PHYSICAL REVIEW B VOLUME 55, NUMBER 19 15 MAY 1997-I

STM study of formic acid adsorption on Cu(110)

Stephen Poulston, Roger A. Bennett, Adrian H. Jones,* and Michael Bowker
Reading Catalysis Centre, University of Reading, Department of Chemistry, Whiteknights, Reading RG6 6AD, United Kingdom

(Received 22 November 1996)

We report a scanning tunneling microscopy (STM) study of formic acid adsorption on clean Cu(110) at 300 K. An ordered structure was observed consisting of short rows parallel to the [110] direction, with an inter-row spacing in the [001] direction of two lattice spacings of the unreconstructed (1×1)-Cu(110) termination. Adjacent domains of this structure were offset in the [001] direction by one lattice spacing giving relatively short-range order in the [110] direction. A structure is proposed to account for the observed STM images. [S0163-1829(97)05220-X]

The adsorption of formic acid on Cu single crystal surfaces, in particular Cu(110), has attracted considerable attention due in part to the identification of formate as a key stable intermediate in methanol synthesis which is carried out commercially using copper based catalysts.[1] Experiments have been concerned with formic acid adsorption on both clean and oxygen precovered surfaces which, at 300 K, respectively, liberate hydrogen and water as well as producing adsorbed formate [Eqs. (1,2)].[1–12] In addition formate on Cu has been the subject of theoretical studies in order to understand the local structure and adsorption geometry.[13]

$$2\mathrm{HCOOH}\rightarrow 2\mathrm{HCOO}_{(\mathrm{ad})}+\mathrm{H}_2, \tag{1}$$

$$2\mathrm{HCOOH}+\mathrm{O}_{(\mathrm{ad})}\rightarrow 2\mathrm{HCOO}_{(\mathrm{ad})}+\mathrm{H}_2\mathrm{O}. \tag{2}$$

Previous spectroscopic studies of formic acid adsorption on clean Cu(110) indicate that the formate is oriented with its molecular plane perpendicular to the surface and parallel to the [110] close-packed direction and that the two oxygens are bound to the surface in locally identical sites.[4] The estimated coverage of the formate has ranged between 0.25 and 0.3 ML.[7,5] Though several formate structures produced by formic acid adsorption on the oxygen precovered Cu(110) surface have been identified using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED),[2,3,14,15] no structures for formate produced by formic acid adsorption on clean Cu(110) have been reported using these techniques. In this paper we report a STM study of formic acid adsorption on clean Cu(110) at 300 K and compare the observed structure with previous work and provide an explanation for the recorded difficulty in observing a LEED pattern for this system.

STM experiments were performed using a WA Technology (now Oxford Instruments) variable temperature STM. The STM was contained within a UHV chamber equipped with additional facilities for Ar^+ ion sputtering, LEED, Auger electron spectroscopy, and temperature programmed desorption (TPD) and has been described in detail elsewhere.[16] Formic acid adsorption was carried out at ~300 K by backfilling the chamber. Gas exposures are quoted in Langmuirs ($1\ \mathrm{L}=1\times10^{-6}$ Torr sec). The Cu(110) sample was cleaned using cycles or Ar^+-ion bombardment at 720 K and annealing. Coverages are quoted in monolayers (ML), where 1 ML is the number density of atoms in the surface layer of Cu(110).

A formic acid exposure of ~10 L at 300 K was required on the clean Cu(110) surface before the observation of an ordered overlayer using STM, a typical image of this structure is shown in Fig. 1 and it is indicative of many other imaged areas. The structure consists of highly segmented domains containing short rows running along the [110] direction with a separation between the rows, in the [001] direction, of ~7 Å i.e., two lattice spacings of the clean Cu(110)-(1×1) termination. We propose that the light rows in Fig. 1 are due to an adsorbed formate aligned along the close-packed Cu rows. The domain boundaries are clearly visible as dark lines aligned approximately along the [001] direction. Closer examination of this structure revealed that the formate rows were significantly wider than the dark rows in between them, this could possibly be due to some vibration of the formate out of the plane perpendicular to the

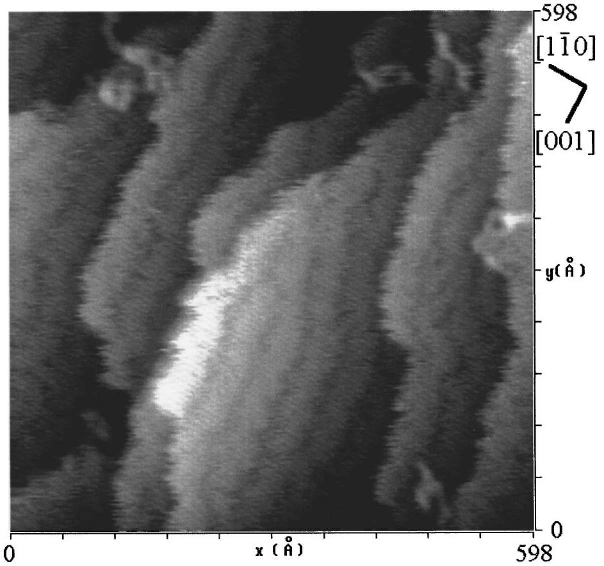

FIG. 1. STM image of formate on Cu(110) formed by exposing clean Cu to formic acid at 300 K. Large area scan showing a large number of domain boundaries running approximately along the [001] direction (598×598 Å^2, 498 mV, 1 nA).

0163-1829/97/55(19)/12888(4)/$10.00

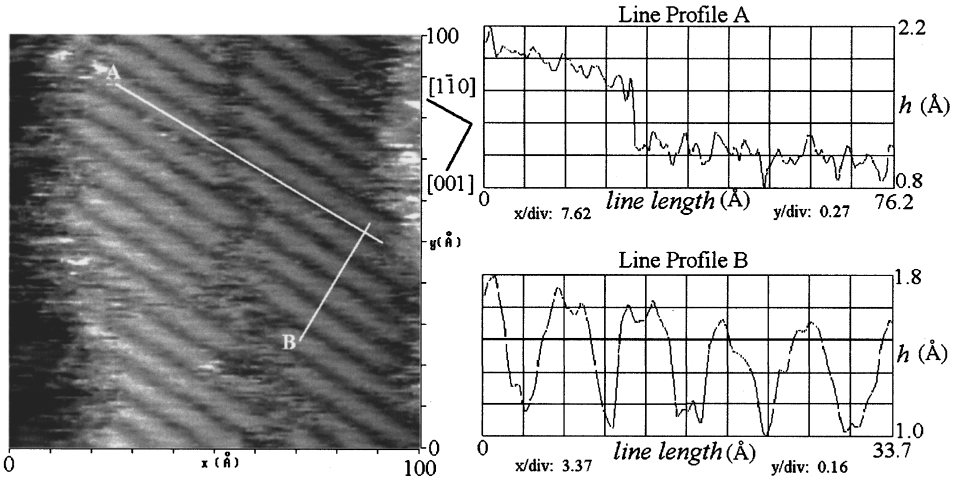

FIG. 2. STM image of formate on Cu(110) formed by exposing clean Cu to formic acid at 300 K together with two line scans (100×100 Å^2, 500 mV, 1 nA). (A) line scan along the [110] direction showing the phase boundary between two domains marked by a drop in the apparent height (h) of $\sim$0.5 Å. (B) line scan along the [001] direction within a single domain showing the peak to trough corrugation across the formate rows (indicated by the value of h) to be $\sim$0.6 Å and the spacing between rows in the [110] direction to be within $\sim$10% of that expected for two lattice spacings, i.e., 7.2 Å.

close-packed rows of the substrate. No structure was observed along the formate rows and a possible explanation for this is presented below. It is interesting that the appearance of this structure occurs fairly suddenly after a formic acid exposure of $\sim$10 L and does not gradually grow across the surface with increasing exposure. It appears therefore that a critical formate coverage must be reached before the ordered overlayer ''condenses out.'' Before this point the formate in the overlayer is too mobile on the time scale of the STM scan ($\sim$40 sec per image) to be imaged. The observation of disordered phases at low coverage due to high adsorbate mobility on the time scale of STM imaging has been reported previously for the S/Re(0001) system.[17] An interesting distinction between the S/Re(0001) system and this one is that in the former case the disordered phase was observed in conjunction with an ordered phase.

No ordered LEED pattern was observed for overlayers giving the STM image shown in Fig. 1. A confirmation of the presence of formate as the adsorbed species in these experiments was obtained using TPD which showed coincident CO_2 and H_2 desorption at $\sim$470 K characteristic of formate decomposition.[8]

The regularity of the formate structure observed using STM is highly anisotropic containing good long-range order in the [001] direction but having only very short-range order in the [110] direction leading to the formation of long thin domains, the adjacent domains being displaced relative to each other by one lattice spacing ($\sim$3.6 Å) in the [001] direction. This is more clearly illustrated in the STM image shown in Fig. 2. Figure 2 also shows a line scan (A) taken along the [110] direction initially running along a formate row and then along the gap between two formate rows clearly showing the offset between the adjacent domains. The transition between these features is signified by a decrease in h, the apparent height above the surface, of $\sim$0.6 Å. Line scan (B) is taken along the [001] direction and shows the regular corrugation across the rows within a domain. The peak-to-trough distance indicating the apparent height of the formate above the surface is $\sim$0.6 Å. The displacement of the formate rows in adjacent domains prevents them from merging to give greater continuity in the [110] direction, and in effect there is an antiphase domain boundary. The similar apparent height of the formate above the Cu in both directions would seem to rule out any large restructuring of the Cu substrate, such as a missing row reconstruction, and suggests the substrate periodicity is close to (1×1).

From analysis of several STM images it is clear that the boundary between ordered formate islands follows the profile of nearby step edges and so does not always follow a particular crystallographic direction. The length distribution of the rows in the [110] direction is shown with a histogram plot in Fig. 3. The mean length of the rows in the [110] direction is 34 Å before a domain boundary is reached. This plot shows the relatively narrow length distribution of the formate rows in the [110] direction. No significant variation in the length of individual formate rows was observed on a time scale of tens of minutes.

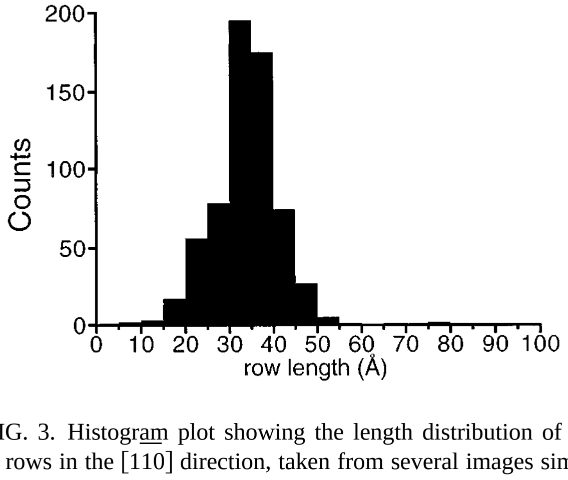

FIG. 3. Histogram plot showing the length distribution of formate rows in the [110] direction, taken from several images similar to those shown in Fig. 1.

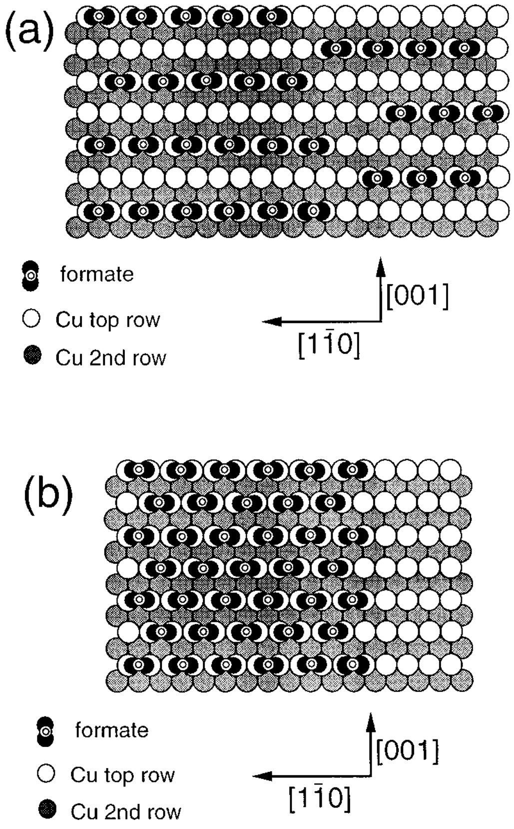

FIG. 4. Schematics of the real-space structures of formate on Cu(110); (a) structure formed by exposing the clean surface to formic acid at 300 K. Note we show no regular arrangement of the formate rows along [110] with respect to either side, unlike the $c(2\times2)$ arrangement where adjacent rows are always offset by one lattice spacing. (b) the $c(2\times2)$ formate structure formed by the adsorption of formic acid on $O_{0.25\,ML}$/Cu(110). The higher local coverage of the $c(2\times2)$ structure may be responsible for the better ordering within the formate rows along the [110] close-packed Cu direction. Thus atomic resolution of the formate $c(2\times2)$ structure can be observed with STM (Ref. 2).

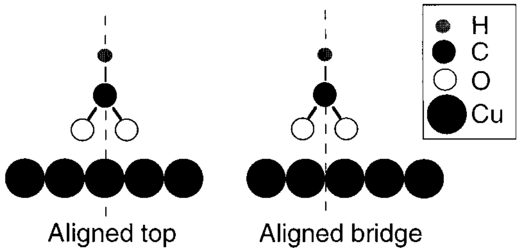

FIG. 5. Schematic illustration of the aligned bridge and aligned top adsorption site for formate on unreconstructed Cu(110).

The formate structure observed with STM would account for the difficulty of obtaining a LEED pattern[2] as the structure displays only relatively short-range order and there are indications of formate movement both parallel and perpendicular to the close-packed substrate rows which is rapid on a STM time scale, as described below. A proposed structure of formate on clean Cu(110) is shown in Fig. 4(a) and is consistent with both the STM results and a large amount of previous work on this system. In this structure the formate molecules are aligned parallel to the [110] direction as suggested by photoelectron diffraction (PhD), surface extended x-ray-adsorption fine-structure (SEXAFS), and near-edge x-ray-adsorption fine-structure[4,18] (NEXAFS) data though only each alternate row is occupied by formate. Therefore if adjacent domains of this structure are offset by one lattice spacing in the [001] direction there is a boundary between the islands as observed with STM. It should be noted that the exact adsorption site of the formate shown in Fig. 4 is that suggested by the PhD work of Woodruff[4] though at variance with that suggested by the SEXAFS and NEXAFS data.[18] Explanations for this discrepancy are discussed elsewhere by Woodruff *et al.*[4] The formate adsorption site suggested by the PhD work as shown in Fig. 4 can be described as an aligned bridge whereas the SEXAFS analysis suggested an aligned top adsorption site with the formate oxygens in between Cu atoms in the close-packed rows rather than directly above them. These two adsorption sites are illustrated schematically in Fig. 5. The energy difference between these two sites might be low and this offers an interesting explanation to account for the absence of atomic resolution along the [110] direction in our STM images, namely, that on the time scale of the STM scan the formate oscillates between the two adsorption sites, even though they may spend the majority of their time on the aligned bridge site. The formate molecules may therefore be regarded as delocalized to some extent along the [110] direction. In addition, as mentioned above, the appearance of broad formate rows may indicate some movement perpendicular to the close-packed substrate rows. In relation to this it is interesting to note that in an STM study of ammonia adsorption on oxygen precovered Cu(110) at 300 K by Guo and Madix[19] also observed similar, very broad adsorbate rows along the [110] direction produced by NH species. Overall, therefore, the formate mobility we have suggested would prevent the observation of an ordered LEED pattern as on the time scale of electron diffraction the formate molecules are to an extent randomly distributed.

The local coverage of the formate structure shown in Fig. 4(a) would be 0.25 ML; consistent with the estimated formate coverage proposed by others. The overall formate coverage would however be slightly lower if the regions between adjacent domains were free of formate. It is possible though that the disordered regions between the ordered domains may contain some formate possibly in a ''lattice-gas''-type state. However, the proposed structure is still in reasonable agreement with the estimated formate coverages reported previously. The clean surface formate structure proposed has similarities to the proposed $c(2\times2)$ formate structure that has been reported for formic acid adsorption on O(0.25)ML/Cu(110).[14] This structure gives a formate coverage of 0.5 ML and is shown for comparison in Fig. 4(b). In particular, both structures have the formate adsorbed on the unreconstructed Cu(110) surface with the formate aligned parallel to the close-packed rows. The $c(2\times2)$ formate structure can be imaged with STM, under similar conditions, with good resolution indicating that the formate species are much more localized than on the clean surface. The reason for formic acid adsorption on clean Cu(110) not forming the higher coverage $c(2\times2)$ structure is likely to be a repulsive interaction between the formate species in the [001] direction. Indeed repulsive intermolecular interactions between the formate molecules are a possible cause of the rapid transition at higher formate coverages which allowed the observation of an ordered overlayer structure. The repulsive interactions may inhibit the growth of increasingly large islands of the ordered, but more closely packed, structure with increasing coverage. This repulsive interaction can be overcome in the case of the oxygen precovered surface. In this case a higher formate coverage is enforced through the energetically favourable reaction of formic acid deprotonation by the preadsorbed oxygen [Eq. (2)]. Further evidence for the existence of repulsive interaction in the formate overlayer can be found in the work of Hayden *et al.*[7] who performed reflection-absorption infrared spectroscopy (RAIRS) and TPD experiments following formic acid adsorption on clean Cu(110). They report a number of changes in the RAIRS spectrum of the formate on Cu(110) at coverages between 0.2 and 0.25 ML which are taken to indicate repulsive interactions in the overlayer. These changes include a broadening of all the adsorption bands and a steep rise in the frequency of the ν_s(COO) and $\nu_{\rm comb}$ bands to higher frequency. It seems likely that the onset of these changes at formate coverages >0.2 ML are linked with our observation of the appearance of an ordered STM image once a critical formate coverage was reached. In addition, Hayden *et al.* suggest a structure consisting of formate molecules tightly packed but locally disordered, again in good agreement with the STM data.

The length distribution of the formate rows shown in Fig. 3 may be determined by repulsive interactions between the formate molecules along the [110] direction. When the row reaches a critical length ($\sim$34 Å or $\sim$7 formate molecules) the repulsive interactions, which may be relatively long range, result in the addition of another formate to the row being unfavorable and a domain boundary results. An alternative explanation for the length distribution of the formate rows in the [110] direction is that the formate molecules cause a small displacement of the Cu atoms in the [110] direction away from their normal lattice positions. This displacement could therefore increase with the length of the formate row until a maximum is reached at which the addition of another formate and further Cu atom displacement is unfavorable thus limiting the row length.

It is interesting to note some similarities between this system and a recent STM study of acetate on Cu(110).[20] For the acetate/Cu(110) system long-range ($\sim$17 Å) repulsive interactions were suggested to account for the relatively low coverage structure observed in STM. For the formate Cu(110) system repulsive intermolecular interactions seem the likely cause of both the low formate coverage (compared with that obtained with an oxygen precovered surface) and the formation of antiphase domain boundaries. In addition, for both systems the structure observed with STM indicates anisotropic intermolecular interactions presumably, in part, as a result of the anisotropic substrate structure.

In summary, we have used STM to identify a real-space structure of formate on Cu(110) formed at 300 K by the adsorption of formic acid on the clean surface. The observed STM structure consisted of domains containing short rows parallel to the [110] direction, with an inter-row spacing in the [001] direction of two lattice spacings of the unreconstructed (1×1)-Cu(110) termination. Adjacent domains were offset in the [001] direction by one lattice spacing giving relatively short-range order in the [110] direction. The STM data are in good agreement with conclusions drawn with the use of other techniques including RAIRS and Ph.D.

---

[*] Present address: Oxford Instruments, Chesterton Mills, French's Road, Cambridge, CB4 3NP, UK.

[1] K. C. Waugh, Catal. Today, **15**, 51 (1992).

[2] M. Bowker, E. Rowbotham, F. M. Leibsle, and S. Haq, Surf. Sci. **349**, 97 (1996).

[3] S. Poulston, A. H. Jones, R. A. Bennett, and M. Bowker, Surf. Sci. **377**, 66 (1997).

[4] D. P. Woodruff, C. F. McConville, A. L. D. Kilcoyne, Th. Lindner, J. Somers, M. Surman, G. Paolucci, and A. M. Bradshaw, Surf. Sci. **201**, 228 (1988).

[5] F. C. Henn, J. A. Rodrigues, and C. T. Campbell, Surf. Sci. **236**, 282 (1990).

[6] M. Bowker and R. J. Madix, Surf. Sci. **102**, 542 (1981).

[7] B. E. Hayden, K. Prince, D. P. Woodruff, and A. M. Bradshaw, Surf. Sci. **133**, 589 (1983).

[8] D. Ying and R. J. Madix, J. Catal. **61**, 48 (1980).

[9] R. J. Madix and S. G. Telford, Surf. Sci. **277**, 246 (1992).

[10] I. Wachs and R. J. Madix, Surf. Sci. **84**, 375 (1979).

[11] B. A. Sexton, A. E. Hughes, and N. R. Avery, Surf. Sci. **155**, 366 (1985).

[12] M. Bowker, S. Haq, R. P. Holroyd, P. M. Parlett, S. Poulston, and N. Richardson, J. Chem. Soc. Faraday Trans. **92**, 4683 (1996).

[13] D. W. Bullett and W. G. Dawson, Prog. Surf. Sci. **25**, 275 (1987).

[14] F. M. Leibsle, Surf. Sci. **311**, 45 (1994).

[15] F. M. Leibsle, S. Haq, B. G. Frederick, M. Bowker, and N. V. Richardson, Surf. Sci. **343**, L1175 (1995).

[16] A. H. Jones, S. Poulston, R. A. Bennett, and M. Bowker, Surf. Sci. **380**, 31 (1997).

[17] J. C. Dunphy, P. Sautet, D. F. Ogletree, O. Dabousi, and M. B. Salmeron, Phys. Rev. B **47**, 2320 (1993).

[18] A. Puschmann, J. Hasse, M. D. Crapper, C. E. Riley, and D. P. Woodruff, Phys. Rev. Lett. **54**, 2250 (1985).

[19] X.-C. Guo and R. J. Madix, J. Chem. Soc. Faraday Discuss. (to be published).

[20] S. Haq and F. M. Leibsle, Surf. Sci. **355**, L345 (1996).