Adsorbate induced kink formation in straight step edges on Cu(5 3 3) and Cu(2 2 1)

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Abstract

Scanning tunneling microscopy (STM) and temperature programmed desorption (TPD) measurements have revealed that the straight step edges of Cu(5 3 3) surfaces are reconstructed by the room temperature adsorption of R-3-methylcyclohexanone (R-3-MCHO). STM and low energy electron diffraction (LEED) investigations have shown that the clean Cu(5 3 3) surface is composed of arrays of narrow (1 1 1) terraces separated by straight (1 0 0) steps. During room temperature adsorption of R-3-MCHO, the (1 0 0) step edges on the Cu(5 3 3) surface reconstruct, adopting a zigzag structure that exposes kinked, high Miller index step edges. The density of step edge and kink adsorption sites on Cu surfaces can be titrated by TPD of R-3-MCHO. TPD experiments also reveal the formation of kinks on the Cu(5 3 3) surface during room temperature adsorption of R-3-MCHO. Furthermore, TPD experiments on the Cu(2 2 1) surface having straight (1 1 0) step edges indicate that these also reconstruct to expose kinked step edges during R-3-MCHO adsorption at room temperature. Although the kinks on such surfaces are chiral, the R- and S-forms appear to be produced in a roughly racemic (equimolar) ratio. Thus, although the reconstruction of the initially achiral Cu surfaces in the presence of a chiral adsorbate could, in principle, lead to a surface with a net chiral structure, R-3-MCHO does not seem to be an effective chiral imprinting agent.
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1. Introduction

The structures of single crystalline surfaces are never those predicted simply by cleavage of the bulk lattice along a given plane. All such surfaces undergo some degree of relaxation and, in severe cases will undergo reconstruction to give surface lattice spacings and periodicities that differ from those of the bulk termination. Such reconstructions occur on clean single crystalline surfaces or surfaces modified by the adsorption of atoms or molecules and there is an enormous literature describing studies of these structures using low energy electron diffraction (LEED), scanning

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tunneling microscopy (STM) and other surface structural tools. The vast majority of these studies have been performed on the low Miller index surfaces of various materials. By comparison, far less work has been done to study the reconstructions of high Miller index surfaces such as those studied in this work.

Surface reconstructions were first observed using LEED and identified by the differences between the periodicity of the real surface lattice and that expected from the termination of the bulk structure. Other forms of surface reconstruction can occur that do not lead to periodic surface structures. For example, at any temperature above 0 K one expects a certain degree of thermal roughening of surfaces due to entropic effects. This occurs on flat low Miller index surfaces and on stepped and kinked high Miller index surfaces. Other forms of surface reconstruction include localized atomic motions induced by atomic and molecular adsorption. Such reconstructions that do not yield surfaces with long range periodicity are most readily observed by local surface imaging methods such as STM [1].

In principle, reconstruction can be used to impart desired properties to surfaces. One possibility is that a surface can be rendered enantioselective by causing it to reconstruct from an achiral to a chiral structure [2–4]. The control of enantioselectivity is the key to the synthesis of enantiomerically pure compounds such as many pharmaceuticals [5]. If one could use surface reconstruction to imprint chiral structures onto surfaces, it might be possible to use these surfaces in enantioselective chemical processes.

The formation of chiral structures by adsorption of chiral molecules onto initially achiral surfaces has been observed on both Cu(1 0 0) and Cu(1 1 0) surfaces. In the case of Cu(1 0 0) the adsorption of the amino acid l-lysine followed by annealing at 430 K has been shown to cause step bunching to produce facets which belong to the {3,1,17} family of surfaces [3,4]. The interesting feature of this observation was that of the eight possible faces in the {3,1,17} family that can appear around the (1 0 0) pole, only four were observed. Such surfaces have chiral structures composed of (1 0 0) terraces separated by kinked step edges. The four surfaces of the {3,1,17} family that were observed on the Cu(1 0 0) surface were all of one handedness and their chirality was dictated by the chirality of the adsorbed l-lysine. A second example of chiral imprinting occurs during the adsorption of hexatertbutyldecacyclene (HtBDC) on the Cu(1 1 0) surface [2]. HtBDC is chiral and, upon adsorption on the Cu(1 1 0) surface, induces the displacement of seven atoms from the top rows of the Cu(1 1 0) structure to leave holes in the topmost atomic layer. Examination of the surface with STM shows that these holes are chiral and that their chirality is dictated by the chirality of the HtBDC molecule which causes their formation. These two examples of chiral imprinting suggest that this might be a general phenomenon occurring during the adsorption of any chiral molecule on a surface.

Past work has shown that high Miller index surfaces with kinked step structures are chiral and that they have enantiospecific properties [6–8]. The adsorption energies of R-3-methylcyclohexanone (R-3-MCHO) at the kinks on the Cu(6 4 3)^R and Cu(6 4 3)^S surfaces have been shown to be enantiospecific [9–11]. Electrochemical measurements have also shown that the rates of d- and l-glucose electro-oxidation on stepped-kinked Pt surfaces are enantiospecific [12–14]. It is the kinks on the step edges that impart chirality to the surface. The work discussed here examines the interaction of R-3-MCHO with high Miller index Cu surfaces having achiral straight step edges. The original intent was simply to determine the adsorption energies at the straight step edges, however, TPD measurements suggest that the adsorption of R-3-MCHO at straight step edges on the Cu(5 3 3) and Cu(2 2 1) surfaces is sufficient to induce the formation of kinks in the step edges [15]. STM has been used in this work to examine the structure of the Cu(5 3 3) surface after adsorption of the R-3-MCHO at 330 K and to reveal the formation of kinks in the step edge. In particular, we wish to determine whether the chirality of the kinks is dictated by the chirality of the 3-MCHO.

2. Experimental

The work described has been done in two laboratories. Desorption measurements on Cu(5 3 3) and Cu(2 2 1) were made at Carnegie Mellon and the STM measurements on Cu(5 3 3) at the University of Houston. Identical procedures were used in both laboratories to prepare the single crystal surfaces and LEED was used in both to ascertain the surface periodicity.

The copper single crystal samples were purchased from Monocrystals Co. with a purity of more than 99.999%. Their surfaces were cleaned using a procedure previously developed to clean the Cu(6 4 3) surfaces on which R-3-MCHO adsorption has been studied. Briefly, they were cleaned in the vacuum chamber by cycles of 1.25 keV Ar^+ ion sputtering while annealing to 1000 K. This was repeated until the surfaces yielded sharp LEED patterns.

R-3-MCHO was purchased from Aldrich Co. with a purity of 98%. Prior to introduction into the vacuum chamber it was purified by several freeze-pump-thaw cycles.

TPD measurements were made using both Cu(5 3 3) and the Cu(2 2 1) surfaces. R-3-MCHO was adsorbed on the surfaces from a 0.75″ diameter dosing tube while the surfaces were held at either 90 K or at 330 K. Following adsorption the samples were positioned immediately in front of the aperture to an Ametek Dycor M200M quadrupole mass spectrometer. The sample was then heated at 1 K/s while the mass spectrometer was used to monitor the signal at $m/q = 39$, a principle ionization fragment of R-3-MCHO.

The Cu(5 3 3) surface was imaged with an Omicron UHV STM system with a base pressure of less than 10^{-10} Torr. R-3-MCHO exposure in the UHV STM system was carried out by backfilling the chamber through a variable leak valve for predetermined time periods at fixed pressures. The STM tips were made by etching 0.2 mm diameter tungsten wires in 2 M NaOH solution. In the STM experiments, a bias voltage was applied to the sample and STM images were obtained in a topographic mode with a tip scan rate of ∼20–200 nm/s. The specific tunneling conditions for the various images are noted in the relevant figure captions.

3. Results

3.1. TPD of R-3-MCHO on Cu(5 3 3) and Cu(2 2 1)

High Miller index surfaces such as Cu(6 4 3) expose three different types of sites for the adsorption of molecules such as R-3-MCHO: terraces, straight step edges and kinks. It is important to point out that not all sites within a given type are equivalent. Kinks for example can be formed at the intersections of step edges of different lengths and, even on a single surface such as Pt(6 4 3), it has been shown that thermal roughening will induce the presence of a variety of different kinks types [16,17]. Similarly, steps on surfaces vicinal to (1 1 1) come in two types: (1 0 0) and (1 1 0). Even the adsorption sites on (1 1 1) terraces are not all equivalent since thermal roughening results in a range of different terrace widths. Nonetheless, one of the nice features about the TPD spectra of R-3-MCHO on the Cu surfaces vicinal to Cu(1 1 1) is that they reveal three distinct features that can be assigned to desorption from the terraces, steps, and kinks. The spectrum of a monolayer of R-3-MCHO adsorbed on the Cu(6 4 3)^R surface at 90 K and then heated at 1 K/s is shown in Fig. 1a. It reveals three well resolved features at 230, 345 and 383 K that have been assigned to desorption of molecules from the terraces, steps and kinks, respectively. The assignment has been made on the basis of comparisons with spectra obtained under identical conditions from the Cu(1 1 1), Cu(5 3 3), and Cu(2 2 1) surfaces. The spectrum from the Cu(1 1 1) surface which only exposes the (1 1 1) terrace structure reveals only a single desorption peak at 230 K [11]. The TPD spectrum of R-3-MCHO adsorbed on the Cu(5 3 3) surface at 90 K and then heated at 1 K/s is shown in Fig. 1b and reveals two peaks. The low temperature peak at 230 K is assigned to desorption from the terraces while the high temperature peak at 350 K is assigned to desorption of R-3-MCHO from the straight (1 0 0) step edges. The TPD spectrum of R-3-MCHO from the Cu(2 2 1) surface (Fig. 1d) is similar to that obtained from the Cu(5 3 3) surface. The desorption from the (1 1 0) step edges on the Cu(2 2 1) surface
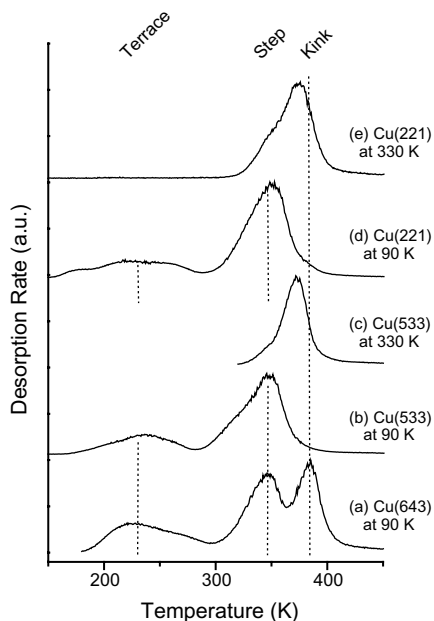
Fig. 1. TPD spectra of R-3-MCHO on the Cu(6 4 3)[R], Cu(2 2 1) and Cu(5 3 3) surfaces. (a) R-3-MCHO adsorbed on Cu(6 4 3)[R] at 90 K. The three peaks are assigned to desorption from the terrace, step edge and kink sites. (b) R-3-MCHO adsorbed on Cu(5 3 3) at 90 K. The two peaks can be assigned to desorption from terrace and straight step edge sites. (c) R-3-MCHO adsorbed on Cu(5 3 3) at 330 K. The single desorption peak now occurs at a temperature associated with desorption from kink sites. (d) R-3-MCHO adsorbed on Cu(2 2 1) at 90 K. The two peaks can be assigned to desorption from terrace and straight step edge sites. (e) R-3-MCHO adsorbed on Cu(2 2 1) at 330 K. Again, the single desorption peak now occurs at a temperature associated with desorption from kink sites. The heating rate was 1 K/s and molecular desorption was monitored using the ionization fragment at $m/q = 39$.

occurs at a slightly higher temperature of 355 K. The key point is that during the adsorption of R-3-MCHO on the Cu(5 3 3) and Cu(2 2 1) surfaces at 90 K and subsequent heating at 1 K/s there is no evidence of reconstruction and the peaks in the desorption spectra can be assigned to desorption from the two principle types of sites that one expects to find: terraces and straight step edges.

Given that desorption from the kinks, steps, and terraces on high Miller index surfaces occurs at three distinct temperatures, one can use the adsorption temperature to limit adsorption to certain sites. For example, adsorption of R-3-MCHO on the Cu(6 4 3) surface at 350 K ought to

result in adsorption at only the kinks. Desorption from the step edges and the terraces is too rapid to allow significant population of either at 350 K. Similarly, exposure of the Cu(5 3 3) surface to R-3-MCHO at 330 K ought to result in adsorption at the step edges only. Fig. 1c shows the TPD spectrum obtained from the Cu(5 3 3) surface after exposure at 330 K. As expected, this reveals only one peak, however, this peak is at 375 K rather than 345 K, the temperature associated with desorption from the straight step edges. The TPD spectrum obtained following exposure of the Cu(2 2 1) surface to R-3-MCHO at 330 K (Fig. 1e) is similar to that obtained from the Cu(5 3 3) surface. It reveals a single desorption feature, but at 372 K, significantly higher than expected for desorption from straight step edges. The simplest interpretation of the TPD spectra obtained following exposure of the Cu(5 3 3) and Cu(2 2 1) surfaces to R-3-MCHO at 330 K is that they arise from desorption from kink sites rather than straight step edges.

If kink sites exist on the Cu(5 3 3) and Cu(2 2 1) surfaces following exposure to R-3-MCHO they must have been induced by the high temperature adsorption process. The interesting question to ask next is whether the chirality of the adsorbate has resulted in the enantioselective production of kinks? Previous work has shown that the adsorption energy of R-3-MCHO onto S-kinks is higher than on R-kinks [11]. This implies that, in principle, there ought to by more S- than R-kinks generated during reconstruction. STM has been used to ascertain that the Cu(5 3 3) surface really is reconstructed after high temperature adsorption of R-3-MCHO and to see if this process is enantioselective and results in a net chirality of the reconstructed surface.

3.2. STM of Cu(5 3 3)

The ideal Cu(5 3 3) surface can be designated as Cu[4(1 1 1)×(1 0 0)], indicating that it is composed of (1 1 1) terraces that are four atoms wide each separated by a one atom (1 0 0) step, as shown by the model in Fig. 2a. STM images of the clean Cu(5 3 3) surface obtained at room temperature and with different spatial resolutions reveal the

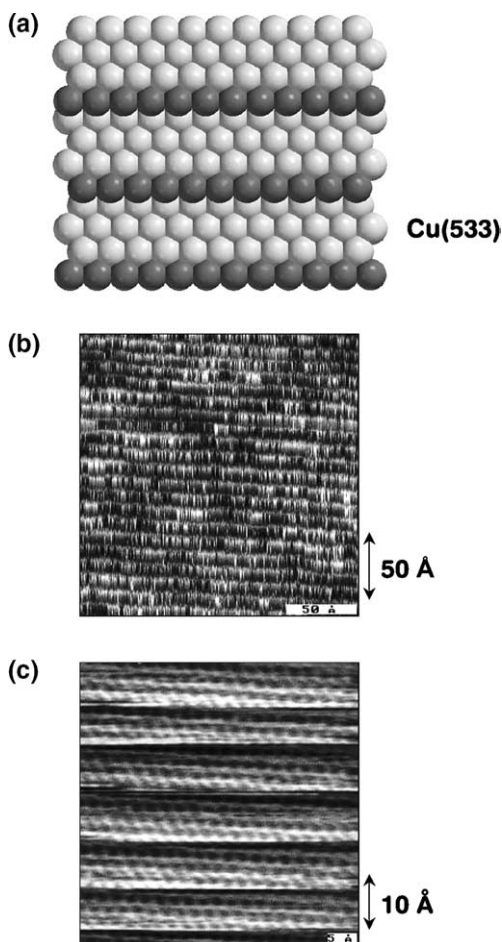Fig. 2. (a) Hard sphere model of Cu(5 3 3) showing straight (1 0 0) step edges separated by (1 1 1) terraces. The step edges run parallel to one another and are separated by 8.5 ± 0.8 Å. (b) STM image obtained from clean Cu(5 3 3) surface. The fuzzy edges are due to atomic motion at the step edges. $(200 \times 200$ Å^2, -1.0 V, 0.7 nA). (c) Atomic resolution STM image of Cu(5 3 3). The terraces have (1 1 1) symmetry. $(50 \times 50$ Å^2, -0.3 V, 1.0 nA).

expected step and terrace structure (Fig. 2b and c). Although the steps appear streaked due to atomic motion, the average step height could be measured from these STM images and corresponded to the ideal single step height of 2.1 Å. The average terrace width in these images is 8.5 ± 0.8 Å, agreeing well with the ideal value of 8.4 Å. The highly streaked appearance of the steps in the STM image collected at room temperature with the fast scan direction oriented perpendicular to the step direc-

tion (Fig. 2b) results from a high mobility of copper atoms along the steps edges [18–20]. When the scan direction is oriented parallel to the step direction, significantly less streaking is observed (the high mobility of Cu atoms at step edges results in the apparent discontinuity at the step edge), atomic resolution is obtained within the terraces (Fig. 2c) revealing their hexagonal symmetry. These images also confirm that the steps are highly aligned along the [0 1 $\bar{1}$] direction. We estimate that the kink density along the (1 0 0) step edge is as low as 2%. The point is that the clean Cu(5 3 3) surface has a structure that is unreconstructed and very close to that expected of an ideal Cu(5 3 3) surface.

If reconstruction occurs as a result of exposure of the Cu(5 3 3) surface to R-3-MCHO, it ought to be revealed in STM images of the surface. Following exposure of the Cu(5 3 3) surface to 20 L of R-3-MCHO (saturation coverage) at room temperature, the surface was imaged with STM (Fig. 3a and b). Close examination of the image in Fig. 3b shows the presence of adsorbed R-3-MCHO along the step edges, however, the step edges are no longer straight. As predicted on the basis of the TPD experiments, the STM images demonstrate that the previously straight steps shown in Fig. 2b have undergone reconstruction. Locally, the steps deviate from the [0 1 $\bar{1}$] direction by $\sim 19°$ (Fig. 3b) indicating that they have been transformed into steps oriented along the [$\bar{1}$ 3 $\bar{2}$] and [$\bar{1}$ $\bar{2}$ 3] directions (see Fig. 4). The step structure consists of one atom kink sites separated by two lattice spacings along the [0 1 $\bar{1}$] direction. This reconstruction does not involve an alteration of the terrace structure; it is merely a reconstruction of the step edges. This reconstructed step orientation corresponds to the step structure found on an ideal Cu(6 4 3) surface. By comparing Fig. 3b to Fig. 2b, we find that the average step density has not changed as a result of the surface reconstruction; however, the long range order of the original step structure has been removed. STM images of the Cu(2 2 1) surface have not been obtained, however, based on the evidence of the TPD spectra, we expect that the straight step edges on the Cu(2 2 1) surface also undergo reconstruction after the room temperatures adsorption of R-3-MCHO and that STM
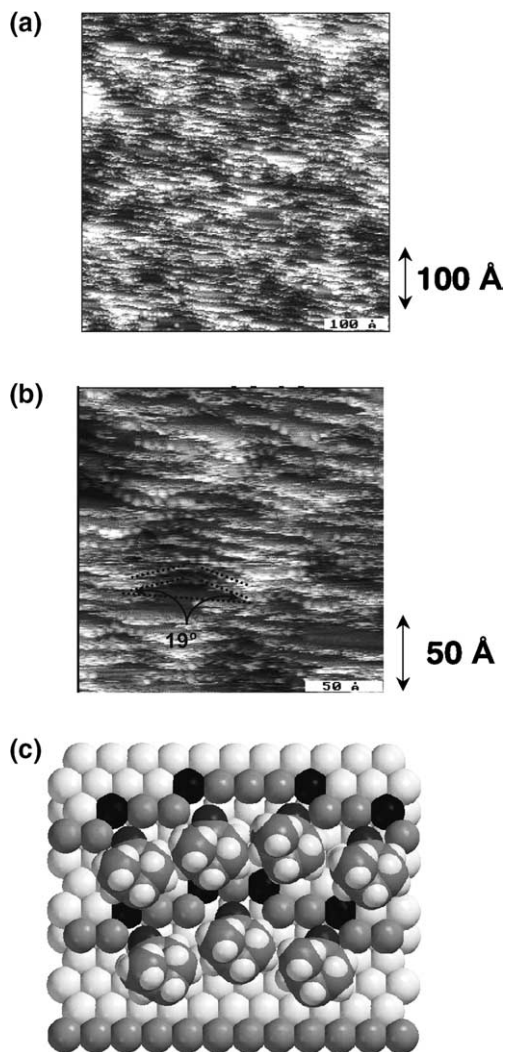
(a)

(b)

(c)

Fig. 3. Structure of Cu(5 3 3) surface roughened by dosing with R-3-MCHO at room temperature. (a) STM image of Cu(5 3 3) dosed with ∼20 L of R-3-MCHO at room temperature. The reorientation of the step edges is clear. (400×400 Å^2, −1.0 V, 0.7 nA). (b) High resolution image of reconstructed Cu(5 3 3) showing the presence of molecules along the step edge. Also highlighted are the directions of the reconstructed step edges forming angles of ∼19° with respect to the [0 1 $\bar{1}$] direction. (c) A model of the reconstructed surface showing the adsorption of R-3-MCHO at kink sites along the newly formed kinked ⟨1 2 3⟩ step edges.

images would reveal the formation of chiral kinks along the step edge.

The adsorption of R-3-MCHO on Cu(5 3 3) induces the formation of chiral step structures
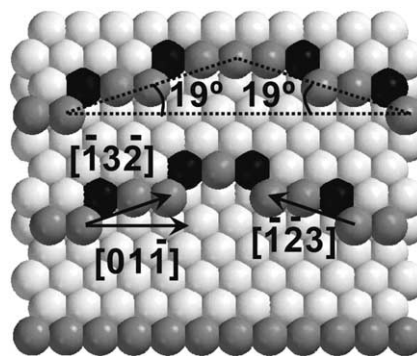

Fig. 4. Hard sphere model of bare roughened Cu(5 3 3) substrate. The step edges have the same structure as those of the ideal Cu(6 4 3) surface with single atom kinks separated by two lattice spacings along the [0 1 $\bar{1}$] direction. The model represents the formation of both R- and S-type kinks.

running along ⟨1 2 3⟩ directions and separating (1 1 1) terraces. We note, however, that both R- and S-kinks co-exist in the reconstruction, as shown by the two related deviations (±19°) from the [0 1 $\bar{1}$] direction. In principle, the net [0 1 $\bar{1}$] orientation of the step edge could have been maintained by the formation of chiral lengths running along either [$\bar{1}$ 3 $\bar{2}$] or [$\bar{1}$ $\bar{2}$ 3] directions separated by achiral lengths running along either the [$\bar{1}$ 1 0] or [1 0 $\bar{1}$] directions. This would have resulted in a surface with a net handedness. In reality it seems that the reconstructed step edges are formed by stretches having both [$\bar{1}$ 3 $\bar{2}$] and [$\bar{1}$ $\bar{2}$ 3] orientations. It is not possible to tell from the images, however, whether these are truly present in equal quantities.

4. Discussion

The TPD measurements suggest the formation of kinks on the Cu(5 3 3) surface during room temperature adsorption of R-3-MCHO and the STM images clearly reveal their presence. The straight (1 0 0) step edges of the Cu(5 3 3) surface have been reconstructed or roughened to include the presence of kinks. The driving force for the production of kinks along the step edge must be the fact that the heat of adsorption of the R-3-MCHO is higher at kink sites than at straight step edges [11,15]. This is revealed clearly by the TPD

spectrum from the $Cu(6\,4\,3)^R$ surface. A rough analysis of the desorption spectra, assuming a first-order desorption pre-exponent of $v = 10^{13}$ s^{-1}, indicates that the difference in the desorption energies from the kinks and step edges is $\Delta\Delta E_{des} = 12$ kJ/mol [21]. Given sufficient mobility of the atoms at the surface this should be sufficient to induce a reconstruction of the step edges.

It is important to realize that reconstruction involves complex atomic motions along the step edge and that there is a kinetic factor that must be considered in addition to the thermodynamic driving force. The TPD spectra obtained by adsorption of R-3-MCHO at 90 K followed by heating at 1 K/s do not reveal any evidence of reconstruction. Clearly the surface must spend some time at temperatures in the vicinity of 300 K in order for the reconstruction to occur. In the TPD experiments using adsorption at 330 K, the Cu(5 3 3) surface was held at the elevated temperature with R-3-MCHO adsorbed for periods on the order of 10 min between initial adsorption and subsequent desorption. Some STM measurements were also conducted by adsorbing the R-3-MCHO at 100 K and then allowing the sample to warm to room temperature at 1 K/s before beginning imaging. Before imaging, however, the sample temperature rested at 300 K for periods on the order of hours. Under these conditions the STM images also revealed reconstruction of the step edges. Unfortunately, in the STM apparatus it was not possible to cycle the temperature rapidly from 100 to 300 K and back down in order to image the surface as it might exist after spending only a short time at 300 K. In summary, we conclude from the TPD spectra that if the surface spends periods of less than 1 minute at temperature in excess of 300 K, then no kinks are formed. However, reconstruction does occur if the surface spends significantly longer periods at these temperatures in the presence of adsorbed R-3-MCHO.

The final issue is whether or not the reconstruction by R-3-MCHO results in net chiral imprinting of the Cu(5 3 3) surface. The heats of adsorption of R-3-MCHO at chiral kinks on Cu surfaces are enantiospecific [11]. Adsorption at the S-kinks is favored by $\Delta\Delta E_{des} \sim 1$ kJ/mol over adsorption at the R-kinks. This means that the generation of S-kinks should, in principle, be favored over the generation of R-kinks and that R-3-MCHO ought to be capable of chirally imprinting the Cu(5 3 3) surface. Unfortunately, if there is any net chirality to the reconstructed Cu(5 3 3) surface it is not detectable in the STM images of Fig. 3. Reconstruction to a surface which had net chirality could be achieved without interlayer or bulk mass transport through the formation of zigzag steps with a combination of $[\bar{1}\,3\,\bar{2}]$ and $[\bar{1}\,1\,0]$ directions. These would have stretches of homochiral, kinked $[\bar{1}\,3\,\bar{2}]$ steps separated by stretches of achiral $[\bar{1}\,1\,0]$ steps and would preserve the net direction of the original $[0\,1\,\bar{1}]$ steps on the (5 3 3) surface. Presumably this is energetically disfavored with respect to the formation of steps running along both $[\bar{1}\,3\,\bar{2}]$ and $[\bar{1}\,\bar{2}\,3]$ directions.

5. Conclusions

Both TPD and STM studies of the room temperature adsorption of R-3-MCHO on the Cu(5 3 3) surface reveal that the straight (1 0 0) step edges undergo adsorbate induced reconstruction to produce short lengths of kinked step edges oriented along the $[\bar{1}\,3\,\bar{2}]$ and $[\bar{1}\,\bar{2}\,3]$ directions and separated by (1 1 1) terraces. TPD measurements on the Cu(2 2 1) surface indicate that its straight (1 1 0) step edges must undergo a similar reconstruction during room temperature adsorption of R-3-MCHO to include kinks. Although the reconstruction should, in principle, result in a surface that has some net chirality, this could not be detected in the STM images.

References

[1] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley Publ., New York, 1994.

[2] M. Schunack, E. Laegsgaard, I. Stensgaard, I. Johannsen, F. Besenbacher, Angewandte Chemie-International Edition 40 (2001) 2623.

[3] X.Y. Zhao, Journal of the American Chemical Society 122 (2000) 12584.

[4] X.Y. Zhao, R.G. Zhao, W.S. Yang, Langmuir 16 (2000) 9812.

[5] E. Polastro, Commercial outlook for chirality. Quo vadis? in: G. Jannes, V. Dubois (Eds.), Chiral Reactions in Heterogeneous Catalysis, Plenum Publ., New York, 1995, p. 5.

[6] D.S. Sholl, A. Asthagiri, T.D. Power, Journal of Physical Chemistry B 105 (2001) 4771.

[7] D.S. Sholl, Langmuir 14 (1998) 862.

[8] C.F. McFadden, P.S. Cremer, A.J. Gellman, Langmuir 12 (1996) 2483.

[9] X.Y. Zhao, S.S. Perry, Journal of Molecular Catalysis A 216 (2004) 257.

[10] J.D. Horvath, A.J. Gellman, D.S. Sholl, T.D. Power, Enantiospecific properties of chiral single crystal surfaces, Chirality: Physical Chemistry, San Francisco, 2000.

[11] J.D. Horvath, A.J. Gellman, Journal of the American Chemical Society 124 (2002) 2384.

[12] G.A. Attard, C. Harris, E. Herrero, J. Feliu, Faraday Discussions 121 (2002) 253.

[13] G.A. Attard, A. Ahmadi, J. Feliu, A. Rodes, E. Herrero, S. Blais, G. Jerkiewicz, Journal of Physical Chemistry B 103 (1999) 1381.

[14] A. Ahmadi, G. Attard, J. Feliu, A. Rodes, Langmuir 15 (1999) 2420.

[15] J.D. Horvath, A.J. Gellman, Topics in Catalysis 25 (2003) 9.

[16] T.D. Power, A. Asthagiri, D.S. Sholl, Langmuir 18 (2002) 3737.

[17] A. Asthagiri, P.J. Feibelman, D.S. Sholl, Topics in Catalysis 18 (2002) 193.

[18] M. Giesen-Seibert, F. Schmitz, R. Jentjens, H. Ibach, Surface Science 329 (1985) 47.

[19] M. Giesen, Surface Science 370 (1997) 55.

[20] J.C. Girard, S. Gauthier, S. Rousset, W. Sacks, S. Decheveigne, J. Klein, Surface Science 301 (1994) 245.

[21] P.A. Redhead, Vacuum 12 (1962) 203.