min, the only change is a slight decrease in the O 1s contribution at 530.8 eV, and a weak additional peak at 533.0 eV that we ascribe to water formed during the reaction. Atomic O over Cu and N over Cu ratios were calculated, after correction for the Scofield factors of the XPS peak intensities, and given in Table 3.

The values of the $I_{N(398\,eV)}/I_{Cu}$ ratio, as well as the weakness of the O 1s contribution at 530.8 eV together with a fully oxidised surface state for copper leads us to conclude that the surface layers are in fact transformed into a copper nitride Cu_3N, partially covered

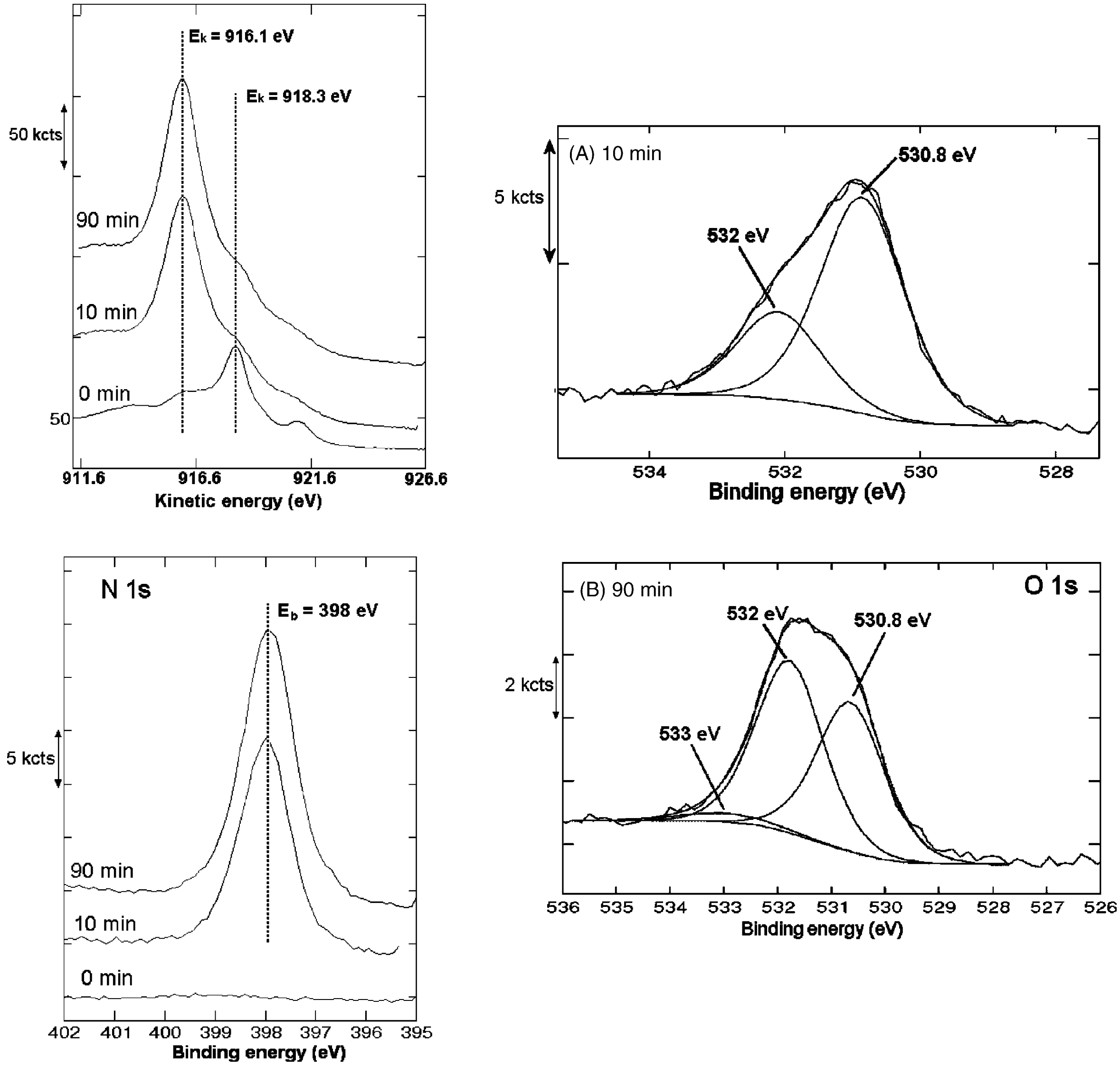


Fig. 9. Cu_{LMM}, N 1s and O 1s regions of the XPS spectra recorded before starting the reaction (stage A) or at stages B and C noted in Fig. 1.

Table 3
Atomic ratios, deduced from corrected XPS intensities after 10 and 90 min of reaction

$T_{reaction}$ (min)	$I_{O(530.8\,eV)}/I_{Cu}$	$I_{O(532.0\,eV)}/I_{Cu}$	$I_{O(533\,eV)}/I_{Cu}$	$I_{N(398\,eV)}/I_{Cu}$
10	0.08	0.03	0	0.25
90	0.04	0.04	0.003	0.24

with oxygen or, a mixed oxynitride species where the nitride is dominant. This is the active state of the catalyst for the reaction.

The copper surface was, for sake of comparison, analysed after the reaction of decomposition of pure ammonia on copper at 650 K (initial state of the reaction mentioned in the preceding section). The corresponding Cu_{LMM} and N 1s regions are shown in Fig. 10. One again observes that the copper is in a

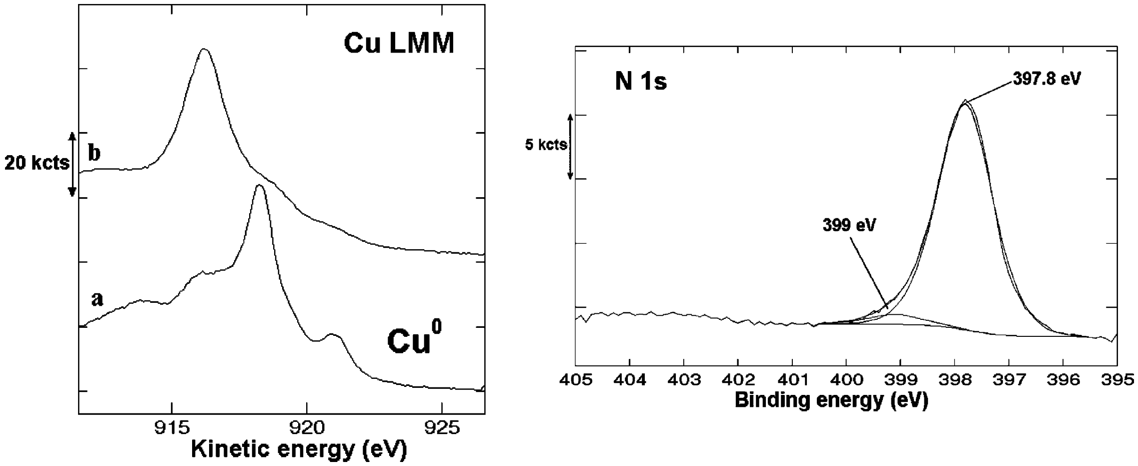


Fig. 10. Cu_{LMM} and N 1s regions of the XPS spectra recorded after decomposition of pure NH_3 at $T = 650\,K$.

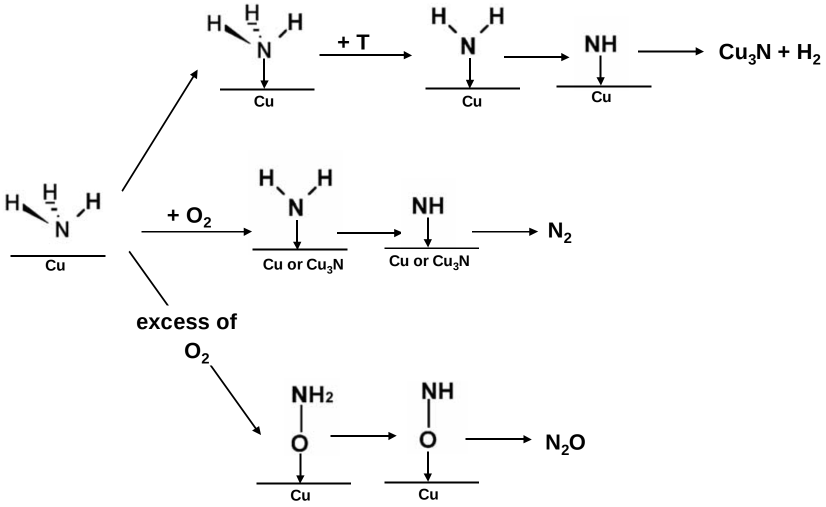
Cu^+ state and the presence of an intense nitrogen peak at BE $= 397.8\,eV$. The $I_{N(398\,eV)}/I_{Cu}$ ratio, equal to 0.28, strongly suggests the formation of Cu_3N on the surface [26].

4. Discussion

The reactivity of NH_3 and O_2 was characterised on a catalytic copper surface both in the 550–720 K temperature range and at room temperature, under a few hundreds Pa of reactants and in the 10^{-5} Pa range, respectively. The combination of kinetics results and surface characterisations opens to a discussion of (i) the nature of the "active" surface under reaction conditions and (ii) the mechanism of the reaction of NH_3 oxy-dehydrogenation.

The main result to emerge from this work is that the reaction of NH_3 oxy-dehydrogenation takes place on a copper surface mainly oxidised to Cu^+ and rich in nitrogen. NH_3 is converted on such a surface and the main product, appearing in the gas phase is N_2, even under oxidising conditions. This new oxidised surface state was identified after 10 min of reaction, when the rate of the reaction increased (change of the slope, see Fig. 1). The data also indicate that the amount of nitrogen formed during the reaction cannot account for the total amount of NH_3 converted at $T = 650\,K$ (see Table 1), for example, when 67% of NH_3 was converted, the yield of N_2 was only equal to 27% which means that 40% of ammonia have been converted in another way. The XPS data tell us that the copper surface is rapidly transformed in a nitride-rich surface, a possibly pure or slightly oxidised nitride; the thickness of this newly formed layer is at least equal to 5 nm since no metallic copper could be detected already after 10 min of reaction. We thus conclude that most of NH_3 is, in the presence of oxygen, was converted into nitride partially covered with oxygen, or a nitride-rich oxynitride, creating an active state of the surface. This finding is in good agreement with Shustorovich and Bell who showed, by Morse potential analysis, that on copper, the presence of oxygen may decrease the enthalpy and activation energy for the reaction of N–H cleavage from NH_3 and consequently facilitate the formation of Cu_3N [27]. Geus and coworkers [28] detected the presence of copper nitride upon admission of NO on a Cu/SiO_2 catalyst. Djega-Mariadassou et al. characterised the catalytic activity of another oxynitride, defined as a nitride containing oxygen, TiN_xO_y, stable at high temperature, up to 950 K, and active for the decomposition of NH_3. The most abundant reaction intermediate was assumed to be atomic nitrogen and, more interesting, titanium oxynitride behaves like a metal possibly catalysing the dehydrogenation of ammonia without requiring oxygen [29].

To check the possible decomposition of NH_3 on copper, the reaction was then carried out in the absence of oxygen or with a pressure of oxygen half that of ammonia, at 650 K; we observed that the rate



Scheme 1. Possible reaction pathways when NH_3 is admitted onto a copper surface, in the absence or in the presence of oxygen.

of NH_3 conversion was only divided by a factor 2 compared to the one measured under slightly oxidising conditions (Fig. 3); this confirms that, when the pressure of oxygen is none, or below the stoichiometric value, the conversion of NH_3 is essentially a decomposition into atomic nitrogen, leading to Cu_3N or gaseous dinitrogen, and hydrogen. The reaction, under stoichiometric or oxidising conditions appears to be a 2-fold process: (i) dissociation of NH_3 into nitrogen and hydrogen, with possible NH_2 and NH intermediates and (ii) oxy-dehydrogenation of NH_3, promoted by the interaction between adsorbed O atoms and the hydrogen atoms of NH_3; the latter reaction leads to H_2O via OH and possibly NO, HNO and N_2O when oxygen is strongly in excess. Scheme 1 summarises the possible reaction pathways taking place on copper upon admission of NH_3.

The role of oxygen is also clear from the IRAS data, recorded at RT: NH_3 adsorbs on the copper surface but does not decompose in the absence of oxygen because that reaction needs to be activated (see Fig. 8). Addition of oxygen permits the abstraction of hydrogen atoms ending in a surface dinitrogen species; HNO and NO intermediates were detected upon heating to 350 K when the reaction was slow; N_2O was detected in the gas phase when the reactant mixture contained an excess of oxygen (Fig. 6). No nitride was formed at RT (Auger N peak very weak). This is not surprising, knowing the high value of the heat of formation of Cu_3N from NH_3 and Cu: $120\,kJ\,mol^{-1}$, a value calculated from Kubaschewski and Evan's data [30].

At 650 K, we measured, under reducing conditions, an order equal to 1.2 with respect to oxygen, confirming (i) the very low amount of oxygen adsorbed, (ii) the promoting effect of oxygen upon the conversion of NH_3 and, (iii) the participation of atomic oxygen in the reaction.

Under oxidising conditions, the order with respect to oxygen becomes close to 0 indicating a high coverage in oxygen. This oxygen-rich surface permits the reaction between adsorbed oxygen and molecular NH_3, the coverage of which remains weak (order = 1). Moreover, N_2O started to be formed, in an amount increasing with the pressure of oxygen. We propose two possible reaction pathways to explain the formation of nitrous oxide: either the reaction of partially dehydrogenated NH_3 with oxygen in excess, followed by the interaction of two surface intermediates; let us note that, even at 350 K, O–NH or NO_x reaction intermediates can be formed under slightly oxidising conditions [24]; the oxidative coupling of two NH_3 molecules to form N_2O on copper zeolites has already been proposed by Coq and coworkers [31]; our second suggestion is the oxidation of copper nitride into copper oxide, according to the following equation:

$$Cu_3N + O_2 = \frac{1}{2}N_2O + \frac{3}{2}Cu_2O$$

The transformation of nitride into oxide has been well documented by several authors [32,33].

At that point, the nature of the active "oxygen" species is questionable. The IRAS data, reported in Figs. 6 and 8, make clear that NH_3 did react with adsorbed oxygen at RT until total, or almost total, consumption since a $p(1 \times 1)$ diagram was recovered at the end of the reaction. This experiment, reaction of NH_3 on an oxygen pre-treated surface, also resulted in parallel decrease of the O/Cu and increase of the N/Cu peak-to-peak Auger ratios.

The conversion of NH_3 also proceeded at RT when O_2 and NH_3 were simultaneously admitted to the surface; the Auger spectra recorded after gas evacuation, showed signals from oxygen and nitrogen suggesting that both species adsorbed and reacted in the adsorbed phase. King and coworkers [23] also showed that pre-dosed oxygen reacts with NH_3 on Cu(1 1 0) at a temperature at which NH_3 would not decompose (250 K). This result is in perfect agreement with our IRAS results that show the formation of dinitrogen at RT.

An apparent discrepancy exists between the lack of activity of Cu_2O towards adsorption, and consequently conversion, of NH_3 at RT and the apparent high activity of a Cu_2O surface towards NH_3 oxy-dehydrogenation at 650 K. Literature is also abundant about the use of copper oxide catalysts for the SCO of NH_3 [3–6]. We believe that, under our experimental conditions, the Cu_2O surface is rapidly transformed into the Cu_3N or mixed Cu_3N/Cu_2O active state. The enthalpy of formation of Cu_3N from Cu_2O and NH_3 is indeed reduced to 9 kJ/mol. An important result of this work is that Cu_2O itself does not promote the reaction of oxy-dehydrogenation of NH_3. Adsorbed oxygen appears to be the active species of that reaction.

5. Conclusions

Combining the results of a kinetic study of the oxy-dehydrogenation of ammonia on copper with an XPS surface characterisation and an in situ IRAS investigation of the reaction enabled to draw the following conclusions:

- Copper is active for the oxy-dehydrogenation of ammonia into dinitrogen, from room temperature to about 700 K with a negligible production of N_xO_y even under slightly oxidising conditions.
- The working surface is enriched in, or possibly pure, copper nitride, Cu_3N. Adsorbed oxygen promotes the abstraction of hydrogen atoms, hence increasing the rate of NH_3 conversion.
- An excess of oxygen leads to the formation of N_2O, either via $O–NH/ONH_2$ intermediates or by oxidation of the copper nitride.

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