

## ADSORPTION AND DECOMPOSITION OF HNCO ON Cu(111) SURFACE STUDIED BY AUGER ELECTRON, ELECTRON ENERGY LOSS AND THERMAL DESORPTION SPECTROSCOPY

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Received 25 June 1980; accepted for publication 13 October 1980

No detectable adsorbed species were observed after exposure of HNCO to a clean Cu(111) surface at 300 K. The presence of adsorbed oxygen, however, exerted a dramatic influence on the adsorptive properties of this surface and caused the dissociative adsorption of HNCO with concomitant release of water. The adsorption of HNCO at 300 K produced two new strong losses at 10.4 and 13.5 eV in electron energy loss spectra, which were not observed during the adsorption of either CO or atomic N. These losses can be attributed to surface NCO on Cu(111). The surface isocyanate was stable up to 400 K. The decomposition in the adsorbed phase began with the evolution of CO<sub>2</sub>. The desorption of nitrogen started at 700 K. Above 800 K, the formation of C<sub>2</sub>N<sub>2</sub> was observed. The characteristics of the CO<sub>2</sub> formation and the ratios of the products sensitively depended on the amount of preadsorbed oxygen. No HNCO was desorbed as such, and neither NCO nor (NCO)<sub>2</sub> were detected during the desorption. From the comparison of adsorption and desorption behaviours of HNCO, N, CO and CO<sub>2</sub> on copper surfaces it was concluded that NCO exists as such on a Cu(111) surface at 300 K. The interaction of HNCO with oxygen covered Cu(111) surface and the reactions of surface NCO with adsorbed oxygen are discussed in detail.

### 1. Introduction

This study is part of our program relating to a better understanding of the surface processes occurring during the metal-catalyzed NO + CO reactions, which is of great technological importance. Detailed infrared spectroscopic measurements in the recent past revealed that during the NO + CO reaction on supported metals an isocyanate (NCO) surface species is formed [1–3]. This reacts rapidly with water to yield ammonia [4], which strongly supports the assumption that surface NCO is primarily responsible for the undesired formation of NH<sub>3</sub> during automobile exhaust catalysis.

Although the infrared spectroscopic measurements provided much information on the formation of NCO species on different supported metals, not much was revealed as to the nature of the bonding between the NCO and the metal, or the reactivity of the NCO species. The reason is that the oxidic supports drastically influence the reactivity of NCO formed on the metal [3–5].

The primary aim of this work is to establish details of the interaction between NCO and the Cu(111) surface. As it is not possible to produce surface isocyanate via the NO + CO reaction at low pressures, we tried to circumvent this problem by using isocyanic acid, HNCO, directly as adsorbing species.

## 2. Experimental

Experiments were performed in a stainless steel UHV chamber equipped with several gas inlets, a single-pass cylindrical mirror analyzer (PHI) for Auger electron spectroscopy, a 3-grid retarding field analyzer (VG) for low-energy electron diffraction and a quadrupole mass analyzer (VG) to monitor gas-phase compositions. The vacuum system was evacuated with ion pumps and a titanium getter. A base pressure of  $7 \times 10^{-11}$  Torr was routinely obtainable in this chamber.

Auger electrons were generated using electron excitation and measured in their usual first derivative mode. Auger spectra were taken with 3 V peak-to-peak modulation, 2.5 kV of incident energy, 1–10  $\mu$ A of beam current and a sweep rate of 3 V/s. The beam area was about 0.4 mm<sup>2</sup>.

Electron energy loss spectra were taken in  $N(E)$  and  $dN(E)/dE$  form at normal incidence of the primary beam, using the Auger optics as a single-pass CMA analyzer. The primary energy used was 20–125 eV. The beam current varied from 0.2 to 1.0  $\mu$ A. A modulation voltage was 200 mV ptp.

The oriented disk-shaped crystal (diameter 6 mm, thickness 1.5 mm) was obtained from Materials Research Corporation. The sample was mechanically polished and was mounted in a copper sample holder. The sample was heated from the rear by the radiation of a tungsten filament. The temperature was measured with a chromel–alumel thermocouple spot-welded to the edge of the crystal. The surface was cleaned by cycles of sputtering (typically 600 eV Ar<sup>+</sup>, 3  $\mu$ A for 10–30 min) and annealing at 970 K for some minutes.

HNCO was prepared by the reaction of saturated aqueous KNCO solution with 95% H<sub>3</sub>PO<sub>4</sub> at 300 K [6]. The product was purified several times by bulb-to-bulb distillation under HV and UHV conditions. HNCO was introduced into the chamber from an auxiliary vacuum system pumped by a small (8 l/s) ion pump through a stainless steel tube with a diameter of 0.8 mm. The crystal face was positioned about 0.5 cm in front of the effusion hole.

## 3. Results

### 3.1. Adsorption on a clean Cu(111) surface

Exposure of the clean Cu(111) surface to HNCO (up to 1200 L) at 300 K resulted in no detectable change in the Auger spectrum, and we could not identify

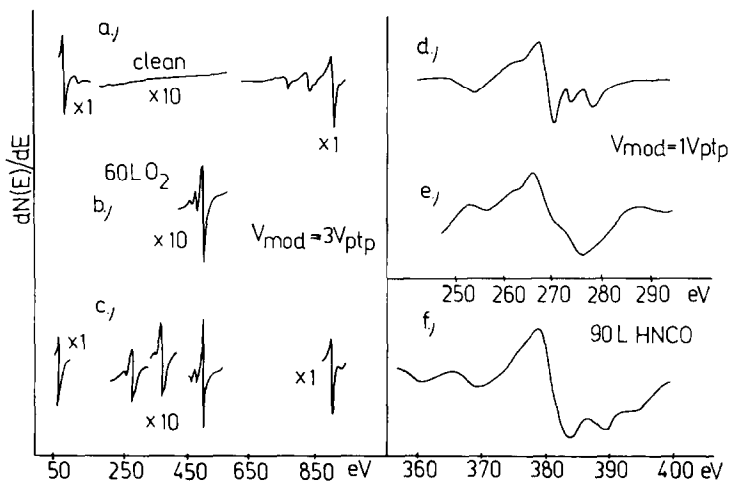


Fig. 1. Auger spectra of the Cu(111) surface taken: (a) with clean surface and after exposure to 100 L HNCO at 300 K; (b) after exposure to 60 L O<sub>2</sub> ( $\theta \approx 0.17$ ) at 300 K; (c) after exposure of the oxygen covered surface ( $\theta \approx 0.17$ ) to 90 L HNCO at 300 K; (d) carbon Auger line shape after HNCO exposure; (e) carbon Auger line shape produced by the dissociation of CO due to electron bombardment; (f) N Auger line shape after HNCO exposure.

any desorbing products on heating the sample up to 1020 K (fig. 1).

In agreement with previous studies, no adsorption or disproportionation of CO on a clean Cu(111) surface was observed by Auger spectroscopy at 300 K (exposure  $2 \times 10^3$  L). No interaction was experienced between CO<sub>2</sub> and a clean Cu(111) surface (exposure  $1 \times 10^3$  L).

### 3.2. Adsorption of HNCO on an oxygen-covered surface, AES studies

The adsorption of oxygen was performed at 300 K. LEED patterns showed no extra spots, but an increase in the background intensity was observed. Fig. 2 shows the ratio  $h_{\text{O}}/h_{\text{Cu}}$  of the oxygen 514 eV to the copper 920 eV peak-to-peak heights in the first derivative Auger spectra versus exposure of oxygen. Higher degrees of coverage were obtained in the pressure range  $10^{-5}$ – $10^{-6}$  Torr. The absolute coverage of oxygen was calculated by using the relationship found by Bootsma et al. [7] between the ratio  $h_{\text{O}}/h_{\text{Cu}}$  in the Auger spectra and  $\delta\Delta$  (ellipsometry), as well as between  $\delta\Delta$  and the oxygen coverage. In this calculation one takes into account that the adsorption of oxygen on the Cu(110) surface leads to a  $(2 \times 1)$  LEED pattern, which means that the ratio of O atoms/Cu surface atom equals 0.5. It is also assumed that the Cu 920 eV Auger signals are equal for Cu(111) and Cu(110).

Exposure of the oxygenated surface ( $\theta \approx 0.17$ ) to HNCO at 300 K resulted in the appearance of the N and C KLL signals at 384 and 271 eV and a slight increase

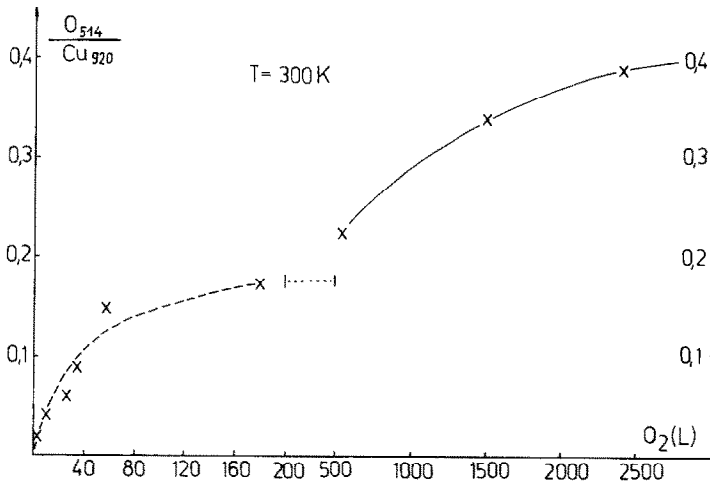


Fig. 2. Ratio of the O 514 eV to Cu 920 eV peak versus exposure of oxygen to a clean Cu(111) surface.

of the O signal at 514 eV (fig. 1). At the same time, mass spectrometric analysis of the gas phase indicated water formation. No other products were identified, however, even when the admission of HNCO onto the sample was performed in the most favourable position, i.e. in front ( $\sim 10$  mm) of the analyzer head of the MS. The adsorption of HNCO did not change the LEED pattern of oxygen covered surface.

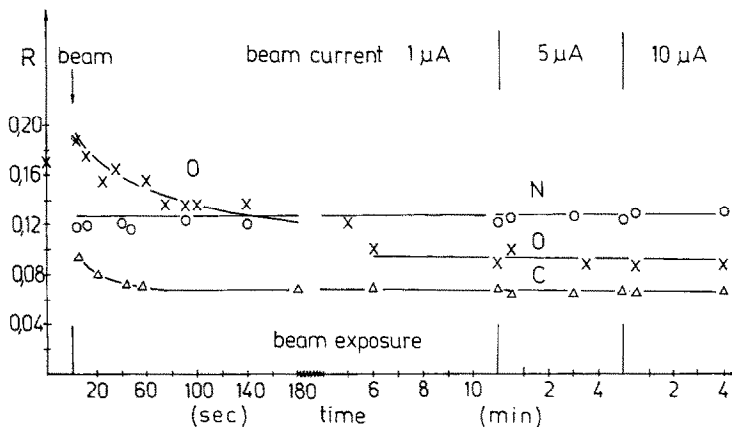


Fig. 3. The effect of the beam current and beam exposure on the relative intensities of N, O and C Auger signals. The oxygen covered ( $\theta \approx 0.17$ ) Cu(111) surface was exposed to 90 L HNCO at 300 K. Auger beam energy 2.5 kV ( $R = O_{514}/Cu_{920}$  (X);  $N_{384}/Cu_{920}$  (O);  $C_{271}/Cu_{920}$  ( $\Delta$ )).

As the C–O bond is very sensitive to an electron beam, detailed studies were performed to establish the effect of an electron beam on the adsorbed NCO. In order to detect the electron beam induced effect a  $1 \mu\text{A}$ , 2.5 keV electron beam was initially used for Auger excitation. Even under these conditions a significant decrease could be observed in the relative intensity of O signal with increasing exposure to the electron beam (fig. 3). With further increase of beam current, only a slight change occurred. When the first Auger spectrum was taken at high beam current ( $\sim 10 \mu\text{A}$ ) the final low O signal was obtained already at the first measurement.

Much less effect was detected in the carbon signal, and no decrease in the N signal was experienced even at high beam current (fig. 3).

In order to minimize the effect of the beam, the important signals were always taken first, and then the other part of the Auger spectrum.

We mention here that, in addition to the main C peak at 271 eV, two smaller ones appeared in the spectra about 3 and 7 eV higher in energy (fig. 1). No such a feature was observed when surface C was produced by the dissociation of CO due

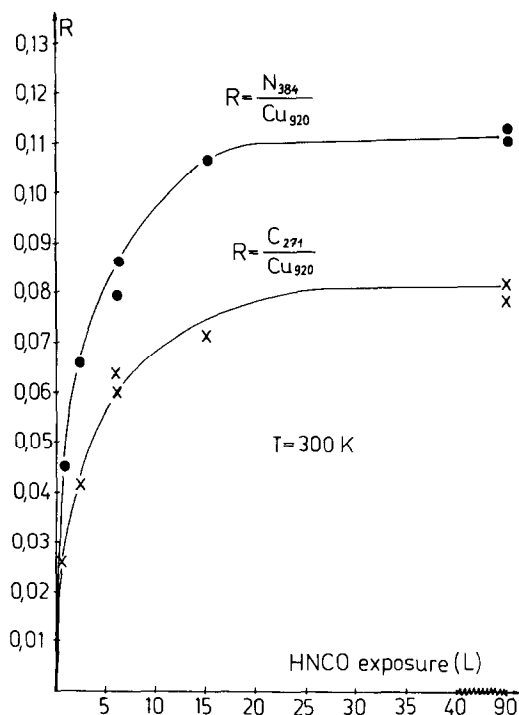


Fig. 4. The dependence of the relative N and C signals on the HNCO exposure. The surface was predeposited with 60 L  $\text{O}_2$  ( $\theta \approx 0.17$ ) at 300 K.

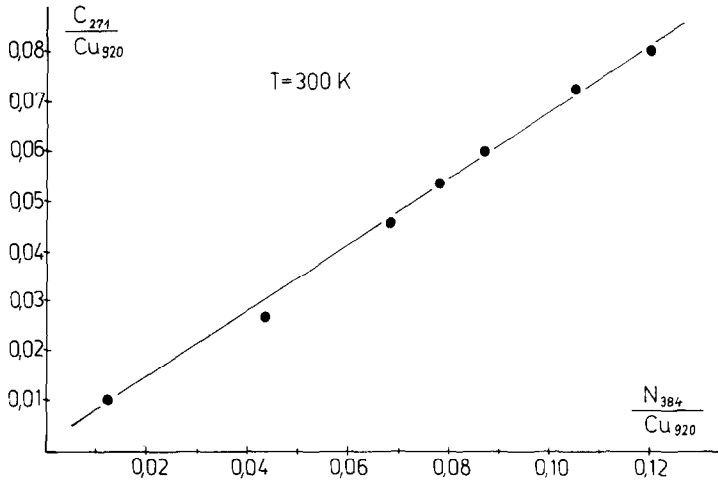


Fig. 5. The relative C Auger signal versus relative N Auger signal on oxygen covered surface ( $\theta \approx 0.17$ ) at different HNCO exposures.

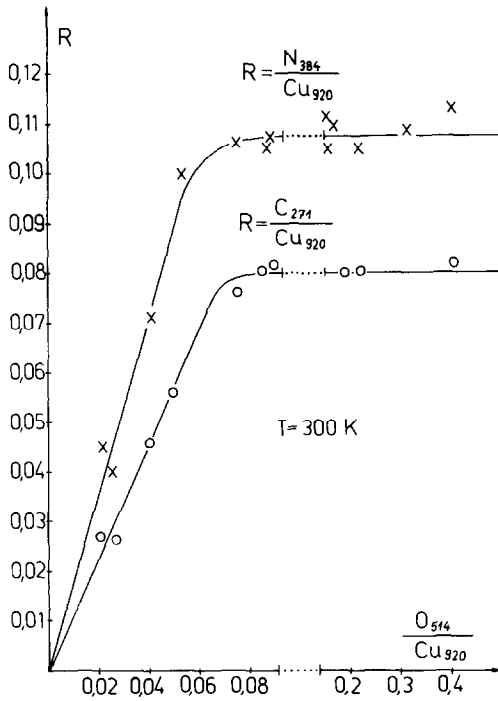


Fig. 6. The effect of oxygen coverage on the relative Auger signals of N and C. The exposition of HNCO was 90 L.

to the electron bombardment (curve e of fig. 1). This results can very likely be attributed to the difference in the chemical environments of the adsorbed molecules which influences the Auger line shapes [8–10]. Similarly, two smaller peaks were observed about 5 and 10 eV above, and about 15 and 23 eV below the main peak of N (384 eV). Comparative studies are in progress in our laboratory to exploit the advantage of NCO as a complex molecule in establishing precisely the effect of the environment on the Auger line shapes of N, C and O atoms on copper and other metals.

In fig. 4 we have plotted the relative N and C signals against HNCO exposure. It can be seen that both signals reached constant values at 20–25 L HNCO exposure. When the relative C signal was plotted against the relative N signal, we obtained a straight line (fig. 5).

Fig. 6 shows the effect of oxygen coverage on the adsorption of HNCO. In this case the exposure to HNCO was constant, at 90 L. The N and C signals increased linearly with the surface concentration of oxygen up to the ratio  $h_{\text{O}}/h_{\text{Cu}} \approx 0.06$ , which corresponds to  $\sim 0.05$  coverage. The highest values were reached at  $\theta \approx 0.07$ . Further increase of the O coverage exerted no observable influence on the adsorption of HNCO.

### 3.3. Thermal desorption measurements

Thermal desorption spectra were taken at a linear heating rate of  $10 \text{ K s}^{-1}$ . The major signals were at 44 amu ( $\text{CO}_2$ ), 28 amu ( $\text{CO} + \text{N}_2$ ) and 52 amu ( $\text{C}_2\text{N}_2$ ) (fig. 7). Care was taken to try to detect signals due to  $\text{H}_2$ ,  $\text{NH}_3$ , HCN, HNCO, NCO,  $(\text{NCO})_2$  and  $\text{H}_2\text{O}$ , without any positive results.

The evolution of carbon dioxide sensitively depended on the amount of pre-adsorbed oxygen. At very low oxygen coverage ( $h_{\text{O}}/h_{\text{Cu}} = 0.018$ ) only one  $\text{CO}_2$  peak ( $\alpha_3$ ) was observed at 670 K. At higher oxygen coverage ( $h_{\text{O}}/h_{\text{Cu}} > 0.10$ ) the amounts of desorbed gases significantly increased. Carbon dioxide desorbed in two main stages, with a peak maximum at 463 K ( $\alpha_1$ ) and 633 K ( $\alpha_2$ ) at saturation. At 670 K only a shoulder was observed (fig. 7).

The desorption of nitrogen started always above 700 K. In order to differentiate between  $\text{N}_2$  and CO, the behaviour of the signal at 14 amu ( $\text{N}^+$ ) was compared with that at 28 amu. Calculation led us to conclude that the 28 amu signal is due to  $\text{N}_2$ , and practically no contribution is made by CO. At higher temperatures, above 800 K, the desorption of  $\text{C}_2\text{N}_2$  was observed. While the ratios of desorbed gases,  $\text{CO}_2/\text{C}_2\text{N}_2$  and  $\text{N}_2/\text{C}_2\text{N}_2$ , increased with the oxygen coverage, the value of  $\text{CO}_2/\text{N}_2$  remained unchanged (table 1).

In the subsequent measurements the oxygen coverage was kept constant ( $h_{\text{O}}/h_{\text{Cu}} = 0.17$ ) and the exposure of HNCO was varied. At a low exposure of HNCO, only the low temperature  $\text{CO}_2$  peak ( $\alpha_1$ ) was observed ( $T_{\text{max}} = 513 \text{ K}$ ). With the increase of HNCO exposure,  $T_{\text{max}}$  was shifted to lower temperatures, and in parallel with this the high temperature peaks ( $\alpha_2$  and  $\alpha_3$ ) developed. Their  $T_{\text{max}}$  seemed to

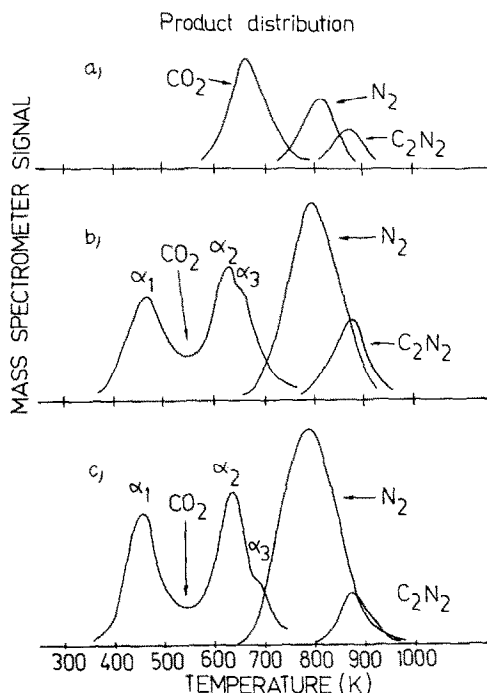


Fig. 7. Temperature programmed desorption spectra following HNCO adsorption at 300 K on a Cu(111) surface predosed with (a) 1.2 L O<sub>2</sub>, (b) 60 L O<sub>2</sub>, (c) 1700 L O<sub>2</sub> at 300 K. The HNCO exposure was 90 L. The curves are uncorrected for detection sensitivities.

be independent of the coverage. The kinetic data calculated by the different methods are listed in table 2.

The peak temperature for the nitrogen signal was 793–803 K; it showed very

Table 1

The effect of oxygen coverage on the CO<sub>2</sub> signal and on the ratios of signals of products (TPD measurements)

	$h_{\text{O}}/h_{\text{Cu}} = 0.018,$ $\theta \sim 0.02$	$h_{\text{O}}/h_{\text{Cu}} = 0.17,$ $\theta \sim 0.17$	$h_{\text{O}}/h_{\text{Cu}} = 0.35,$ $\theta \sim 0.35$
CO <sub>2</sub>	0.51	1.30	1.43
CO <sub>2</sub> /C <sub>2</sub> N <sub>2</sub>	3.1	4.0	5.9
N <sub>2</sub> /C <sub>2</sub> N <sub>2</sub>	2.5	3.5	5.7
N <sub>2</sub> /CO <sub>2</sub>	0.80	0.78	0.87

The above values are not corrected for detection sensitivities.



Table 2

Summary of the results observed for the decomposition of surface isocyanate on oxygen-covered Cu(111) face

State <sup>a</sup>	$T_p$ (K)	$E^b$ (kJ/mol)	$k_0^b$ (s <sup>-1</sup> )	$E^c$ (kJ/mol)	$k_0^c$ (s <sup>-1</sup> )
CO <sub>2</sub> ( $\alpha_1$ )/HNCO	513–463	46.0		66.0	
CO <sub>2</sub> ( $\alpha_2$ )/HNCO	633	82.9	$7 \times 10^5$	98.0	$1.2 \times 10^7$
N <sub>2</sub> /HNCO	793	146.5	$5.1 \times 10^9$		
C <sub>2</sub> N <sub>2</sub> /HNCO	874	169.8	$4 \times 10^{11}$	158.3	$1.4 \times 10^9$

<sup>a</sup> The notation of A( $\alpha$ )/B refers to the  $\alpha$  state or desorption peak for gas A following adsorption of gas B.

<sup>b</sup> Calculated on base of heating rate variation method [11].

<sup>c</sup> Calculated according to approximation method of Chan et al. [12].

little variation with the coverage (fig. 8). The activation energy for the desorption of nitrogen (146.5 kJ/mol) was considerably higher than that for CO<sub>2</sub> evolution. The desorption maximum of C<sub>2</sub>N<sub>2</sub> occurred at 874 K; it showed no dependence on the HNCO coverage (fig. 8). We obtained 169.8 kJ/mol for the activation energy for C<sub>2</sub>N<sub>2</sub> formation (table 2).

The Auger spectra of the sample covered with HNCO and heated to different temperatures are in good agreement with the results of TPD measurements. No decrease in the N signal was experienced below 700 K. Decreases in the C and O signals were observed above 400 K. In the final stage, above 750 K, only the signals

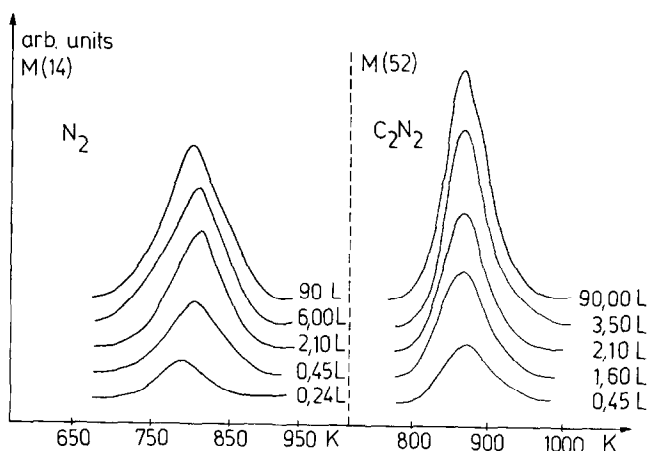


Fig. 8. Nitrogen (14 amu) and C<sub>2</sub>N<sub>2</sub> (52 amu) desorption spectra subsequent to the adsorption of HNCO on Cu(111) at 300 K. The Cu(111) surface was preadsorbed with 60 L O<sub>2</sub> ( $\theta \sim 0.17$ ) at 300 K.

due to C and N were detected, and these were eliminated together on further heating.

### 3.4. Electron energy loss studies

EELS provide a good picture of the electronic structures of the clean metal and the metal–gas system. From the point of view of gas adsorption and surface contamination, the surface plasmon losses are important. As the adsorption of gases mainly influences the losses due to surface plasmon, the effect of gas adsorption may help in differentiating between bulk and surface losses.

We first determined the dependence of the elastic peak height reflected from a clean Cu(111) surface on the primary energy at 20–125 eV. The maximum of the reflectance appeared at 70 eV, in good agreement with the results of Kessler and Thieme [13]. Further measurements were performed at a primary electron energy of 70 eV. In this case the beam current was 0.2  $\mu\text{A}$ .

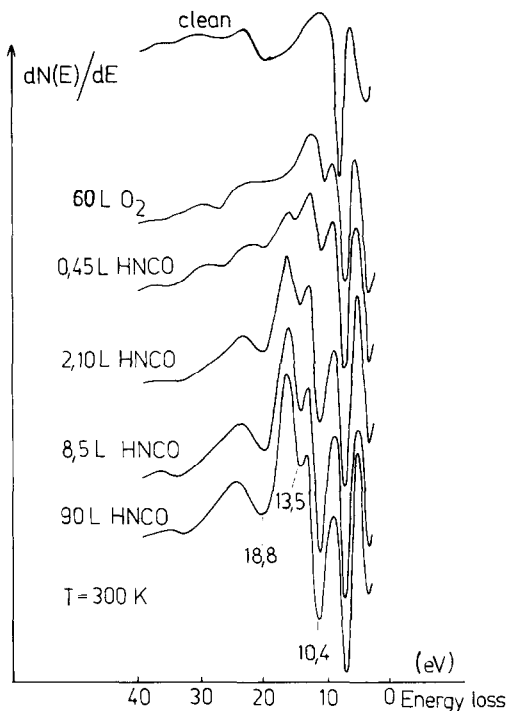


Fig. 9. Electron energy loss spectra of Cu(111) surface covered with oxygen ( $\theta \approx 0.17$ ) as a function of HNCO exposition, the ELS of clean Cu(111) surface is also shown ( $E_p = 70 \text{ eV}$ ,  $I = 0.2 \mu\text{A}$ ).

The characteristic loss energies of a Cu(111) surface appeared at 2.7, 4.8, 7.1, 18.8 and 26 eV. These losses did not vary with the primary electron energy. Admission of oxygen onto the surface (60 L, at  $10^{-8}$  Torr) enhanced the intensity of the elastic peak and that of the 2.7 eV peak, and markedly reduced the intensity of the peak at 18.8 eV. The peak at 7.1 eV was shifted to 6.5 eV. At 9.3 eV a new loss appeared (fig. 9).

The introduction of HNCO onto a Cu(111) surface predosed with 60 L  $O_2$  at 300 K, produced new intensive loss peaks at 10.4 and 13.5 eV (fig. 9). The intensities of these peaks at 10.4 and 13.5 eV, and also that of the elastic peak, increased up to an exposure of 10 L HNCO. At the same time the intensity of the peak at 9.3 eV, developed due to the adsorption of oxygen, decreased and appeared as a shoulder. It should also be noted that the intensity of the peak at 18.8 eV, which decreased following the adsorption of oxygen, became higher upon the introduction of HNCO, and at 10 L reached its original value.

The electron energy loss spectra were also taken after heating the sample exposed to 90 L HNCO to different temperatures. Spectra are shown in fig. 10.

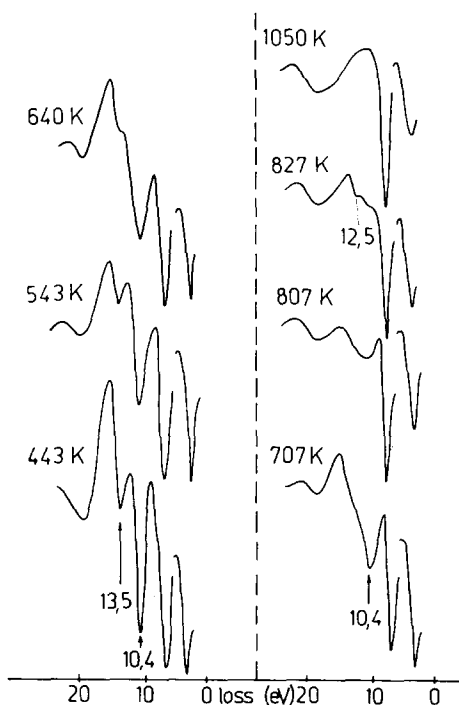


Fig. 10. Electron energy loss spectra taken after heating the sample exposed to 90 L HNCO to different temperatures. Heating rate was  $10 \text{ K s}^{-1}$ .

Table 3  
Characteristic energy losses of copper covered with different adsorbates

Clean metal losses (eV)	New losses after adsorption of				Ref.						
	HNCO	CO	O	C <sub>2</sub> N <sub>2</sub>							
2.7	4.8	7.1	18.8	26	10.4	13.5	9.3	10.4	12.5	This work	
	4.5	7.7	10.5	19.0	27.5	39		4.5	13.5	[28]	
	3.4	4.7	7.7	19.8				4.7	(10)	13.8	[13]

Heating the sample exposed to HNCO to above 443 K decreased the intensities of both the 10.4 and the 13.5 eV peaks. The 13.5 eV peak disappeared at 650–707 K. The peak at 10.4 eV was more stable. It was present up to 874 K. A new feature of the spectrum was that above 707 K a shoulder appeared at 12.6 eV. This was eliminated only above 874 K.

Exposure of the clean and oxidized Cu(111) surface to 100 L CO, CO<sub>2</sub> and activated nitrogen at 300 K caused no change in the electron energy loss spectra.

Table 3 gives the loss energies observed in the present work, together with some data from the literature for comparison.

#### 4. Discussion

The adsorption of HNCO was earlier investigated on Pt(110) and Pt(111) surfaces [14]. In contrast to these surfaces, no adsorption of HNCO was observed on a clean Cu(111) surface at 300 K. The presence of adsorbed oxygen, however, exerted a dramatic influence on the adsorptive properties of this surface and caused HNCO adsorption. Based on the N and C signals in the Auger spectra, the adsorption of HNCO increased linearly with the extent of the surface concentration of oxygen up to  $\sim 0.05$  coverage (fig. 6). The saturation coverage of HNCO was calculated to be  $(9.5 \pm 0.5) \times 10^{13}$  at 300 K. This calculation was based on the relationship found between the ratio  $h_N/h_{Cu}$  in the Auger spectra and the nitrogen coverage in the study of the adsorption of atomic nitrogen on Cu(111) surface [26]. The initial sticking probability for the adsorption of HNCO, determined from the change of the N signal on the Auger spectra (fig. 4), is 0.11.

The marked influence of oxygen adsorbed on Cu(110) on the subsequent adsorption of CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, HCHO and HCOOH has been nicely demonstrated by Madix et al. [15]. Recently the interaction of oxygen chemisorbed on a Cu(100) surface with alcohols was investigated by means of high resolution electron energy loss spectroscopy, and CH<sub>3</sub>O–Cu and C<sub>2</sub>H<sub>5</sub>O–Cu stable surface species were identified [16].

Before attempting a discussion of the results, we should deal briefly with the Cu–O<sub>2</sub> interaction. The adsorption of O<sub>2</sub> on a Cu(111) surface has been less extensively investigated than on other Cu surfaces. No ordered superstructure was observed in LEED studies [17–20]. Bootsma et al. [7] recently examined the interactions of O<sub>2</sub> and N<sub>2</sub>O in the low temperature range with a Cu(111) surface by ellipsometry, Auger electron spectroscopy and LEED. They found that O<sub>2</sub> chemisorbed dissociatively, with an initial sticking probability of about  $10^{-3}$  and an apparent activation energy of 9–16 kJ/mol. The oxygen coverage was maximum at  $\theta = 0.45 \pm 0.05$ . The LEED patterns indicated that the adsorption takes place in a disordered, random fashion.

#### 4.1. Interaction of adsorbed oxygen with HNCO

A possible role of the adsorbed oxygen in causing the adsorption of HNCO on copper is to promote the dissociative adsorption of HNCO. This may occur through the following transition state

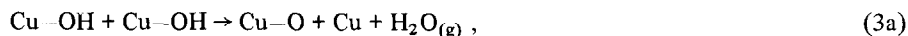


The hydrogen is then bonded to adsorbed oxygen, while NCO is adsorbed on an adjacent vacant adsorption site:

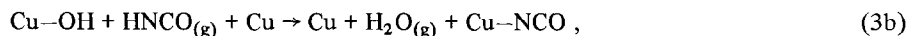


In the light of the results of IR spectroscopic measurements [1–6] we assume that NCO is bonded to the metal via the nitrogen end of the molecule.

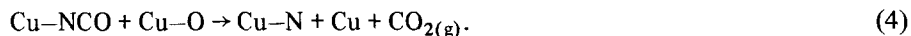
The adsorption of HNCO was accompanied by the evolution of water, indicating that the dehydration of the surface



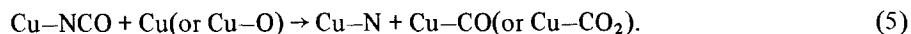
or



occurred rapidly and simultaneously with the adsorption. This process was practically complete at 300 K, as neither H<sub>2</sub>O nor hydrogenated products were found in the desorbing products. This result is in harmony with the observations of Roberts et al. [21] on the stability of OH groups on Cu(111) surface. As we could not identify either HNCO, NCO or (NCO)<sub>2</sub> in the desorbing gases, we may infer that NCO is strongly bonded to the Cu and does not desorb as such. With the increase of the temperature, CO<sub>2</sub> evolution was first observed, showing that reactions occurred in the adsorbed phase. It is very likely that adsorbed NCO groups reacted with adsorbed oxygen on the neighbouring site and that CO<sub>2</sub> desorbed:



An alternative explanation for these results is that NCO is also dissociated on the copper surface during the adsorption at 300 K:



This process probably occurs on Pt surfaces [14]. The adsorption behaviour of CO and CO<sub>2</sub> on copper surfaces, however, make this explanation very unlikely. No, or only an extremely small interaction of these molecules with a clean Cu(111) surface was detected at 300 K in the present work. The adsorption of CO on a clean

Cu(111) surface was observed only at low temperature, at 140 K [13,22–24]. It gave a  $\sqrt{3} \times \sqrt{3}$  R30° LEED pattern [24]. It could be pumped off around 170 K. From this result an adsorption energy of about 50 kJ/mol was estimated. Work function changes during desorption of CO also indicated that CO desorbed completely around 190 K [13].

One may argue that the surface oxygen on the copper increases the sticking coefficient and the adsorption of CO and CO<sub>2</sub>. However, we could not detect the adsorption of CO or CO<sub>2</sub> on a partially oxidized Cu(111) surface at 300 K. This is in harmony with the experimental finding of Wachs and Madix [25] on a Cu(110) surface. From a comparison of the adsorption characteristics of CO and CO<sub>2</sub> on clean and partially oxidized surfaces at 180 K, they found that the total amount of CO and CO<sub>2</sub> adsorbed decreased following initial exposure to oxygen. The presence of oxygen atoms on the copper surface diminished the sticking probabilities of CO and CO<sub>2</sub>; this is very probably due to the decreased number of adsorption sites available to the CO and CO<sub>2</sub>.

Accordingly, we may conclude that NCO exists as such on a Cu(111) surface.

We note that our recent infrared spectroscopic measurements on the stability of NCO species on partially oxidized copper, provide additional evidence for the existence of NCO on Cu in a moderate temperature range. The adsorption of HNCO on Cu/SiO<sub>2</sub> produced a band at 2210 cm<sup>-1</sup>, which can be attributed to Cu–NCO. The location of this band agrees well with that observed in the NO + CO reaction on a CuO/SiO<sub>2</sub> catalyst [2]. The assignment of this band is confirmed by the IR spectra of Cu(NCO)<sub>2</sub>. The intensity of the 2210 cm<sup>-1</sup> band started to decrease above 403 K, and it disappeared completely above 600 K.

The fact that CO<sub>2</sub> desorbed in two main stages can be explained by the assumption that – from the point of view of reactivity – two different kinds of adsorbed oxygen (or adsorbed HNCO) exist on the surface. In our opinion the most probable reason for the two stages is that in the low temperature stage NCO reacts with the adjacent adsorbed O in a second order process, while migration of the reactants is necessary for the second stage of the reaction, which requires somewhat higher activation energy. The relatively low activation energies and preexponential factor of the CO<sub>2</sub> evolution seem to be in harmony with this consideration.

The nitrogen formed in the surface reaction of the NCO species remains bonded to the copper; it desorbs above 700 K with an activation energy of 146.5 kJ/mol. Accurate determination of the ratio of the signals at 28 and 14 amu indicate that nitrogen atoms recombine before desorption. We have recently studied the interaction of atomic N on a Cu(111) surface [26]. The peak temperature and the activation energy for the desorption of nitrogen agreed very well with the data obtained in this work.

A surprising result of the thermal desorption measurements was the identification of C<sub>2</sub>N<sub>2</sub> in the desorbing gases. It was the most stable surface compound, desorbing only above 800 K. The fact that the relative amount of C<sub>2</sub>N<sub>2</sub> increased

with the decrease of the O coverage may suggest that it is formed mainly after the consumption of surface oxygen in reaction (2). We may assume that in this stage the process occurs



As we could not detect CN radicals in gas phase we may assume that CN groups recombined before desorption. The desorption characteristics of  $\text{C}_2\text{N}_2$  agreed with those determined in a separate study of the interaction of  $\text{C}_2\text{N}_2$  with Cu(111) [27]. ( $\text{C}_2\text{N}_2$  desorbed in one stage;  $T_{\text{max}}$  was 860 K. No desorption of CN (26 amu) was observed. The value of the activation energy for the desorption of  $\text{C}_2\text{N}_2$  was 160 kJ/mol.)

#### 4.2 Electron energy loss spectra

EEL spectra provide further evidences for the proposed model of HNCO adsorption and reactions. Before attempting to discuss the losses due to HNCO adsorption, it is instructive to summarize the previous results obtained for CO adsorption on copper surfaces.

The adsorption of CO on a Cu(311) surface at 77 K caused two strong maxima, at 4.5 and 13.5 eV, and the disappearance of copper losses at 7.7 and 19 eV [28]. The small loss peak at 10.5 eV was also removed by CO adsorption. On warming of the crystal to room temperature, the loss spectrum of the clean surface was always recovered, indicating the total desorption of CO, as found by surface potential measurements [29].

Kessler and Thieme [13] observed a decrease in the intensities of the 4.7 and 7.7 eV peaks due to the adsorption of CO on a Cu(111) surface at 150 K. A new loss peak was produced at 13.8 eV, and also a small one at 10 eV. The 10 eV peak was stable up to 450 K and was attributed to adsorbed oxygen, which was assumed to be produced by the dissociation of CO in the electron beam.

Our results showed that the adsorption of oxygen also influenced the 7.1 eV loss, indicating that this loss is probably due to surface plasmon [30,31] and not to bulk plasmon [32–34]. The fact that the adsorption of oxygen also decreased the loss at 18.8 eV, similarly as in the adsorption of CO at low temperature [28], may support the idea of Wehenkel [35] that, in contrast to the former interpretation [30,33,34], the losses below 35 eV are largely of a hybrid character, containing both a surface and a bulk contribution; the surface contribution is stronger below 10 eV. A new loss appeared at 9.3 eV, which may confirm the interpretation of Kessler and Thieme [13] for the origin of the 10 eV loss in their spectra.

The adsorption of HNCO at 300 K caused two strong new losses, at 10.4 and 13.5 eV. In addition, the intensity of the peak at 18.8 eV, which greatly decreased on the adsorption of oxygen, was recovered; this clearly demonstrated the occurrence of a reaction between adsorbed oxygen and HNCO. The loss at 9.3 eV caused by the adsorption of oxygen appears as a shoulder at low exposure of HNCO; at



higher exposures it can not be discerned, partly due to the large peak at 10.4 eV, but, in our opinion, mainly due to the reaction between adsorbed oxygen and HNCO.

As adsorbed CO produced a loss at 13.5–13.8 eV, it would be tempting to attribute the 13.5 eV loss to the adsorbed CO formed in the dissociation of NCO. We believe, however, that the arguments mentioned previously against the existence of CO on the surface are strong enough to exclude this possibility. In addition, we did not find the strong loss at 4.5 eV observed by Papp [28] during CO adsorption at 140 K, which was larger than the 13.5 eV feature, but we identified a new loss at 10.4 eV.

Accordingly, we may attribute these losses to the adsorbed NCO. Unfortunately, as regards the electron structure and levels of NCO very little is known which may be of help in the interpretation of these losses. The fact that the highest energy NCO loss feature is close to that of adsorbed CO on different metals makes it likely that the same electron transition occurs in the present case, too.

Heating the sample exposed to HNCO upto 650–707 K caused the disappearance of the peak at 13.5 eV and the appearance of a shoulder at 12.6 eV. Taking into account the results of the thermal desorption measurements, it seemed very likely that formation of the cyanide group is responsible for the appearance of this new loss. Our recent ELS measurements seem to prove this assumption. Adsorption of  $C_2N_2$  (0.36 L) on a clean Cu(111) surface produced a loss at 12.6 eV. With the increase of the  $C_2N_2$  exposure this peak became larger, and a strong peak also developed at 10.3 eV [27].

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