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By DAVID W. JOHNSON, MOHAMMED H. MATLOOB, and M. WYN ROBERTS*
(School of Chemistry, University of Bradford, Bradford BD7 1DP)



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Adsorption of Nitric Oxide on Cu(100) Surfaces; an Electron Spectroscopic Study

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Summary The adsorption of nitric oxide on Cu(100) has been investigated by high resolution X-ray photoelectron spectroscopy; at 85 K a number of distinct molecular processes have been recognised including dissociation, oxygen chemisorption, and the catalytic formation of nitrous oxide, which desorbs at 110 K leaving at 295 K only chemisorbed oxygen which exhibits a $\sqrt{2} \times \sqrt{2} R$ 45° low energy electron diffraction pattern.

We have studied recently¹ the adsorption of nitric oxide on polycrystalline copper using X-ray and u.v. photoelectron spectroscopies. At 85 K adsorption was suggested to be molecular, two distinct surface species being observed with O(1s) binding energies of 535 and 531.7 eV and N(1s) values of 406 and 401 eV. This adlayer was thermally unstable and dissociation of the surface species was observed above about 150 K to give an adlayer at 295 K which was exclusively chemisorbed oxygen. In order to obtain further details regarding the mechanism of the formation of the adlayer at 85 K and its thermal stability we have investigated the interaction of nitric oxide with a single crystal Cu(100) surface. Furthermore the X-ray-induced spectra have been obtained at a higher resolution with a view to exploring in greater detail the profiles of the core-level spectra which in our earlier work had full width at half-maximum height (FWHM) values of about 4 eV. The possibility of overlapping peaks, not resolved in our earlier studies, therefore required closer investigation.

The experimental approach using combined *in situ* low energy electron diffraction and electron spectroscopic facilities and the preparation of the well defined 'clean' Cu(100) surface has been described.² For example, the Cu(100) surface showed no evidence for chemisorbed oxygen (Figure 1, curve a). Nitric oxide was prepared as before.¹

Figure 1 (curves b and c) shows the development of the O(1s) spectrum with increasing exposure to NO at 85 K, curve b after 6 L, and curve c after 24 L. † N(1s) spectra are shown in Figure 2. It is clear that when adsorption is studied with increasing extents of exposure and at high resolution three distinct O(1s) peaks are present: 529.6, 531.2, and 534.5 eV, all three peaks increasing in intensity with exposure. After 24 L exposure the N(1s) spectrum (Figure 2, curve c) showed a rather broad peak centred at 401 eV and a second one at 406 eV. Both these peaks are at similar binding energies to those observed with polycrystalline copper and assigned to $\text{NO}^{\delta-}$ (ads) and $\text{NO}^{\delta+}$ (ads) respectively¹. There is, however, an important difference between the O(1s) spectra observed with Cu(100) and polycrystalline copper in that the previously observed¹ broad single peak at about 531 eV is resolved with Cu(100) into two distinct peaks, one centred at about 529.5 eV and the other at 531 eV. Furthermore the intensity of the former is greater than the latter at low exposure (*e.g.* after 6 L, Figure 1, curve b) but with increasing NO exposure all three

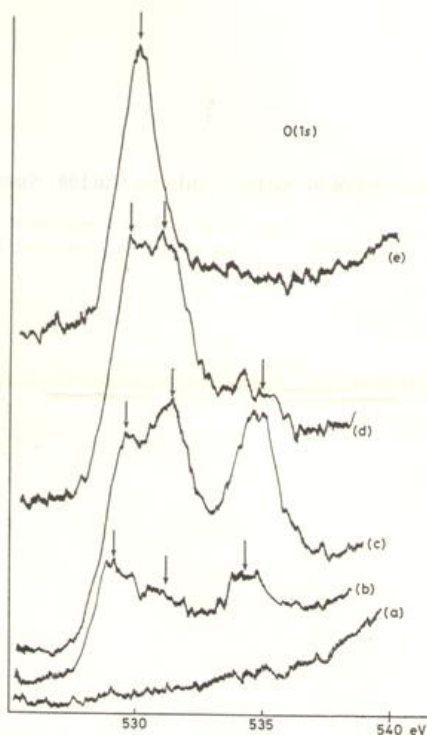


FIGURE 1. O(1s) spectral region: curve (a) clean Cu(100) surface; curve (b) after exposure (6 L) of Cu(100) surface to NO at 85 K; curve (c) after exposure (24 L) of Cu(100) surface to NO at 85 K; curve (d) after warming adlayer (curve c) to 110 K and then to 295 K (curve e). † designate the peak positions. Analysing conditions: 20 eV; 3×10^6 counts s^{-1} (full scale deflection).

O(1s) peaks increase in intensity (Figure 1, curve c). We should recall that for oxygen chemisorbed on copper³ the O(1s) peak is centred at about 529.6 ± 0.3 eV so that the high resolution O(1s) spectra are therefore strongly suggestive of the dissociative chemisorption of NO on Cu(100) even at 85 K and low exposure. It should, however, be emphasised that no N(1s) peak at about 397 eV is observed (Figure 2); this would be expected if N(ads) were present.¹

† 1 L (Langmuir) = 10^{-4} Torr s.

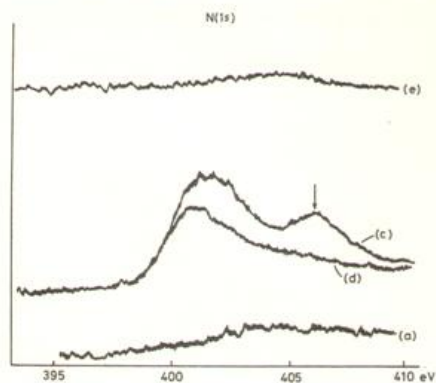
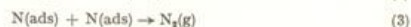
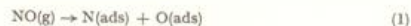


FIGURE 2. N(1s) spectra corresponding to curves (a), (c), (d), and (e) of Figure 1. Analysing conditions: 50 eV, 1×10^4 counts s^{-1} (full scale deflection).

On warming the adlayer to 110 K the main point to note is the almost complete disappearance of the O(1s) peak at 535 eV (Figure 1, curve d). Further warming to 295 K (Figure 1, curve e) resulted in just the O(1s) peak at 529.5 eV remaining. When we examine the corresponding N(1s) spectra (Figure 2, curves c, d, and e) we find that at 110 K the 406 eV peak has disappeared while the profile of the broad 401 eV peak has changed. The change is, however, only in the higher binding energy component region of the peak. This suggests that the lower binding energy N(1s) peak observed at 85 K and centred at about 401 eV is composite and that on warming to 110 K the higher binding energy component as well as the peak at 406 eV disappear. On further warming of the adlayer to 295 K no detectable N(1s) peak was present indicating the absence of adsorbed 'nitrogen' on the Cu(100) surface (Figure 2, curve e). This oxygen chemisorbed layer exhibited a $\sqrt{2} \times \sqrt{2} R 45^\circ$ low energy electron diffraction pattern; a similar structure is formed² from O₂(g) at 295 K.

When the areas of the O(1s) and N(1s) components lost between 85 and 110 K (Figure 2, curves b and d) are compared and estimates then made of the corresponding nitrogen and oxygen atom concentrations the N:O atom ratio is about 2:1. This suggests that N₂O could be present in a molecularly adsorbed state at 85 K and that it desorbs on warming to 110 K. The 2:1 ratio may, however, arise from other molecular processes and is in itself not conclusive evidence for N₂O desorption. The binding energies of the two N(1s) peaks 'lost' on thermal activation of the adlayer formed at 85 K are at 402 and 406 eV and since these are virtually identical with the N(1s) values for molecularly adsorbed³ nitrous oxide, there is very strong evidence for N₂O(ads) being formed from NO within the saturated adlayer at 85 K. Furthermore its desorption on warming to 110 K is in keeping with a heat of adsorption of no more than 25 kJ mol⁻¹. In our previous studies¹ with polycrystalline copper we tentatively assigned the weakly adsorbed surface species characterised by N(1s) and O(1s) values of 406 and 535 eV respectively as NO²⁺. The present high resolution spectra and stoichiometric data as well as similar observations^{4,5} with aluminium suggest however that what we had previously designated as NO²⁺ we now attribute to N₂O(ads), the 'missing' low binding energy N(1s) peak being hidden within the broad peak centred at 401 eV. In view of the low vapour pressure (*ca.* 10⁻⁵ Pa) of N₂O(g) at 85 K the molecule, once formed by the interaction of N(ads) and NO(ads), remains physically adsorbed at this temperature.

We therefore have strong evidence for the sequence of molecular events in reactions (1)–(4) occurring at 85 K with negligible activation energy. On warming the adlayer to 110 K desorption of N₂O (reaction 5) occurs.



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