An STM–XPS study of ammonia oxidation: the molecular architecture of chemisorbed imide 'strings' at Cu(110) surfaces

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The structural characteristics of imide strings formed when a Cu(110) surface is exposed to an ammonia rich NH_3–O_2 mixture at 325 K have been determined by STM. The spacing of the NH units within a string is 5 Å and at complete coverage the strings are separated by 7.2 Å.

Here we provide a detailed insight into the structure of the imide overlayer that results from the oxidation of ammonia at a Cu(110) surface. The experiment was carried out under dynamic co-adsorption conditions where there is no evidence at the surface of either of the two reactants, ammonia and oxygen, and investigated using X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The combination of STM with *in situ* XPS provides a unique and powerful approach to the study of the mechanism of surface reactions: STM provides structural information at the atomic level and XPS allows chemical identification of the surface species. The dual function ultra high vacuum spectrometer was supplied by Omicron Vakuumphysik.

The formation of a chemisorbed imide adlayer at a Cu(110) surface exposed to an ammonia-rich (30 : 1) mixture of ammonia and dioxygen was first established by us using XPS and high resolution electron energy loss spectroscopy (HREELS).[1,2] Subsequently, Bradshaw *et al.*[3] showed using photoelectron diffraction that the imide species are adsorbed in the short-bridge site on Cu(110). Previous STM studies by Madix's group[4] have concentrated on the reaction of pre-adsorbed oxygen atoms on Cu(110) by ammonia. Chemisorptive replacement of oxygen occurs primarily at Cu–O chain ends[4,5] leading to a mixed imide–oxygen adlayer.

An STM image of the Cu(110) surface saturated with imide species (Fig. 1) shows close-packed, broad NH(a) 'strings' with a uniform separation between strings of 7.2 Å, which is close to twice the copper lattice spacing in the $< 100 >$ direction. Since individual NH species are generally not resolved along the strings, STM alone cannot determine the packing density of the imide moieties in the $< 1\bar{1}0 >$ direction. However, quantification[6] of the observed XP N(1s) spectrum gives a saturation coverage of 2.6×10^{14} cm^{-2}. Population of all the short bridge sites (*i.e.* a 2×1 structure) would lead to a saturation imide coverage of *ca.* 5×10^{14} cm^{-2}. We conclude that the imide species are adsorbed in alternate short bridge sites, with a NH–NH spacing of *ca.* 5 Å. This is in excellent agreement with recent density functional calculations.[7] Whether the imide species are adsorbed in a p(2×2) or a c(2×4) surface structure cannot be determined from the present data.

Corroboration of the intermolecular spacing of the imide molecules comes from an analysis of the string labelled '6' in Fig. 2, observed during the real-time study of the growth of imide strings on the copper surface at 325 K. Unusually, discrete features within the string are resolved in this case, with a spacing of 5.2 Å. We were able to observe this particular feature develop alongside the already completed NH string labelled '5' at approximately the same rate as other NH strings. The feature was stable (as were all the features recorded in this

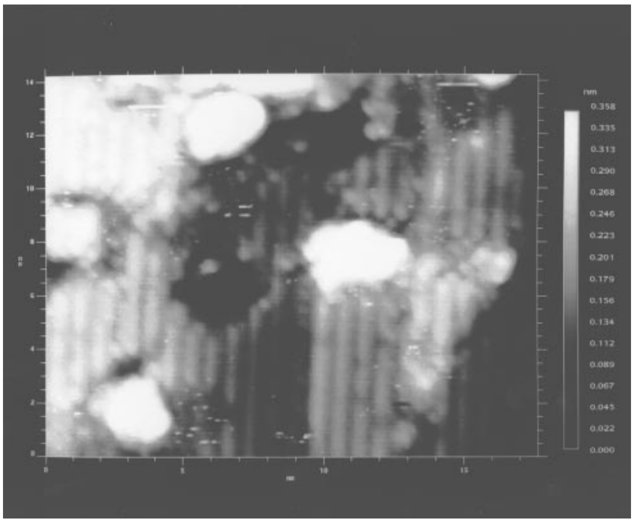

Fig. 1 STM image of a Cu(110) surface saturated with imide species after several hours exposure to the 30 : 1 ammonia–dioxygen mixture. Note the regular spacing of the imide rows. STM imaging conditions: sample bias −0.62 V, tunneling current 0.24 nA, scan speed 215 nm s^{-1}.

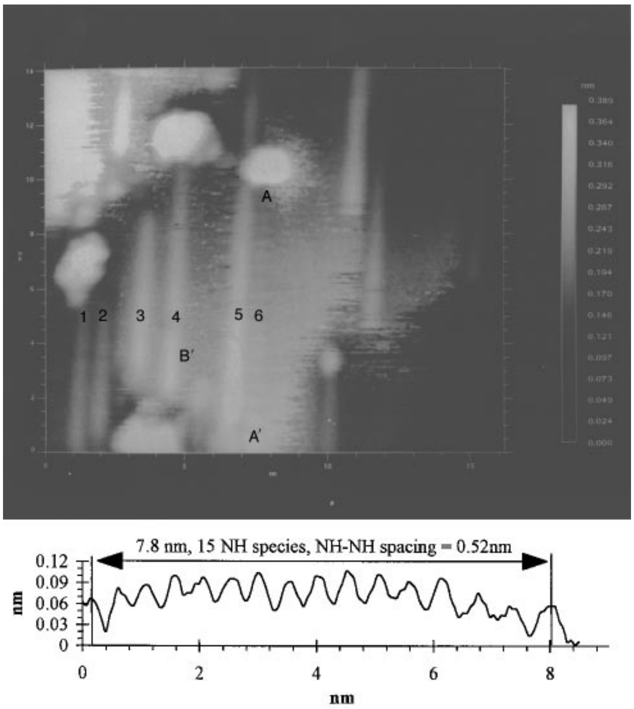

Fig. 2 STM image recorded during exposure of a Cu(110) surface at 325 K to a 30 : 1 ammonia–dioxygen mixture; the image was recorded after 2300 s at a mixture pressure of 1.5×10^{-8} mbar. The characteristically broad imide rows are aligned in the $< 110 >$ direction. Selected NH strings are numbered 1–6; the line profile below the image was obtained between the points A and A' and shows a corrugation reflecting the individual imide species in row 6. STM imaging conditions: sample bias −1.00 V, tunneling current 0.25 nA, scan speed 91 nm s^{-1}.

experiment) for at least 40 minutes and was identical in both the forward and the reverse scan. Why the NH molecules should be resolved in this particular feature (and a few others) but not in the majority of cases is not clear. We have already reported[1,2] that XPS shows that only NH is present at the surface, as reflected in an N 1s feature with a binding energy of 397.8 eV, during exposure of Cu(110) to such an ammonia–dioxygen mixture.

It is significant that the NH species form extended strings at the surface, rather than simply adsorbing randomly. We have previously established that under dynamic co-adsorption conditions novel surface chemistry can be observed through the interaction of weakly adsorbed species, possessing a short surface life-time, with reactive co-adsorbates (see the reviews in ref. 8). In this case, NH formation results from the interaction of ammonia molecules (present at immeasurably low coverages under the reaction conditions and undergoing rapid surface diffusion) with transient oxygen species. The NH (possibly radical-like) species then diffuse across the terraces and are trapped at sites adjacent to the ends of NH strings, where they are energetically most stable.[7] We have not however been able to progress further the debate[1,9] as to whether at the Cu(110) surface the reactive oxygen species are atomic [eqns. (1) and (2)] or molecular [eqn. (3)] in nature (s = surface transient; a = chemisorbed species):

$$O_2(g) \rightarrow 2\,O^{\delta-}(s) \qquad (1)$$

$$NH_3\,(s) + O^{\delta-}\,(s) \rightarrow NH\,(a) + H_2O\,(g) \qquad (2)$$

$$NH_3\,(s) + O_2^{\delta-}\,(s) \rightarrow NH\,(a) + O\,(a) + H_2O\,(g) \qquad (3)$$

Both atomic[10] and molecular[11] transient oxygen species have been implicated in the surface chemistry observed at other metal surfaces under dynamic coadsorption conditions.

A further observation that can be made in Fig. 1 is that during the early stages of the development of the NH overlayer, nucleation of NH strings frequently occurs not at the ideal close-packed spacing of 7.2 Å but one lattice spacing further apart giving a spacing of 10.8 Å. (Compare for example the separation between NH strings 1 and 2, and 3 and 4.) This observation is interesting because although these NH strings appear very stable even at 325 K, continual exposure to the ammonia–dioxygen mixture generates a close-packed layer with a uniform 7.2 Å string separation. This can only result from a displacement of some of the NH chains due to lateral interactions between imide species, as newly formed NH groups diffuse to short-bridge sites located between imide chains separated by 10.8 Å.

In summary, the mechanism of the selective oxidation of ammonia at Cu(110), first investigated using X-ray and electron energy loss spectroscopies,[1,2] has been developed through STM to provide a model at the molecular level. Details of the interatomic spacing of the NH units within an imide string and the spacings between the rows of strings have been obtained for the first time.

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