

INTERACTION OF HNCO WITH Cu(111) SURFACE 205

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Abstract

When clean Cu(111) was exposed to HNCO at 300 K, no adsorption occurred. When the surface was predosed with oxygen, however, HNCO adsorbed with concomitant release of water. Auger analysis of the sample showed signals of C, N and O. The ratio of the relative intensities of the N and C signals remained the same with the increase of the coverage. ELS showed losses which were not observed during the adsorption of either CO or atomic N. No HNCO was desorbed as such, and neither NCO nor  $(\text{NCO})_2$  were detected during the desorption. The main products were  $\text{CO}_2$  (463 and 633 K),  $\text{N}_2$  (793) and  $\text{C}_2\text{N}_2$  (874 K).

Introduction

The isocyanate (NCO) complex identified by i.r. spectroscopy on supported metals plays an important role in the  $\text{NO}+\text{CO}$  reaction [1-3]. However, its surface behaviour on metals has not been established on an atomic scale, very probably due to the difficulty in producing it by the  $\text{NO}+\text{CO}$  reaction at low pressures. In the present work a report is given on its surface chemistry on Cu(111), studied by LEED, AES, ELS and temperature-programmed reaction spectroscopy.

Experimental

Experiments were performed in a stainless steel UHV chamber described in detail in our other paper [4]. The difference was that the Auger and electron energy loss spectra were taken by a single-pass CMA analyzer.

The oriented disk-shaped crystal (diameter 6 mm, thickness 1.5 mm) was obtained from Materials Research Corporation. 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  $\text{Ar}^+$  bombardment and annealing at 973 K for some min. HNCO was prepared by the reaction of saturated aqueous HNCO solution with 95%  $\text{H}_3\text{PO}_4$  at 300 K [5].

Results

Adsorption of HNCO on an Oxygen-Covered 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 any desorbing products on

heating the sample up to 1020 K. When the clean surface was predosed with oxygen at 300 K, however, a significant adsorption of HNCO was observed. The absolute coverage of oxygen was calculated by using the relationship found by Bootsma et al. [6] between the ratio  $h_{O}/h_{Cu}$  in the Auger spectra and  $\delta\Delta$  (ellipsometry), as well as between  $\delta\Delta$  and the oxygen coverage. Exposure of the oxygenated surface ( $\theta \sim 0.17$ ) to HNCO at 300 K resulted in the appearance of the N and C KLL signals at 384 and 270 eV and a decrease of the O signal at 514 eV. At the same time, mass spectrometric analysis of the gas phase indicated water formation. No other products were, however, identified. As regards the effect of the beam, we found that it exerted only a slight influence on the intensities of the N and C signals. It caused, however, the dissociation of C-O bond pre- $\sqrt{V}$ . In Fig. 1 we have plotted the relative N, C and O signals against HNCO exposure. It can be seen that the N and C signals reached constant values at 20-30 L HNCO exposure. When the relative C signal was plotted against the relative N signal, we obtained a straight line. The extent of the decrease in the oxygen signal during the adsorption of HNCO depended on the oxygen coverage. At the coverage  $\theta \sim 0.17$ , it decreased to approximately half its initial value. Figure 2 shows the effect of oxygen coverage on the adsorption of HNCO.

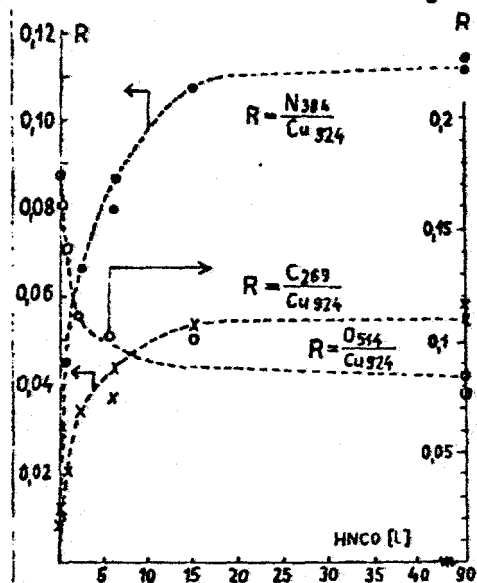


Fig. 1 - The dependence of the relative N, C and O signals on the HNCO exposure.

#### Thermal Desorption Measurements

Thermal desorption spectra were taken at a linear heating rate of  $10 \text{ Ks}^{-1}$ . 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. 3). Care was taken to try to detect signals due to  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{NCO}$ ,  $(\text{NCO})_2$ , HNCO and  $\text{H}_2\text{O}$ , without any positive results. Carbon dioxide desorbed in two stages, with a peak maximum at 463 and 633 K. At a low exposure of HNCO, only the low temperature peak was observed. With the increase of the HNCO exposure,  $T_{\text{max}}$  was shifted to lower temperatures, and in parallel with this the high temperature peak developed. Its  $T_{\text{max}}$  seemed to be independent of the coverage. The thermal desorption data were analyzed by the method of heating rate variation. Activation energies for  $\text{CO}_2$  evolution were 11.3 and 19.8 kcal/mol. The desorption of nitrogen started 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. Calculations led us to conclude that the 28 amu signal is due to  $\text{N}_2$ , and practically no contribution is made by CO. The peak temperature for both signals was 793-803 K; it showed very little variation with the coverage. The activation energy for venting to detect an increase of O signal due to the adsorption of HNCO.

the desorption of nitrogen (35 kcal/mol) was considerably higher than that for CO<sub>2</sub> evolution. At higher temperatures, above 800 K, the desorption of cyanogen was observed. Its amount was about 20% of the N<sub>2</sub> formed. The desorption maximum occurred at 874 K; it showed no dependence on the HNCO coverage. The activation energy for C<sub>2</sub>N<sub>2</sub> formation was 39.3 kcal/mol.

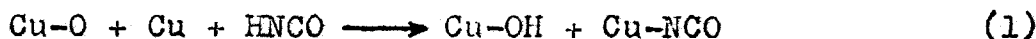
### Electron Energy Loss Spectra

Detailed ELS measurements were carried out. We can report here only on the main results. The introduction of HNCO onto a Cu(111) surface predosed with 60 L O<sub>2</sub> at 300 K, produced new intensive loss peaks at 10.4 and 13.5 eV (Fig. 4). 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.

### Discussion

The adsorption of HNCO was earlier investigated on Pt(110) and Pt(111) surfaces [7]. 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. The marked influence of oxygen

adsorbed on copper surfaces on the subsequent adsorption of many organic compounds has been nicely demonstrated by Maddix et al. [8]. A possible role of the adsorbed oxygen in causing the adsorption of HNCO on copper is to promote the dissociative adsorption of HNCO. The hydrogen is bonded to adsorbed oxygen, while NCO is adsorbed on an adjacent vacant adsorption site:



The adsorption of HNCO was accompanied by the evolution of

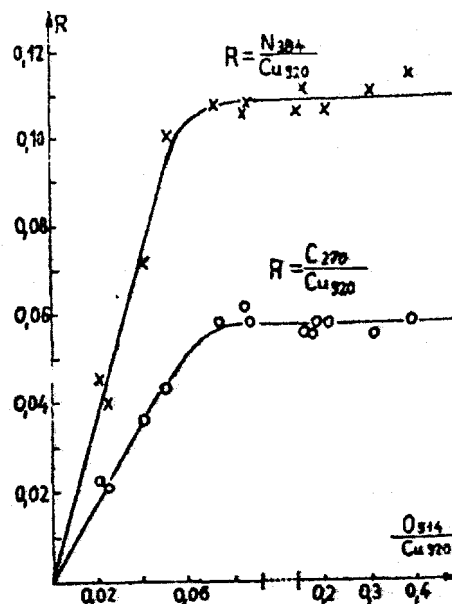


Fig. 2 - The effect of oxygen coverage on the relative signals of N and C.

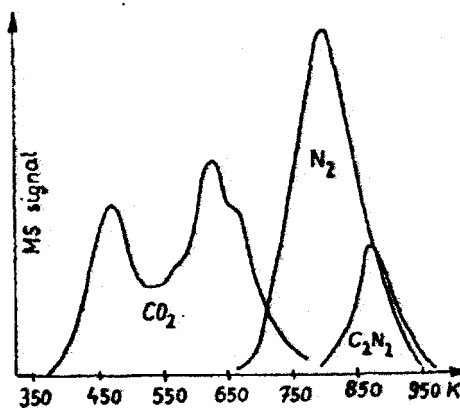
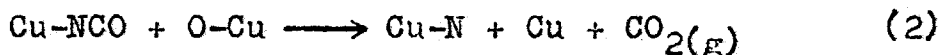
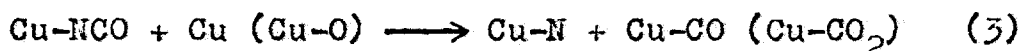


Fig. 3 - Temperature programmed spectra following HNCO adsorption at 300 K on a Cu(111) surface predosed with 60 L O<sub>2</sub>.

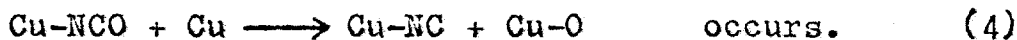
water, indicating that the dehydration of the surface occurred rapidly and simultaneously with the adsorption. This process was practically complete at 300 K, as neither H<sub>2</sub>O nor hydrogenated products were found in the desorbing products. As we could not identify either HNCO, NCO or (NCO)<sub>2</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 [7]. The adsorption behaviours 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 copper surface was detected at 300 K in the present and previous works [8]. Accordingly, we may conclude that NCO exists as such on a Cu(111) surface. The fact that CO<sub>2</sub> desorbed in two stages can be explained by the assumption that in the low temperature stage NCO reacts with the adjacent adsorbed O, while migration of the reactants is required for the second stage of the reaction. A surprising result of the TPD measurements was the identification of C<sub>2</sub>N<sub>2</sub>. 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 O in the reaction (2). We may assume that in this stage the process



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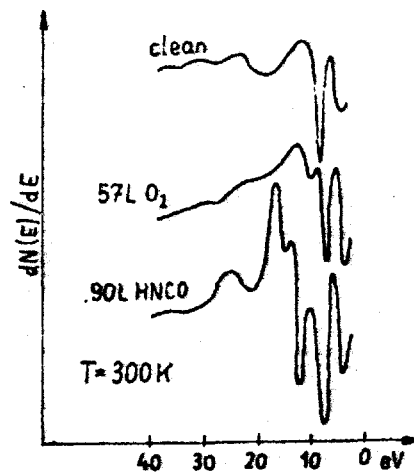


Fig. 4 - ELS spectra.