CIENCIA 14 (Special Number on Adsorption and Catalysis), 114 - 124, 2006
Maracaibo, República Bolivariana de Venezuela

Two-dimensional chiral assemblies of chiral modifiers at metal surfaces: Alanine succinic acid adsorption on Cu(110)

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Received: 13-09-05 Accepted: 21-10-05

Abstract

Creating successful heterogeneous enantioselective catalysts remains an important goal for the chemicals and pharmaceuticals industry, with considerable attention being focused on chirally modified metals as promising candidates. By suitable adsorption of organic molecules, a metal surface can become chiral, existing in one of two distinguishable mirror forms that cannot be superimposed. However, the behaviour of such complex adsorption systems is difficult to predict and only recently have surface science studies begun to provide a more detailed understanding. Here, extended chiral adsorption phases of two successful chiral modifiers, tartaric acid and alanine on a Cu(1 10) surface are reviewed. The chiral organisation created by the tartaric acid molecule is further contrasted with the behaviour of the similar, but achiral, succinic acid molecule. The 2-dimensional assembly at the surface is shown to be strongly dependent on molecule-metal bonding interactions with the driving force for creating chiral organisations arising from adsorption-induced asymmetrisation.

Key words: Alanine; Cu (110); chirality; succinic acid; surfaces; tartaric acid.

Ensamblajes quirales en dos dimensiones de modificadores quirales en superficies metálicas: La adsorción de alanina, ácido succionico sobre Cu (110)

Resumen

El desarrollo de catalizadores heterogéneos enantioselectivos exitosos es aun de interés capital para la industria química y farmacéutica, con una atención considerable enfocada en metales modificados quiralmente como candidatos prometedores. Una adsorción adecuada de moléculas orgánicas sobre una superficie metálica puede convertirse en quiral, existiendo en una de dos formas pequeñas distinguibles que pueden ser superpuestas. Sin embargo, el comportamiento de tal sistema de adsorción complejo es difícil de predecir y solo recientemente se han comenzado estudios de ciencia de superficie que provean una comprensión más detallada. En este trabajo se revisan fases de adsorción quirales extendidas de dos modificadores quirales exitosos, ácido tartárico y alanina, sobre una superficie de Cu [110]. La organización quiral creada por las moléculas de ácido tartárico contrasta con el comportamiento similar presenta-

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do por la molécula de ácido succínico, que es aquiral. El ensamblaje en dos dimensiones en la superficie muestra ser fuertemente dependiente de las interacciones del enlace molécula-metal con una fuerza impulsora que crea organizaciones quirales que se originan a partir de asimetrizaciones de adsorción inducidas.

Palabras clave: Ácido tartárico; ácido succínico; alanina; Cu (110); superficies; quiralidad.

1. Introduction

Chirality is a simple geometric property that dictates that the mirror transformation of an object that does not possess any inverse symmetry elements is a non-identity operation, i.e. the object and its mirror image are non-superimposable. As a result, a chiral object can exist in two distinguishable mirror, or enantiomeric, forms. Since the thalidomide tragedy, which starkly demonstrated the different physiological effects opposite enantiomers can have on a biological system, there has been a major momentum within the chemicals and pharmaceuticals industries to establish enantioselective catalytic methods (1) whereby pure enantiomeric forms of products can be produced. At present, most commercial-scale operations are based on homogeneous catalytic systems (1) but heterogeneous systems offer significant advantages with non-stoichiometric production of chiral molecules being combined with ease of handling and separation. A number of different approaches have been adopted for creating heterogeneous chiral catalysts (2-5), and we have concentrated on the approach of introducing asymmetry by adsorbing chiral molecules at achiral metal surfaces. At present, such systems have had their best successes reported for the hydrogenation of β-ketoesters over supported Ni catalysts (6-10). The central feature of these, and related systems, is that enantioselectivity is only manifested if the metal surfaces are first modified by the adsorption of chiral organic "modifier" molecules. For hydrogenation reactions at Ni, Cu and Co surfaces (3-7,9), modifiers based on either the chiral dicarboxylic acid, tartaric acid, or the simplest chiral amino acid, alanine, are well-known for stereodirecting the hydrogenation of methylacetoacetate (MAA) to give R-methyl-3-hydroxybutrate or S-methyl-3-hydroxybutrate as shown in Figure 1. Since MAA is a planar molecule, the optical activity of the product is simply determined by the molecular face at which the hydrogen attack occurs. For the unmodified metal, the probability of hydrogen attack on the prochiral substrate is identical for each face, yielding a racemic product mixture. However, the final product created on modified metal surfaces is governed by the chirality of the modifier. Thus, modification of a nickel surface by R,R-tartaric acid yields the R-product in >90% enantiomeric excess (*e.e*), while S,S-tartaric acid favours the S-product.

It is now appreciated that the metal-organic interface can result in a wealth of adsorption phases for any given system, dependent on coverage and thermodynamic conditions, with the adsorbed molecules displaying a range of chemical states, orientations, molecular arrangements and bonding interactions at the surface (11-16). The results presented in this paper concentrate on adsorption phases where chiral domains are seen as these are likely to be the most relevant to asymmetric catalytic systems. In particular, we discuss the creation of surface chirality for two chiral modifiers shown in Figure 2, tartaric acid (HOOC-C*HOH-C*HOH-COOH) and alanine ($NH_2C^*H(CH_3)COOH$) on the model achiral metal surface, Cu(110). In addition, further understanding of the underlying forces and mechanisms that generate chirality at surfaces, is provided by the adsorption of the achiral molecule, succinic acid

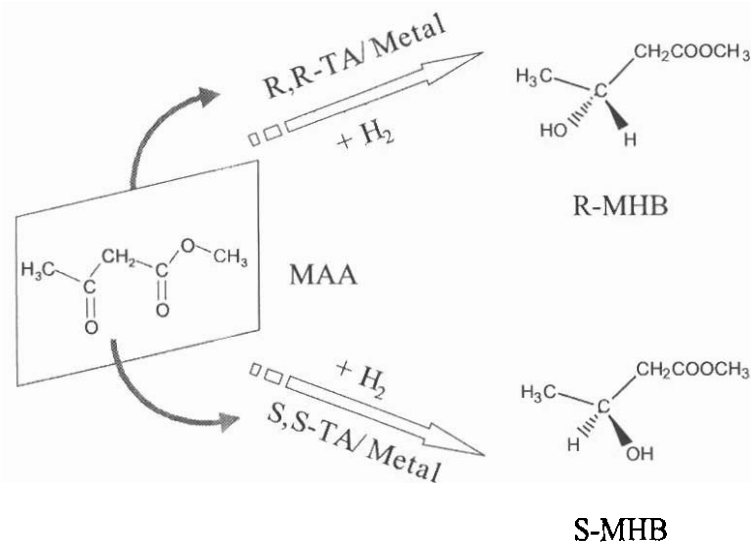

Figure 1. The stereodirected hydrogenation of methylacetoacetate (MAA) to give methyl-3-hydroxy-butrate (MHB) on Tartaric acid (TA) chirally-modified Ni catalysts.

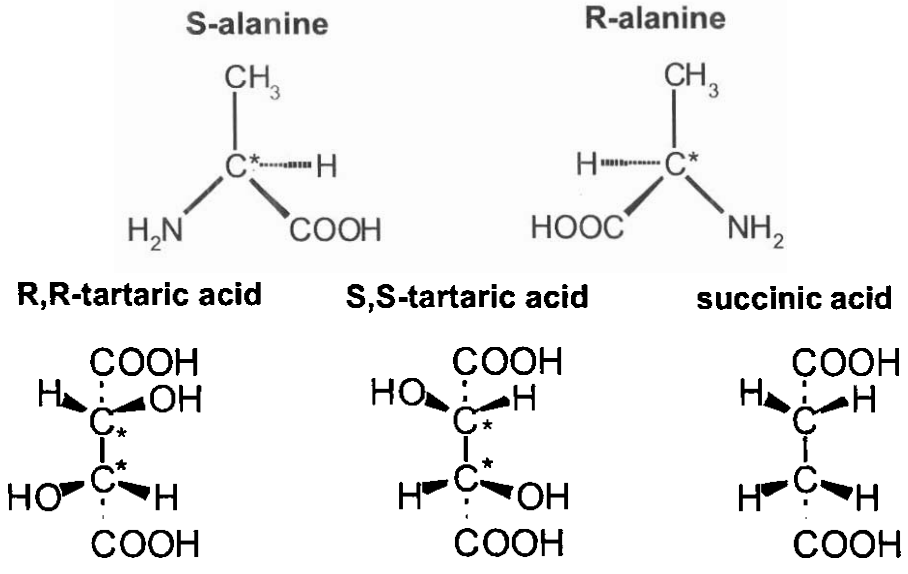

Figure 2. Structures of (a) R-alanine, (b) S-alanine, (c) (R,R)-tartaric acid, (d) (S,S)- tartaric acid and (e) succinic acid.

(HOOC-CH_2-CH_2-COOH), which despite a lack of inherent chirality, can also form chiral domains on the Cu(110) surface. Succinic acid is a very similar molecule to tartaric acid, with the only difference being that the two hydroxyl groups present in tartaric acid are replaced by hydrogen atoms leading to the loss of both chiral centres.

The chiral surfaces created were probed using three main techniques: Reflection Absorption Infrared Spectroscopy (RAIRS), Low Energy Electron Diffraction

(LEED) and Scanning Tunnelling Microscopy (STM). Each technique provides complementary information on the interface. The high sensitivity, high resolution vibrational data obtained by Fourier-transform RAIRS provides direct information on the chemical nature of the adsorbed molecules, their perturbation by the surface, and their orientation at the surface. LEED monitors the long-range 2-dimensional periodicity of the adlayer while STM provides information on the local arrangements of the molecules within the domains formed at the surface.

2. Experimental

Experiments were carried out in an Omicron Vakuumphysik variable temperature-STM chamber with facilities for STM, LEED, Auger Electron Spectroscopy (AES) and sample cleaning. All STM experiments were carried out with the sample at room temperature. The images were acquired in constant current mode. Complementary RAIRS experiments identified the nature of the adsorbed species imaged by STM. The Cu(110) crystal was cleaned by cycles of Ar^+ ion sputtering, flashing and annealing to 700 K. The surface ordering and cleanliness were monitored by LEED and AES. Alanine, succinic acid (99%) and tartaric acid (99%) were obtained from Sigma Aldrich and used without further purification. The adsorbate was introduced into the chamber via sublimation from a Knudsen cell. During sublimation the main chamber pressure was typically 2×10^{-9} mbar.

Adsorbate coverage at the surface is given in terms of fractional monolayers (ML), quoted with respect to the number density of surface metal atoms. The adlayer unit mesh is given in standard matrix notation and quoted in the text as (G_{11} G_{12} , G_{21} G_{22}):

$$\begin{pmatrix} a_0 \\ b_0 \end{pmatrix} = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \begin{pmatrix} a_s \\ b_s \end{pmatrix}$$

where $\mathbf{a_0}$, $\mathbf{b_0}$ are the overlayer unit vectors, $\mathbf{a_s}$, $\mathbf{b_s}$ are the substrate unit vectors and $|\mathbf{a_s}| < |\mathbf{b_s}|$ with the vectors all defined by a right handed axis system (11).

3. Results and Discussion

There are two major manifestations of chirality at surfaces. The first, leading to the creation of chiral motifs at surfaces, arises because adsorption of the molecule essentially creates a molecule-metal complex which locally destroys all mirror planes. Such point chirality is the most basic manifestation of chirality and leads to a local chiral motif that is restricted to possessing the point group symmetries C_1, C_2, C_3, C_4, or C_6. Alternatively, chirality arises when adsorbates assemble into clusters, 1D chains or ordered 2D structures where the self-assembly of individual motifs destroys the reflection symmetry planes of the underlying surface, leading to the creation of organisational chirality. Such chirally ordered domains belong to one of the five possible chiral space groups, C_1, C_2, C_3, C_4, C_6, that can exist at a surface. Here, we discuss these two aspects for the phases showing chiral domains for alanine, tartaric acid and succinic acid on Cu(110).

3.1. Alanine on Cu(110)

RAIRS shows that on the adsorption of molecules of S-alanine, or the opposite enantiomer R-alanine, on the Cu(110) surface between temperatures of 300 and 470 K, the alaninate species is always present (17-19). The carboxylic acid group is deprotonated to give the carboxylate COO^- and the amino group is neutral, NH_2, with the integrity of the chiral centre preserved i.e. the system always has a chiral adsorption motif. Interestingly, the alaninate/Cu(110) system is found to be polymorphic with the singularly preferred alaninate unit self-assembling into a variety of chiral surface superstructures (19). However, although the chiral nature of the alanine molecule determines that all the surface phases ob-

tained remain overall chiral, only the phase obtained at high coverage, at temperatures between 300 and 430 K, shows a true long-range chiral organisation, exhibiting global organisational chirality. i.e. for each enantiomer a single growth direction and arrangement is maintained over the entire surface with no reflection domains of the opposite chirality tolerated, Figure 3(a). In this phase, the molecule is present as two differently orientated alaninate species, bound either to the copper surface through both oxygens of the ionised carboxylate group and the nitrogen of the neutral amino group (μ3 species) or through the amino group and only one of the carboxylate oxygen atoms (μ2 species). The bonding geometry and preferred adsorption footprint of the μ3 species has been further examined by DFT calculations performed by Rankin and Sholl (20, 21) and photoelectron diffraction measurements made by Woodruff and co-workers (22). These have determined that the preferred geometry is one where the nitrogen bonds almost atop to a copper atom in one close packed <1 1 0> row and the two oxygen atoms bond to two adjacent copper atoms in the next close packed row but in off-top positions.

A small area STM image, Figure 3(b), for the S-alanine/Cu(1 1 0) system reveals that the individual molecules are self-assembled into defined chiral clusters. Each cluster consists of either six or eight molecules lined up in pairs in the <1 1 0> direction with the same overall growth direction, broadly parallel to the non-symmetric (1 2) direction. The area scanned in Figure 3(b) mainly consists of octamer clusters whereas other areas of the surface show rows of hexamer clusters e.g. Figure 3(a) and Figure 4(c). The organisational integrity of this self-assembly is seen with LEED, which is sensitive to the long-range order of the interface. Figure 4(a) displays the LEED pattern associated with this phase for S-alanine, with the real space unit cell described by the matrix (2 -2, 5 3). The two dimensional chi-

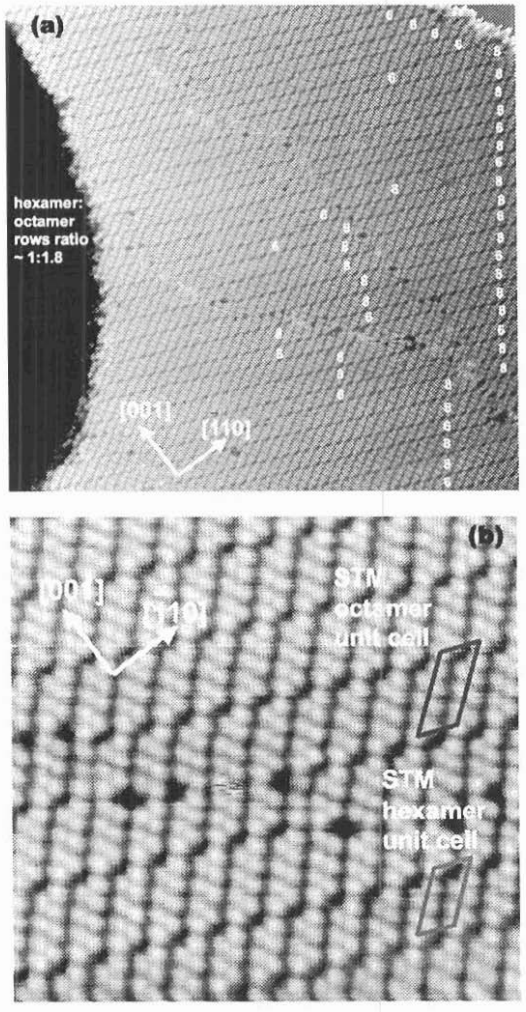

Figure 3. STM images of S-alaninate/Cu(110) for the chiral phase III at 403 K. a) Large area image showing the organised chiral surface. (Image size 508 Å x 492 Å, V= -2.08V, I=1.97 nA.) Rows of hexamer and octamer clusters are marked with 6 or 8 respectively.

rality of this phase can be switched, with the opposite enantiomer, R-alanine, showing defined hexamer or octamer chiral clusters that self-assemble broadly in the mirror (1 2) direction, and an overall chiral surface which is the mirror image of that created by S-alanine. The mirror LEED and STM im-

ages of S- and R-alanine are presented in Figure 4 with R-alanine showing a real space LEED unit cell of (5 -3, 2 2).

The cluster structures are obviously highly complex and there is no direct information on where specific μ3 and μ2 alaninate species are located within a structure, which particular adsorption footprint they adopt and what intermolecular interactions they participate in. These questions represent huge challenges within this field and, even within the boundaries imposed by our multi-technique data set, a large number of permutations can be envisaged. Some of these are presented in reference (19) where we propose that the formation of the size-selected cluster assemblies arise from the stress of maintaining both optimum adsorption sites for the alaninate molecules and maximising the intermolecular interactions. This stress becomes too great once a critical cluster size is reached, leading to a fracture in the assembly of the chains. There are two possible scenarios for chain fractures: either intermolecular interactions progressively force subsequent pairs of molecules

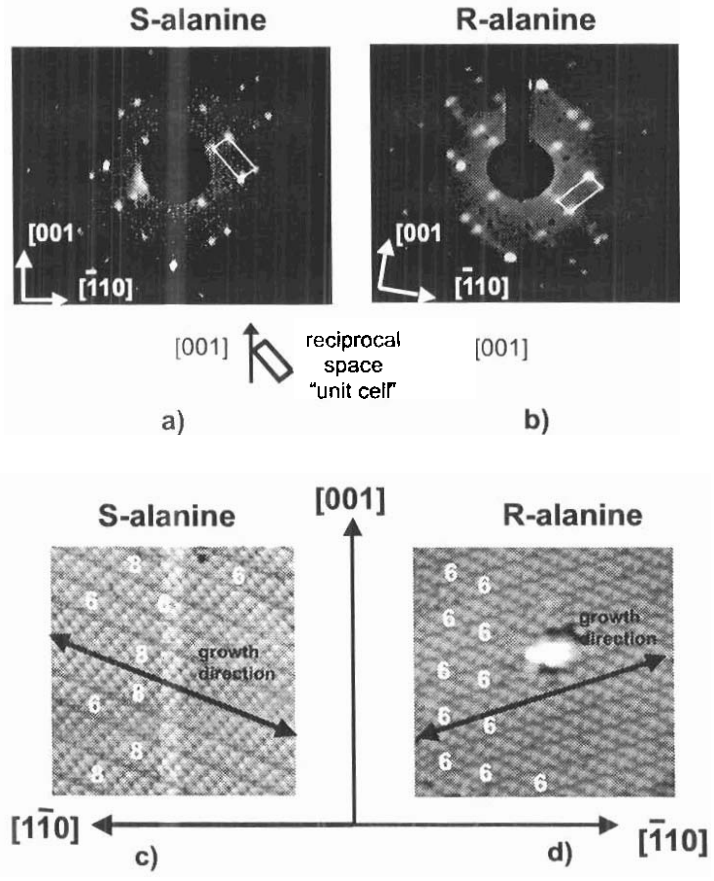

Figure 4. LEED patterns and STM images obtained for the chiral phase III of the S- and R-alaninate/ Cu(110) systems. a) S-alaninate LEED (LEED energy 52 eV, annealing temperature 395 K). b) R-alaninate LEED (LEED energy 54eV, annealing temperature 423 K). c) S-alaninate STM (165 Å x 160 Å, V=-2.08V, I=1.97nA, annealing temperature 403 K). d) R-alaninate STM (165 Å x 160 Å, V=-2.08V, I=1.04nA, annealing temperature 413 K). Rows of hexamer and octamer clusters are marked with 6 or 8 respectively.

further away from their optimum bonding positions, until adsorption is no longer favourable and a new cluster is nucleated; or the strength of the chemisorption bond forces surface reconstruction of the copper atoms in order to optimise adsorption geometry.

Thus, for both S- and R-alanine adsorbed on Cu(110), a surface is created in which size-defined chiral clusters self-assemble into a defined chiral array with channels and spaces of bare metal left between the chiral clusters that are themselves chiral. The nature of these chiral spaces and channels on the extended surface depends sensitively on the details of both the cluster and the repeat unit which are not yet fully understood. These chiral areas of exposed metal may, however, hold the clue to the success of alanine as a chiral modifier. What is certain is that, overall, under the specific adsorption conditions of high coverage and a temperature between 300 and 430 K, either S- or R-alanine adsorbed on Cu(110) create a surface with true global organisational chirality.

3.2. Tartaric and succinic acid on Cu(110)

Unlike alanine with its single alaninate form, tartaric and succinic acid exhibit a range of chemical states at the Cu(110) surface (23-25). Detailed RAIR spectroscopic data (23,11) show that the doubly deprotonated form of the molecules is thermodynamically preferred on Cu(110) at low coverages with both carboxylate ends of the molecule involved in bonding to the surface and the two oxygen atoms in each COO^- unit held almost equidistant from the surface, leaving the C_2-C_3 bond almost parallel to the surface and yielding a fairly rigid adsorption geometry. This general geometry has recently been confirmed by periodic density functional theory calculations for both bitartrate and bisuccinate on Cu(110)(26). These calculations also show that, in both cases, the molecule is adsorbed across the long-bridge site, and that the carboxylate oxygens of the bitartrate and the bisuccinate occupy the on-top Cu positions across the two-fold short bridge site, Figures 5 and 6.

LEED and STM data show that both these two bicarboxylate molecules form chiral domains on the Cu(110) surface. The *(R,R)*-bitartrate phase (24) possesses a [1 2, -90] structure, Figure 5, with rows of three bitartrate molecules assembling at the surface to form long chains, which are aligned along the (14) surface direction. Significantly, this structure annihilates both reflection symmetry planes of the underlying Cu(110) and, as a result, creates a system where chirality is present at both the molecular adsorption motif (point group) level and at the organisational (space group) level i.e. it displays global organisational chirality. In fact, the chirality of the bitartrate system can only be switched by creating the same phase but using the twin enantiomer, *(S,S)*-tartaric acid, which leads to a perfect image chiral surface in which all molecular positions and growth directions are reflected in space (24), Figure 5.

STM images from the bisuccinate phase (25), Figure 6(a), clearly show that it produces two domains at the surface with both the chiral [90, -22] phase and its mirror image [22, -90] phase coexisting at the surface. Thus, this system does not exhibit global organisational chirality. As the succinic acid molecule possesses no inherent chirality, any chiral behaviour it displays is adsorption-induced. Important clues on this spontaneous creation of chirality in the bisuccinate phase comes from the LEED data which show diffraction patterns with a slightly different repeat structure to that picked up by the STM experiment, namely a [11, -90] and [90, -11] structure, Figure 6. This halving of the repeat distance in the (12) and (12) directions, respectively, can only arise if asymmetry is introduced for the local adsorption unit, i.e. the achiral bisuccinate adopts a local chiral adsorption motif. Detailed structural models (25) show that

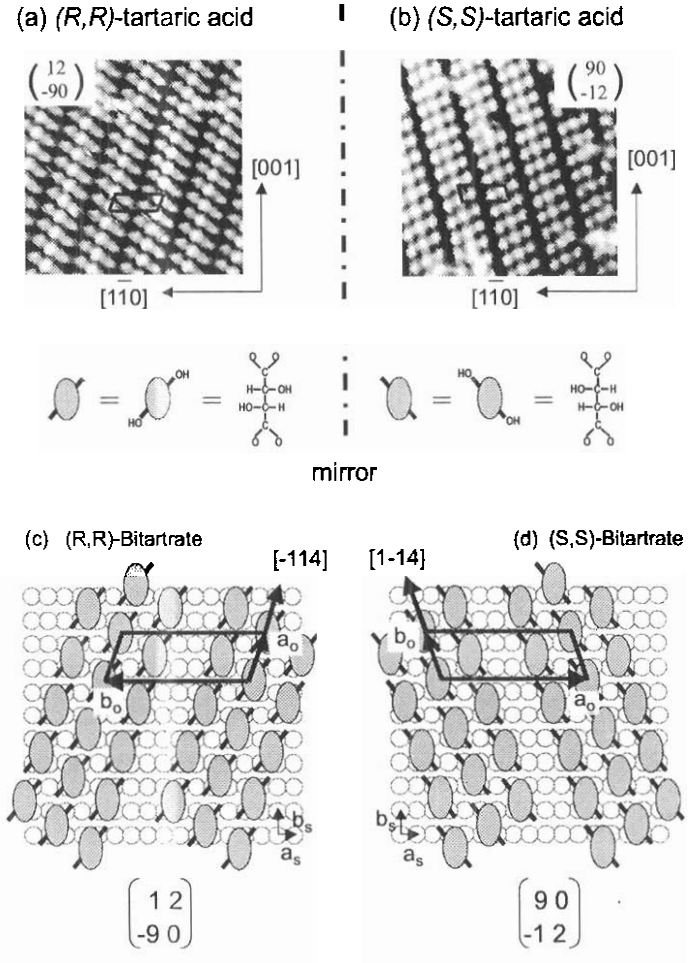

Figure 5. Depiction of the [12, -90] and [90 -12] bitartrate phases formed for the adsorption of Tartaric Acid on Cu(110). (a) and (b) STM images (108 Å x 108 Å) (V = -1.7 V; I = 1.18 nA) showing the *(R,R)*-bitartrate [12, -90] phase and (108 Å x 108 Å) (V = -2.73 V; I = 1.02 nA) showing the *(S,S)*-bitartrate [90, -12] phase. c) and (d) Structural models for each of the tartrate phases: *(R,R)*- bitartrate [90, -12] and *(S,S)*- bitartrate [12, -90].

each domain consists of rows of three bisuccinate molecules that assemble at the surface to form long chains with chiral organisations. The overall similarity in the trimer chain structures adopted by both the bitartrate and the bisuccinate phases, suggests that it is the molecule-metal interactions that determine the general nature of the self-organisation and that the presence/absence of the chiral OH groups does not affect the overall type of supramolecular assembly that is adopted. For the bisuccinate system, the achirality of the adsorbing molecule makes the nucleation of point chirality of one-handedness (via a chiral molecular distortion/reconstruction) energetically degenerate to that of creating point chirality of the opposite handedness (via a mirror chiral molecular distortion/reconstruction), so random adsorption processes will produce equal numbers of each adsorption motif from which local chiral domains will be

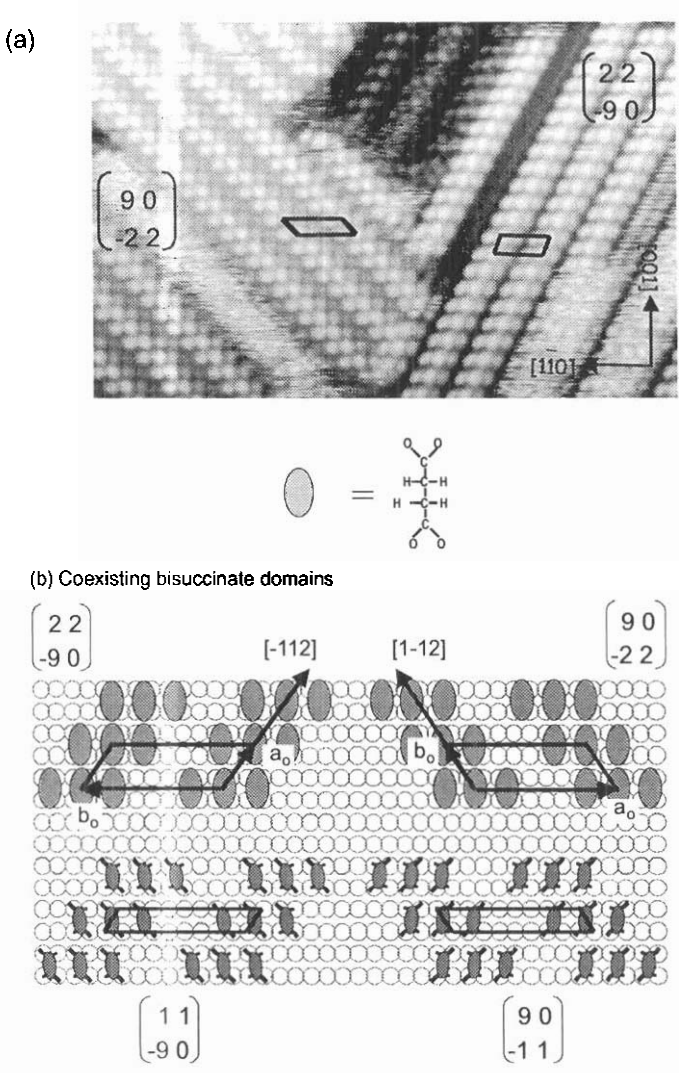

Figure 6. Depiction of the bisuccinate phases. (a) STM images (260 Å x 170 Å) (V = -0.21 V; I = 0.15 nA) showing the coexistence of the [22, -90] and [90, -22] phases (b) Structural models are presented for each of the phases. The [22, -90] and [90, -22] unit cells of the overall structure are shown on the top part, while the lower part presents the model that could lead to the [11, -90] and [90, -11] periodicities by molecular distortions of the bisuccinate adsorbate.

propagated. Thus, the succinate system can only maintain chirality at the local level and is globally a racemic conglomerate. However, for the bitartrate adsorption, the rigid adsorption of the bitartrate unit in which both carboxylate functionalities are bonded to the surface forces the chiral OH groups to adopt a uniquely defined direction with respect to the surface for each enantiomer. This breaks the degeneracy between one chiral molecular distortion/reconstruction vis-a-vis its mirror chiral molecular distortion/reconstruction, restricting each enantiomer to a single chiral adsorption motif and producing a single chiral domain with global organisational chirality.

Conclusion

Detailed studies of the adsorption of the chiral modifiers, alanine and tartaric acid on Cu(110) show that each of the individual enantiomers possess a phase with global organisational chirality i.e. each enantiomer adopts a single chiral adsorption motif (point chirality) and a chiral growth direction which is sustained across the entire surface (space group chirality) with the organisation being the mirror image of that for the opposite enantiomer. In the case of alanine, the chiral organisation proceeds via adsorption of individual alaninate molecules with chiral footprints, to the formation of size-defined chiral clusters which then assemble into an overall single chiral domain for each enantiomer. For tartaric acid, the chiral adsorption motifs are formed by bitartrate molecules that form a chiral trimer chain structure giving a single chiral domain for each enantiomer. The achiral succininc acid molecule adsorbs as a bisuccinate on Cu(110) with a similar trimer chain structure to the bitartrate which points to the dominance of molecule-metal bonding in dictating the overall type of superstructures adopted. However, for the bisuccinate system, the inherently achiral nature of the molecule means that two equally probable mirror adsorption motifs are possible, leading to an overall racemic conglomerate.

Acknowledgements

It is a great pleasure to acknowledge the substantial contributions that our coresearchers have made to this research effort: Maria Ortega-Lorenzo, Chris Baddeley, Chris Muryn, Paul Murray, Souheila Louafi, Delphine Le-Roux and Jamie Williams. Financial support has been provided by EPSRC, BBSRC and the University of Liverpool.

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