Interaction of NH₃ and oxygen with Cu(1 1 0), investigated by FT-IRAS

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Abstract

Adsorption of ammonia, on the Cu(1 1 0) surface, has been investigated in situ, at room temperature, by Fourier-transformed infrared reflection–absorption spectroscopy (FT-IRAS). The role of oxygen in the reaction of oxy-dehydrogenation of ammonia was made clear by successively characterising the interaction of ammonia, co-adsorbed with oxygen on metallic Cu(1 1 0) or adsorbed on an oxygen-pre-dosed Cu(1 1 0) surface. Auger electron spectroscopy was used to check the chemical state of the surface after oxygen and/or ammonia exposure.

NH₃ was observed to adsorb in a molecular form on the metallic Cu(1 1 0) surface. When co-adsorbed with ammonia or pre-adsorbed on the surface, oxygen favours abstraction of hydrogen from NH₃, eventually yielding dinitrogen. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Numerous studies have been devoted to the interaction of NH₃ with metallic surfaces providing important information about its mode of adsorption and stabilisation by the metal. These data constitute a useful basis for understanding nitriding processes [1], ammonia synthesis and decomposition [2]. On well-defined metallic surfaces, like Pt(1 1 1) [3], Fe(1 1 0) [4], Ni(1 1 0) [5], the adsorption of ammonia

has been characterised by combining UHV techniques, HREELS, LEED and/or TDS, as well as utilising a theoretical approach [6]. On all these surfaces, NH₃ adsorbs molecularly at ≈100 K, and decomposes under low pressure ($\leq 10^{-8}$ Torr), at higher temperature. On copper, at low temperature (below 150 K), the NH₃ molecule strongly binds to copper via electrostatic interactions due its large dipole moment [7]. On Cu(1 1 1), like on Ni(1 1 0), the molecule adopts the atop sites with H atoms pointing away from the surface [8,9]. Under these conditions, no dehydrogenation of ammonia could be evidenced [10]. On Cu(1 1 0), at 80 K, NH₃ is physisorbed; it totally desorbs at 200 K in UHV, whereas imide, NH, species were shown to be thermally stable up to at least 400 K [11]. Note also that adsorption of molecular nitrogen proceeds

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at room temperature on copper-ion-exchanged zeolites, this material being possibly used for the direct decomposition of NO_x [12].

On the other hand, numerous studies report the role of dioxygen, either in the gas phase or pre-adsorbed onto the metallic surface, upon dissociation and oxy-dehydrogenation of ammonia. The chemical reactivity of "hot" oxygen in H-abstraction has already been demonstrated. Isolated $O^{\delta-}$ adatoms, originating from impinging or weakly adsorbed molecules, are in fact more active than pre-chemisorbed oxygen [11,13]. At 80 K, the main species resulting from the oxy-dehydrogenation of NH_3 are OH(a) and NH_2(a), whereas at 295 K, imide species are predominant. The imide species are possible intermediates to the formation of surface nitroxyls or adsorbed nitrogen atoms [14]. The role of isolated oxygen in the oxy-dehydrogenation of ammonia on Cu(1 1 0) has been confirmed by an STM study at 300 K [15].

The reaction of oxidation of ammonia also yields N_2O as a by-product, having a strong green house effect, and defining the conditions for its formation upon activation of NH_3 by oxygen is an accurate challenge [16].

Although many studies have addressed adsorption of ammonia to probe the acido-basic properties of oxide surfaces [17–19], only very few adsorption experiments have been reported on well-defined surfaces modified with oxygen. On a well-defined NiO(1 0 0) surface, at 90 K, ammonia was shown to be bonded to the surface cations via the N-free electron doublet [20]. Finally, there have been so far very few studies of the adsorption of NH_3 at room temperature and above. One concerning Ni(1 1 0) surface, mentions a partial fragmentation of NH_3 into NH_2 and NH species at T above 300 K [21].

IR measurements, performed in situ and correlated to the surface structure, enable to account for the properties of a metallic or oxygen-pre-dosed surface under "real" conditions and to get a better understanding of its reactivity. In that respect, the in situ characterisation of the surface species by infrared reflection–absorption spectroscopy (IRAS) is a significant step towards filling the gap between high vacuum surface studies and real catalysis. Within this objective, we characterised by Fourier-transformed IRAS (FT-IRAS) the molecular species adsorbed on a well-defined Cu(1 1 0) surface, in the presence of NH_3

or $NH_3 + O_2$, at pressures ranging from 7×10^{-6} to 3×10^{-3} Pa (i.e. from 5×10^{-8} to 10^{-5} Torr). The role of surface oxygen was eventually addressed by characterising the interaction of NH_3 after pre-adsorption of oxygen on the Cu(1 1 0) surface.

2. Experimental

All experiments were performed in a vacuum chamber in which the surface was cleaned and subsequently analysed by AES before and after adsorption experiments. The copper(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. IR measurements were carried out in situ at grazing incidence ($6°$) using a FT-IR spectrometer (NICOLET, Magna 550) equipped with a MCT wide-band detector, 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 300 scans at a resolution of $4 \, cm^{-1}$. Some spectra were recorded at $8 \, cm^{-1}$ or after only 100 scans when kinetics data were searched. These conditions enabled to record a spectrum every minute. 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. When needed, oxygen was pre-adsorbed by heating the sample to 600 K under 1.3 Pa (10^{-2} Torr) of oxygen. This procedure led to a $I_{Cu(60 \, eV)}/I_{O(506 \, eV)}$ ratio equal to 1.8; in that case, copper was kept in a metallic state as checked by an independent XPS analysis and in agreement with previous works [22,23].

3. Results and discussion

3.1. Adsorption of NH_3 on metallic copper

Spectra recorded in the presence of ammonia (10^{-5} Torr) on a metallic Cu(1 1 0) surface are shown
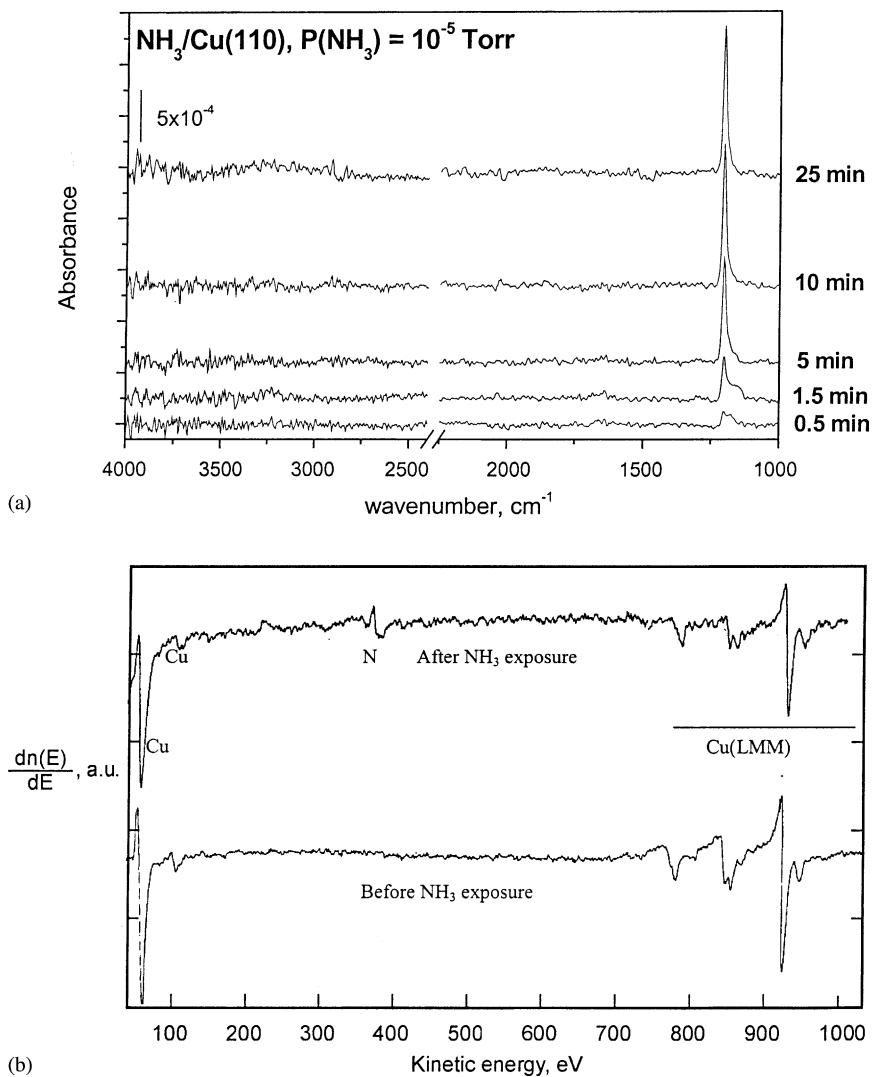
Fig. 1. (a) IRAS spectra of the clean metallic Cu(1 1 0) surface recorded as a function of time in the presence of NH$_3$ ($P = 10^{-5}$ Torr). The x-axis has been broken between 2250 and 2400 cm^{-1} in order to eliminate the signal from residual gaseous CO$_2$ in the beam path outside the UHV chamber. (b) Auger spectra before and after NH$_3$ adsorption.

in Fig. 1a. From the beginning of the interaction, a vibration band appears at 1180 and 1200 cm^{-1}, easily ascribed to the symmetric deformation (umbrella mode) δ_{NH} in NH$_3$ molecules coordinated to metal atoms [24]. For short times of interaction, the δ_S band is clearly made of two contributions; one, at 1180 cm^{-1} remains roughly constant in intensity and can be attributed to the immediate interaction of ammonia molecules with some defect sites of the

surface. The second one, at 1200 cm^{-1}, rapidly grows and reaches a plateau after 10 min, indicating a saturation of the amount of NH$_3$ adsorbed. This mode is shifted upward compared to gaseous ammonia (950 cm^{-1}) indicating some electron transfer from the N atom to the metal (weak acidic character of the surface).

After 1 h, the gas was evacuated, inducing an almost total disappearance of the vibration band at

$1200 \, cm^{-1}$. An Auger spectrum was recorded when the pressure was lowered to 10^{-8} Torr (see Fig. 1b); a peak was detected at $380 \, eV$ suggesting that a fraction of ammonia has been decomposed leaving atomic nitrogen on the surface.

The absence of the asymmetric deformation mode of NH_3, at ca. $1580 \, cm^{-1}$, indicates that ammonia is adsorbed with its C_{3v}-axis normal to the surface. The fact that, even for long exposure times corresponding to a saturation of the δ_S band, no band at ca. $1600 \, cm^{-1}$ could be observed is an indication that the coverage of ammonia, remains low at RT under our conditions. As a matter of fact, ammonia was said to adopt a tilted configuration for coverages higher than $0.2 \, ML$ and this would make the asymmetric deformation band IRAS active [25]. Moreover, the symmetric and asymmetric ν_{N-H} modes, expected at ca. $3300 \, cm^{-1}$, are also absent as expected for low ammonia coverages. The latter has been observed for adsorption of molecular NH_3 at $80–100 \, K$ when multilayers, and consequently hydrogen-bonded species, are formed [26,27]. Other studies of NH_3 adsorption on metals also failed to

show the presence of a band in the N–H stretching region [8].

This experiment was repeated at lower pressures, 10^{-6} and 10^{-7} Torr; similar spectra were observed with corresponding decreases in the intensity of the band at $1200 \, cm^{-1}$. Fig. 2 shows the $1100–1250 \, cm^{-1}$ region recorded after $10 \, min$ of NH_3 interaction at various pressures. The evolution of the δ_S band area is plotted as a function of time in the insert of Fig. 2. The kinetics curves have a Langmuir or a Fowler line-shape suggesting that an equilibrium can be reached between the surface and the gas phase with the amount of adsorbed ammonia depending on the pressure. The surface is not saturated at 10^{-6} and 10^{-7} Torr. The constant value of the frequency of the main contribution, at $1200 \, cm^{-1}$, suggests weak or constant interactions when increasing the ammonia coverage. Weak attractive interactions were indeed invoked by other authors to account for some displacement of ammonia molecules from exact on-top sites [28]. At lower pressure, 10^{-7} Torr, the intensity after $10 \, min$ is very low and the δ_S band is again clearly made of two contributions confirming some site heterogeneity.
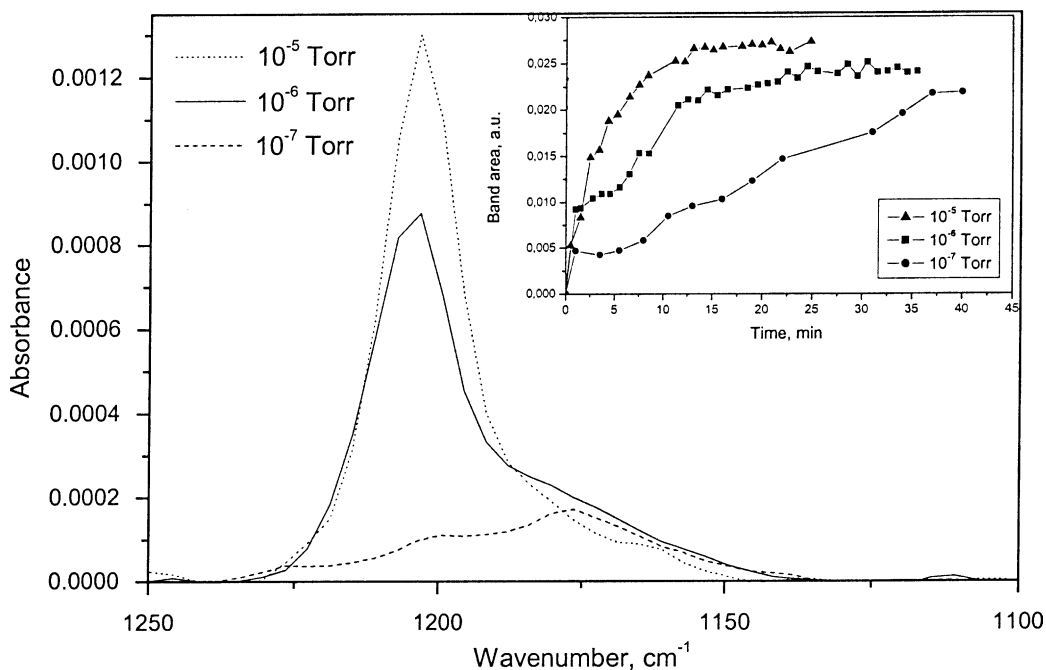

Fig. 2. The $1100–1250 \, cm^{-1}$ spectral region recorded after $10 \, min$ of ammonia interaction under $P_{NH_3} = 10^{-7}$, 10^{-6} and 10^{-5} Torr. Insert: plot of ca. $1200 \, cm^{-1}$ band area as a function of time for the corresponding pressures of NH_3.
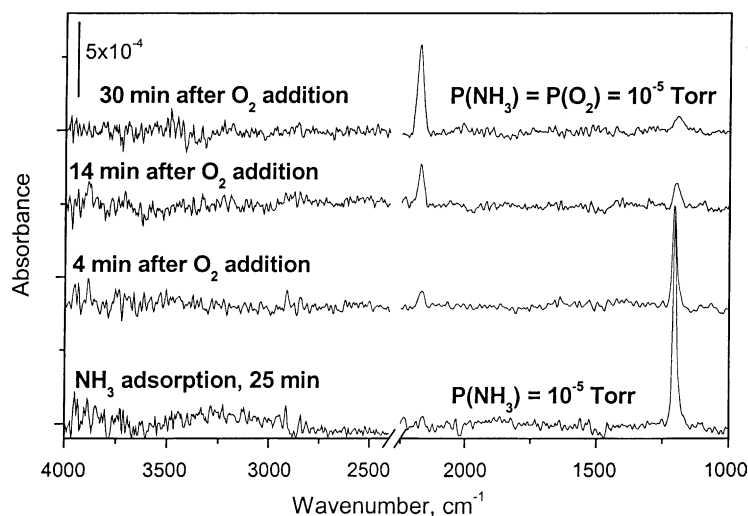
Fig. 3. IRAS spectra of the metallic Cu(1 1 0) surface; the surface was exposed to NH$_3$ at RT for 25 min and then to an equimolecular ammonia–oxygen mixture ($P_{NH_3} = P_{O_2} = 10^{-5}$ Torr) during 4, 14 and 30 min. The x-axis has been broken between 2250 and 2400 cm^{-1} in order to eliminate the signal from residual gaseous CO$_2$ in the beam path outside the UHV chamber.

3.2. Co-adsorption of NH$_3$ + O$_2$ on metallic Cu(1 1 0)

In order to test the reactivity induced by oxygen, a first experiment was performed; it consisted in adding oxygen after having let NH$_3$ interact on the Cu(1 1 0) surface at RT for 25 min at $P = 10^{-5}$ Torr

(saturation). The corresponding IRAS spectra are displayed in Fig. 3. Remarkable is the decrease of the NH$_3$ δ_S vibration band at 1200 cm^{-1}, observed as soon as oxygen is admitted, to the benefit of an IR signal at 2180 cm^{-1}. The evolution of the two intensities is reported in Fig. 4. The band at 2180 cm^{-1} grows continuously with time in the presence of an
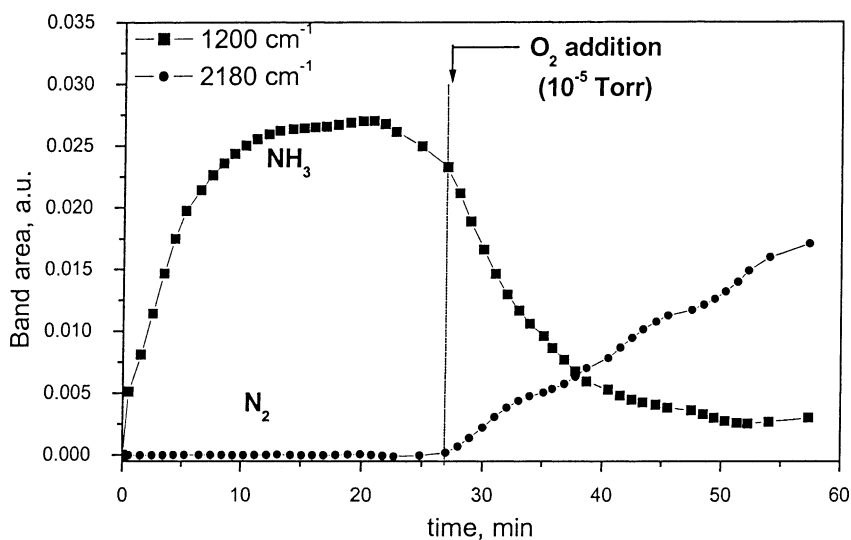

Fig. 4. Plot of the 1200 and 2180 cm^{-1} IR band areas as a function of time. Oxygen was added after 25 min of ammonia exposure.

O_2/NH_3 equimolecular mixture, whereas the NH_3 δ_S bands decreases down to a plateau corresponding to a very weak intensity. Appearance of this new signal proves that a chemical reaction between oxygen and adsorbed ammonia did occur. A plausible mechanism in agreement with Afsin et al.'s and Busca and coworkers' recent results is the following: oxygen adsorbs in a reactive $O^{\delta-}$ form that can abstract H atoms from NH_3 [11]; amide (NH_2) and imide (NH) species may either undergo a further dehydrogenation to N(a) or recombine into N_2H_4 or N_2H_2 species; these molecules may in turn react with $O^{\delta-}$ and lose their hydrogen atoms leaving $N_2^{\delta-}$ on the surface [29–31]. Note that dehydrogenation of NH_3, exposed to oxygen, already proceeds at 80 K on Cu(1 1 0) [11]. At RT, the reaction is rapid as shown by the evolution of the IR spectra. This may explain why, at RT, no signals at ca. 1430 and 1540 cm^{-1}, normally expected for respectively NH and NH_2 groups, are visible on the spectra [29]. We will see later on that, under certain conditions, amide and imide intermediates will be detected. The growing IR signal at 2180 cm^{-1} is hence assigned to the N–N stretching frequency of $N_2^{\delta-}$, a ionised form of dinitrogen adsorbed on metal atoms. This attribution is in agreement with the value of the N–N stretching frequency, in metal complexes containing N≡N ligands [32]. The considerable downward frequency shift, observed for adsorbed N_2 species, compared to gaseous dinitrogen (2331 cm^{-1}), can be considered as a proof of chemisorption which involves an electron transfer from the N≡N bonding σ orbital to the metal and to the π* back-bonding from the metal surface [33]. Hollins and Pritchard [34] and Heskett et al. [35] suggested that, for weakly bound N_2, only the 5σ orbital, also slightly antibonding, is involved in the process of back-donation from the substrate [34,35].

Another possible assignment for this signal would be the N–N stretching frequency of N_2O species. N_2O was shown to be stable on copper up to 220 K [36]. This molecular compound was identified by a N–N stretch at 2227 cm^{-1}, a slightly higher value than the frequency we observe. N_2O has been evidenced on Cu(1 1 1) [37] and on Cu(1 1 0) [38] upon adsorption of NO. The mechanism proposed by the authors implies either the formation of NO dimers which, in turn, partially decompose into N_2O and O or the reaction of N(a) with NO(a). According to those results, once

the surface is covered with O(a), the decomposition of $(NO)_2$ into $N_2O(a)$ and O(a) is blocked and $(NO)_2$ accumulates on the surface. In our case, the reaction is not likely to proceed this way since (i) though the IRAS band at ca 2200 cm^{-1} is still present after gas evacuation, almost no oxygen was detected on the surface by AES and (ii) expected bands for NO or NO_2 were never observed. We consider that the absence of any signal in the 1700–2000 cm^{-1} region rules out the formation of NO or any NO-containing coordinative species, under these conditions.

Ramis et al. investigated the adsorption and the SCO of ammonia on several oxides; they came to the conclusion that, in the absence of NO, the main path of ammonia oxidation by oxygen is the formation of NH_2 and N_2H_4 intermediates [39]; this supports our first interpretation. More recently, the same team suggested the formation of hydroxylamine, $O–NH_2$ species from ammonia adsorption on Fe_2O_3/TiO_2 SCR catalyst as intermediates to the formation of N_2O [40]. Again, we cannot exclude such a mechanism on copper in the presence of oxygen though no bands of hydroxylamine were detected (1620, 1175 cm^{-1}). To summarise the situation, the position of the observed signal, 2180 cm^{-1}, as well as the mechanisms discussed in the literature, lead us to assign the latter to dinitrogen. Molecular dinitrogen was identified on isolated Cu$^+$ sites inside a zeolite with a N≡N stretching vibration at 2290 cm^{-1}. It is also known that the N≡N frequency is very much sensitive to the metal and charge site, varying in the 2200–1700 cm^{-1} spectral range on different transition metal centres [41]. A more important π* back-donation is expected on neutral copper centres compared to cations and this may explain why a lower frequency value is observed on metallic copper. This explanation disregards the possible polarisation associated with the electric field considering that, on metallic copper, the latter is weak. On Ni(1 1 0), the N–N vibrational band of chemisorbed N_2 was observed at 2200 cm^{-1} at low coverage with a shift downward to 2192 cm^{-1} at high coverage [42]. These figures are well below those observed on metal cations and very close to our finding. Unlike the situation for CO, a weak shift, only 16 cm^{-1}, was observed when the N_2 coverage was increased. The limited change in the N≡N stretch frequency, reported for N_2 on Ni(1 1 0), was simply ascribed to an almost perfect compensation between

dipole induced and chemical shifts. Note that, like for CO, the shifts are opposite signs on nickel, a group VIII metal and on copper, a group IB one. This is merely coincidental and well discussed by Grunze for N_2 [43] and by Hollins and Pritchard for CO [44].

Note finally that very weak nitrogen and oxygen peaks were observed on the Auger spectrum recorded after gas evacuation ($I_{O,506\,eV}/I_{Cu,60\,eV} = 0.05$ and $I_{N,398\,eV}/I_{Cu,60\,eV} = 0.1$).

In a second series of experiments, the clean Cu(1 1 0) surface was exposed to an equimolecular mixture of NH_3 and O_2 at a total pressure of $3 \times 10^{-3}\,Pa$ ($2 \times 10^{-5}\,Torr$). The spectra, recorded for increasing times of interaction, are presented in Fig. 5. All spectra are dominated by a sharp, strong band at $2180\,cm^{-1}$ that increases in intensity and slightly shifts toward higher wavenumber ($\approx 15\,cm^{-1}$) with further exposure. Another band, almost constant in intensity, is present at $1200\,cm^{-1}$; it is assigned to the symmetric deformation stretch of NH_3, which continuously adsorbs and reacts, whereas the former is attributed to the formation of dinitrogen, similarly as above. In that case, the oxygen and nitrogen Auger peaks, after gas evacuation, were very small ($I_{O,506\,eV}/I_{Cu,60\,eV} = 0.11$ and $I_{N,398\,eV}/I_{Cu,60\,eV} = 0.12$).

In none of these experiments where NH_3 was dehydrogenated, OH could be detected on the surface. The sensitivity of the IRAS device is poor in that region. Another possible explanation is that hydroxyls recombined into water and desorbed. Dehydroxylation of the Cu(1 1 0) surface has already been observed at temperature as low as 200 K by Carley et al. [45]. The OH groups might also be very much tilted towards NH_2 groups and hence IR-inactive, but this is unlikely since a very little amount of oxygen was left on the surface after pumping.

3.3. Adsorption of NH_3 on oxygen-pre-dosed Cu(1 1 0)

A final experiment consisted in the adsorption of ammonia on an oxygen-pre-dosed Cu(1 1 0) surface ($P_{O_2} = 10^{-5}\,Torr$, $T = 600\,K$, 30 min, leading to $I_{O,506\,eV}/I_{Cu,60\,eV} = 0.16$) before admission of ammonia. The corresponding Auger spectrum, recorded at room temperature after oxygen evacuation, is shown in Fig. 6(a). The spectra recorded under ammonia ($P_{NH_3} = 10^{-5}\,Torr$) are shown in Fig. 6(b) and significant spectral changes were observed compared to the two above described experiments. The symmetric deformation mode of NH_3, at $1200\,cm^{-1}$ is detected over
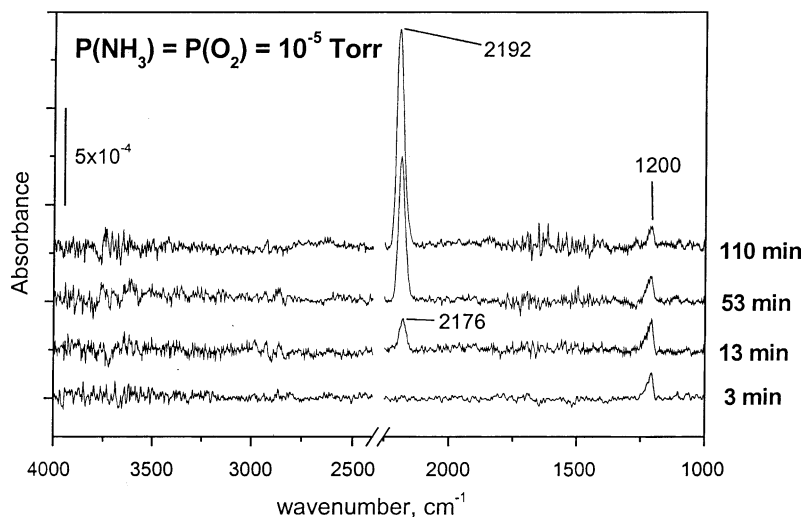

Fig. 5. IRAS spectra of the metallic Cu(1 1 0) surface; the surface was exposed to $NH_3 + O_2$ at RT ($P_{NH_3} = P_{O_2} = 10^{-5}\,Torr$) for 3, 13, 53 and 110 min. The x-axis has been broken between 2250 and 2400 cm^{-1} in order to eliminate the signal from residual gaseous CO_2 in the beam path outside the UHV chamber.
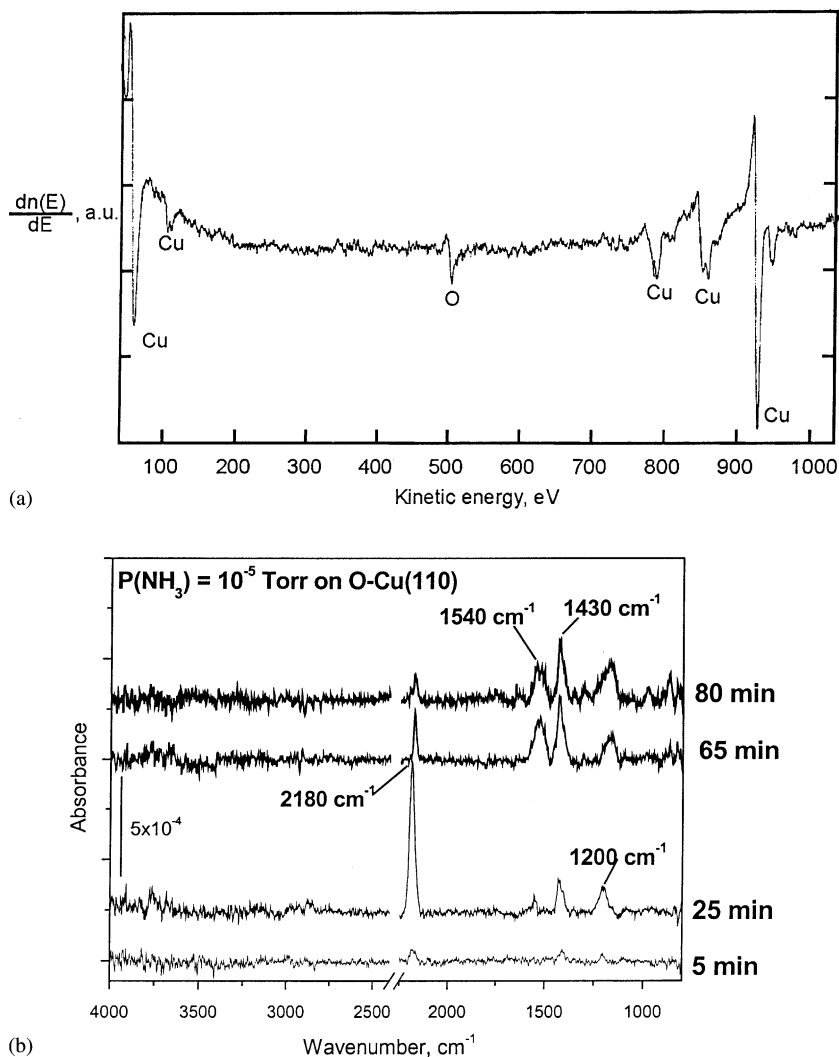
Fig. 6. (a) Auger spectrum of the Cu(1 1 0) after oxygen pre-dosing before NH$_3$ interaction. (b) IRAS spectrum of the oxygen-pre-dosed Cu(1 1 0) surface; the surface was exposed to NH$_3$ at $P_{NH_3} = 10^{-5}$ Torr for 5, 25, 65 and 80 min. The *x*-axis has been broken between 2250 and 2400 cm^{-1} in order to eliminate the signal from residual gaseous CO$_2$ in the beam path outside the UHV chamber.

more than 1 h of interaction and the 2180 cm^{-1} signal grows during the first 25 min and decreases down to almost zero intensity after 80 min. The appearance of vibration bands at 1430 and 1540 cm^{-1}, and their roughly constant intensity throughout the reaction process, suggest the dehydrogenation of NH$_3$ into NH$_2$(a) and NH(a). These intermediates are here detected because, in the absence of oxygen in the gas phase, the reaction process to N$_2$ formation is slow. For times of interaction longer than 80 min, the only vibrations

were those two, plus one at 1200 cm^{-1} assigned to the NH$_3$ δ_S stretching mode. Ammonia and NH$_x$ species do not react any further probably because the surface oxygen atoms have either been consumed or hydroxylated. The Auger spectrum, after this experiment, exhibits a very weak nitrogen peak ($I_{N,398\,eV}/I_{Cu,60\,eV} = 0.07$) and an oxygen signal slightly lower than before NH$_3$ interaction ($I_{O,506\,eV}/I_{Cu,60\,eV} = 0.11$). These figures tend to show that, part of the oxygen stays on the surface, probably in a hydroxylated form, upon

NH_3 interaction. This was not the case when oxygen and ammonia were admitted simultaneously.

4. Conclusion

To better understand the reactivity of ammonia on copper, its adsorption and oxy-dehydrogenation was investigated by FT-IRAS on model, oriented, Cu(1 1 0) surface. These processes are highly sensitive to the reaction conditions, like oxygen pressure or initial oxygen coverage of the surface. In the presence of pure ammonia ($P > 10^{-7}$ Torr), weakly bond molecular NH_3 was observed by FT-IRAS. Admission of oxygen, either before, after, or simultaneously with ammonia, revealed the role of this element in the dehydrogenation process. NH_2 and NH species could be postulated as the intermediates for N_2 formation. No NO-containing species, like N_2O, HNO or NO_x, were ever detected at RT, under moderate oxygen pressure.

FT-IRAS measurements enabled us to monitor the reactivity of a copper surface in situ and the dynamics of the reaction of NH_3 oxy-dehydrogenation.

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