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Chiral reconstruction of Cu(110) after adsorption of fumaric acid

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ABSTRACT

The interaction of fumaric acid with the Cu(110) has been investigated in UHV by means of low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD), scanning tunneling microscopy (STM) and density functional theory (DFT). Different long-range ordered structures appear in LEED after gently annealing. It is found that rows consisting of metal adatoms are strung along the <1, ±1> directions, thus breaking locally the mirror symmetry of the surface. Models proposed by DFT are in good agreement with the STM appearance.

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1. Introduction

Restructuring and faceting of surfaces after adsorption of organic molecules is a common phenomenon [1]. This process may involve mirror symmetry breaking, either because the adsorbed molecule is an enantiomer of a chiral species or spontaneous symmetry breaking occurs locally [2]. For the latter, opposite handed facets will inevitably co-exist on the surface. Prominent examples for faceting or step edge restructuring include amino acids on Cu(100) [3–6], or PVBA on Ag(110) [7]. Tartaric acid (TA, Fig. 1), a C4 dicarboxylic acid available in a chiral and an achiral meso form (Fig. 1), has previously been studied on Cu(110) [8–12]. Based on theoretical modeling, it was concluded that reconstruction must be involved for TA adsorbed on Ni(110) [13], but in the case of the C4 carboxylic acids TA, *m*-TA and succinic acid (SU, Fig. 1) on Cu(110) it was only speculated that this might be also the case [14–16]. Chiral reconstructions of Cu(110) induced by malic acid (Fig. 1b) have been identified by Roth et al. via STM [17,18], and Gellman, Sykes and coworkers recently reported a chiral reconstructed phase of Cu(110) induced by TA [19,20].

In general, C4-carboxylic acids offer the unique opportunity to study reshaping of crystals, because they impose a chiral footprint onto the surface [21]. That is, both carboxylate groups may strongly interact with the surface, while the backbone takes a zigzag distortion that breaks mirror symmetry. For TA on Cu(110), this molecular structure was experimentally confirmed by XPD studies [22,23]. Interestingly, homochiral doping of the SU and *m*-TA systems with chiral TA induced symmetry breaking at the global scale, turning the entire surface into a homochiral arrangement via the so-called Sergeant-and-Soldiers principle [24,25]. Because SU, when adsorbed as succinate with both carboxyl groups attached to the surface, cannot establish intermolecular hydrogen bonds, it was assumed that this type of chiral amplification must be mediated by the substrate [26,27]. Noteworthy here also is the suppression of the minority enantiomorph of TA at enantiomeric excess or by diastereospecific recognition [28,29].

In order to shine more light into the principles of interaction of C4 carboxylic acids with the Cu(110) surface, we studied the adsorption of trans-butenedioic acid (fumaric acid, FUA, Fig. 1). All four carbon atoms of this molecule are sp^2-hybridized and lie within a single plane. This should eliminate any chiral distortion via the zigzag

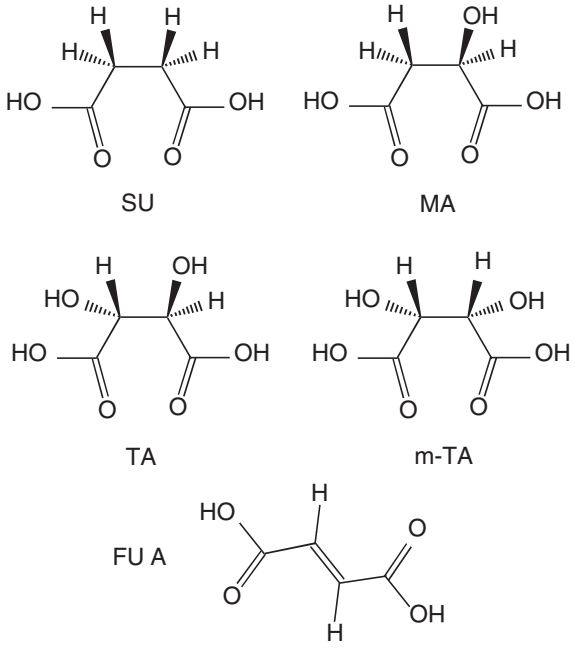

Fig. 1. Structural formulas for succinic acid (SU), malic acid (MA), tartaric acid (TA), *meso*-tartaric acid (*m*-TA) and fumaric acid (FUA).

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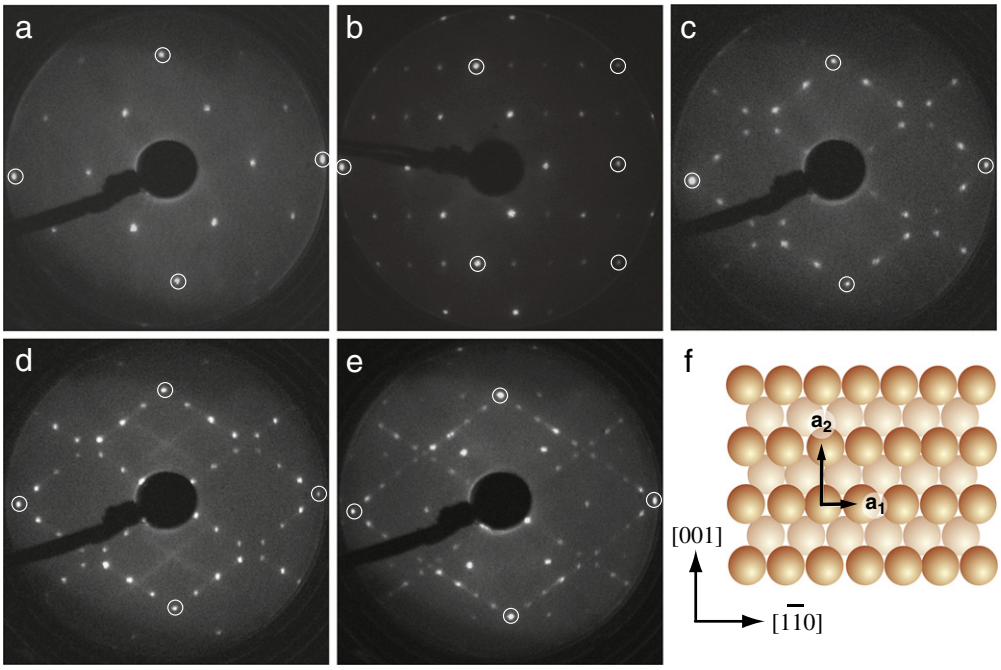

Fig. 2. LEED patterns of FUA on Cu(110). The (1 × 1) clean surface spots are marked with circles. a) c(2 × 4), E_P = 48 eV; b) p(2 × 4) with missing spots along the high symmetry directions, E_P = 53 eV; c) (1 −1, 3 2), E_P = 56 eV; d) (1 1, −5 2), E_P = 53 eV, with faint features suggesting also a <2, 2> periodicity instead of <1, 1> ; e) (1 1, −6 3) phase, coexisting with the c(2 × 4) phase, E_P = 52 eV; f) Real space lattice with identical orientation as in the LEED patterns.

footprint mechanism. However, we observe the same structures for FUA as previously reported for SU [13]. Some of these structures are reconstructed surfaces with Cu adatom rows aligned such that the mirror symmetry of the substrate is broken.

2. Experimental and theory

The experiments were carried out in UHV chambers (p = $5 \cdot 10^{-10}$ mbar), equipped with facilities for XPS, TPD, LEED, RAIRS and VT-STM. Experimental set-ups and sample preparation have been performed as described in detail previously [30]. FUA (Sigma Aldrich, ≥99%) was used without further purification and evaporated from differentially turbo-molecular-pumped homemade Knudsen cells, separated from the main chambers by gate valves. Prior to deposition, FUA was degassed for 20 min at 343 K before opening the valve and exposing the copper crystal surface to the FUA vapor. All annealing treatments were performed with a 50 °C/min heating rate until reaching the target temperature, where the crystal was kept constant for the indicated time. STM (in constant current mode) and LEED measurements were then performed at room temperature. Coverage calibration has been performed with XPS in combination with LEED. Where mentioned, STM images were filtered after fast Fourier transformation (FFT) with a first order low pass Butterworth filter to remove the higher frequency noise followed by inverse FFT.

DFT calculations were performed using the CP2K software within the Gaussian and plane wave mixed scheme where the wavefunction is expanded in a triple zeta valence Gaussian basis set with two sets of polarization functions (TZV2P), adapted for molecular systems, and the charge density in plane waves with a cutoff of 400 Ry. The PBE exchange-correlation functional was used, and the core electrons were described by using norm-conserving Goedecker–Teter–Hutter pseudopotentials. Moreover, the 2010 Grimme parametrization (DFT-D3) was applied. The Cu(110) substrate was modeled within a slab geometry, using periodic boundary conditions in all directions and a vacuum region of 20 Å in the direction orthogonal to the surface. The slab was 8 layers thick, with the 4 lower layers kept fixed, whereas the coordinates of all other atoms and the adsorbed molecules (in the mono- or dicarboxylate configuration) were fully optimized up to a threshold of $5 \cdot 10^{-4}$ a.u. in the forces. STM contrast simulations were performed in the Tersoff–Hamann approximation [31,32].

3. Results

3.1. LEED

Adsorption of FUA at room temperature (RT) does not result in ordered structures, except of a low quality c(2 × 4) structure at monolayer saturation (≈1 ML, θ = 0.25). Upon annealing (373 K for 15 min.), however, the saturated monolayer turns into a well-ordered c(2 × 4) structure, as judged by sharp diffraction spots and low background intensity (Fig. 2a). Further annealing for 15 min at 423 K changes the pattern from c(2 × 4) to p(2 × 4), with missing (0, n) spots, n = ½, ³/₂, etc. and missing (n, 0) spots, n = ¼, ¾, etc., indicating glide planes parallel to [001] and [1$\bar{1}$0] (Fig. 2b). This structure belongs therefore to the p2gg plane group. No ordered structures were observed at coverages below 0.7 ML. At coverages between 70% and 81% of the saturated monolayer, three enantiomorphous phases are observed after annealing (15 min., 423 K). That is, the LEED patterns constitute superpositions of two mirror domains. These are a (1 −1, 3 2)[1] phase (0.7 ML, θ = 0.175, Fig. 2c), a (1 1, −5 2) phase (0.78 ML, θ = 0.195, Fig. 2d)), and a (1 1, −6 3)[2] phase, the latter coexisting with the c(2 × 4) phase (0.81 ML, θ =0.203, Fig. 2e). At intermediate coverages (1 1, −5 2) and (1 1, −6 3) coexist, but prolonged annealing (30 min., 423 K) leaves only the (1 1, −5 2) phase on the surface. The LEED pattern of the (1 1, −5 2) structure shows weak stripes, dividing the reciprocal lattice in <1, ±1> direction, suggesting that there is a (2, ±2) periodicity as well. All structures reported here have been previously reported for SU and in part for *racemic* MA [15,17,24]. Both (1 1, −5 2) and (1 1, −6 3) structures are stable until 473 K. When the crystal is

[1] The (2 × 2) transformation matrix [33], linking the adsorbate lattice vectors (b_1, b_2) to the substrate lattice vectors (a_1, a_2) via $b_1 = m^{11}a_1 + m^{12}a_2$ and $b_2 = m^{21}a_1 + m^{22}a_2$, is written here in the form (m^{11} m^{12}, m^{21} m^{22}).

[2] These structures have previously been denoted as (5 0, ±1 1), (7 0, ±1 1) and (9 0, ±1 1) [15,22]. We use here a more consistent assignment strategy for unit cell definition and the master matrix formalism [34].

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