CHIRALITY IN AMINO ACID OVERLAYERSAT METAL CRYSTAL SURFACES

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Chirality

Chirality ("handedness") is the property of an object that it cannot be superimposed on its mirror image. Chiral objects, by definition, have no mirror symmetry.

Many molecules are chiral, occurring in left- and right-handed forms, or **enantiomers**. In an organic molecule, for example, a carbon atom bonded to four different functional groups is a **chiral centre**.

The building blocks of living organisms - amino acids and sugars - exhibit chirality. Moreover, naturally occurring amino acids all occur in just one of the two enantiomeric forms: amino acids occur in the L form (except glycine, which is achiral), sugars in the D form.

Getting the chirality right can be critical in pharmaceutical manufacture. One enantiomer of a drug molecule may have therapeutic effects, whereas the other may have no effect, or even be harmful.

The challenge: can metal surfaces be tailored to promote enantioselective heterogeneous catalysis? This is a key motivation for investigating the various manifestations of chirality that can occur at solid metal surfaces.

Catalysis

A **catalyst** is a substance that controls the activity (rate of reaction) and/or selectivity (balance of products) of a chemical reaction without itself being a reactant or a product.

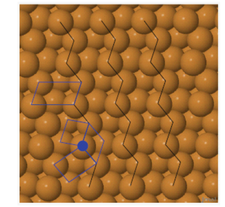
In **homogeneous catalysis**, the catalyst is in the same phase as the reactants and products. Typically, this means that the catalyst, reactants and products are all liquids. This can make separation and re-use of the catalyst challenging.

In **heterogeneous catalysis,** by contrast, the catalyst is in a different phase to the reactants and products. Typically, the catalyst takes the form of solid metal nanoparticles, whereas the reactants and products are liquids or gases.

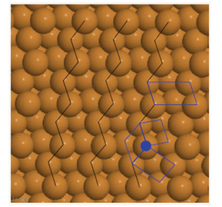
We study the interactions of molecules with solid metal surfaces in order to understand better how heterogeneous catalysis works. Real-world examples include the Haber-Bosch process (ammonia synthesis over Fe catalysts); the Fischer-Tropsch process (synthesis of hydrocarbon fuels from CO and H_2 over Co, Fe or Ru catalysts); and car exhaust catalytic converters (CO and HC oxidation, NO_x reduction over Pt/Pd/Ru catalysts).

Amino acids on a chiral surface: Cu{531}

A face-centred cubic material has high symmetry, but a surface of such a crystal may or may not be mirror-symmetric, depending on surface orientation. A surface cut to an orientation that has no mirror symmetry is an example of an **intrinsically chiral surface**. As with all chiral objects, such surfaces exist in either of two enantiomeric forms. Cu{531} is an example of an intrinsically chiral surface.

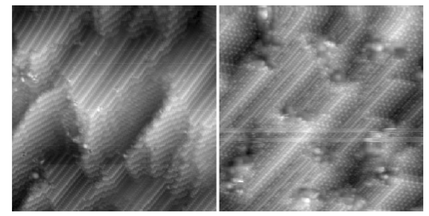


Cu{531}-S



Cu{531}-D

Because the surface is chiral, one can anticipate that a chiral molecule might behave differently on a particular enantiomer of the surface. For example, Cu{531}-S might offer a more suitable binding site for L-alanine than for D-alanine, and *vice versa* on Cu{531}-D. In fact, chiral fcc surfaces are highly prone to atomic-scale roughening, so this picture is too simplistic. However, the flexibility of the Cu{531} surface allows it to restructure to new orientations in the presence of alanine, and ordered structures form on the re-oriented facets. Crucially, the ordered structures seen with L-and D-alanine on Cu{531}-S are not the same: there is clear **enantiospecific restructuring** behaviour. This is potentially a very promising way forward for enantiospecific heterogeneous catalysis [9, 12].



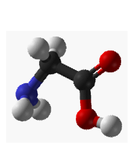
STM images 50 nm x 50 nm

L-alanine on Cu{531}-S

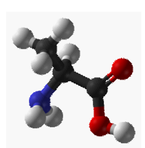
D-alanine on Cu{531}-S

Amino acids on a mirror-symmetric surface: Cu{311}

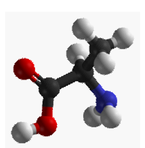
Glycine and alanine are the two simplest amino acids. Each has an amine group, NH_2, and a carboxylic acid group, COOH. Alanine has a methyl group, CH_3, bonded to the backbone C atom. This makes the backbone C atom a chiral centre: alanine exhibits **molecular chirality**. Glycine, by contrast, has two H atoms on the backbone C atom, making it the only achiral amino acid.



glycine



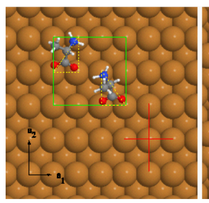
L-alanine



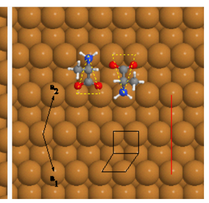
D-alanine

C: grey
N: blue
O: red
H: white

Glycine and alanine bond to Cu surfaces in anionic COO^- form, typically bonding through the amine group and the carboxylate O atoms. On Cu{110} surfaces, this 3-point bonding defines a right-angled triangle which breaks the mirror symmetry of the substrate, leading to **footprint chirality**. Adjacent molecules adopt footprints of opposite chirality. The same behaviour is seen with enantiopure alanine, racemic alanine (an equal mix of L and D), and with glycine [1-8]. Thus there is no strong coupling between molecular chirality and footprint chirality.

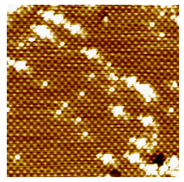


L-alanine on Cu{110}.

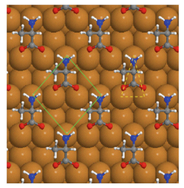


L-alanine on Cu{311}.

Cu{311} has different symmetry to Cu{110} - one mirror plane instead of two - and offers an isosceles triangular bonding site instead of a rectangular one. This subtle change in the surface crystal structure eliminates footprint chirality for 3-point bound amino acids. All molecules are now bound with identical, symmetric footprints, and the same ordered structure is seen for enantiopure alanine, racemic alanine and glycine, irrespective of any molecular chirality [9, 10].



Scanning tunnelling microscope image (20 nm x 20 nm) of ordered layer of 3-point bound glycinate on Cu{311}.



Ordered L-alanine on Cu{311}

If more amino acid molecules are added to Cu{311}, some of them are forced to adopt a 2-point bonding configuration, in which one of the carboxylate O atoms is not bonded to the surface. With enantiopure alanine, high-resolution Scanning tunnelling microscope images reveal a network of linear boundaries whose direction breaks the substrate mirror symmetry. Switching between L- and D-alanine causes the boundaries to switch between the two mirror-equivalent directions [9-11].

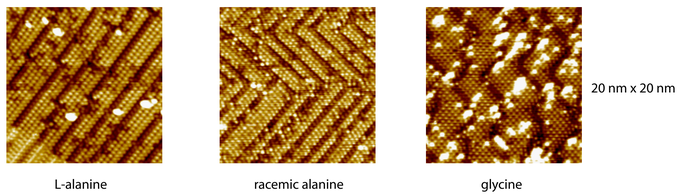
STM images 20 nm x 20 nm

L-alanine

D-alanine

These boundaries exhibit **long-range self-organisational chirality**. The local structure within the boundary is chiral, and this chirality propagates from one pair of neighbouring molecules to the next, causing the chiral boundary orientation to extend over long distances on the surface.

With racemic alanine, domains exhibiting both boundary directions are seen, and the distance over which boundaries propagate in a single direction is considerably shorter. Perhaps surprisingly, chiral boundaries are also seen with glycine, but over much shorter distances again [11].



20 nm x 20 nm

L-alanine

racemic alanine

glycine

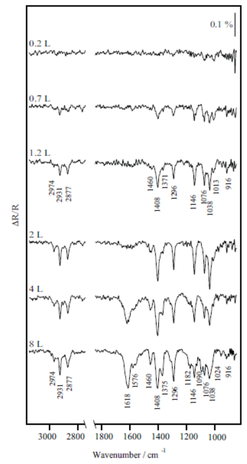
The fact that chiral boundaries are seen with glycine, which has no molecular chirality, means that the local chirality must emerge as a consequence of the molecule-substrate bonding configuration, inter-molecular hydrogen-bonding interactions, and steric interactions between nearest neighbours. The influence of the molecular chirality of alanine is secondary: the presence of the methyl group presumably influences the steric interactions, and its main impact is to increase the boundary lengths.

Determining the bonding

STM images give a great deal of information about surface crystalline structure, but do not directly indicate the bonding configurations - although they may provide important clues.

We determine the bonding from characteristic vibrational 'fingerprints', by means of reflection-absorption infrared spectroscopy (RAIRS). The spectrum at 2 L exposure is characteristic of 3-point binding. In particular, the symmetric O-C-O stretch at 1408 cm^{-1} shows that both carboxylate O atoms occupy essentially identical bonding sites. At higher exposures, by contrast, the new band at 1618 cm^{-1} is the C=O stretch associated with the non-surface-bound O atom of the 2-point binding configuration [10].

To make the band assignments, we performed ab initio calculations within the framework of density functional theory (DFT), then calculated phonon spectra via the finite displacement method [10].



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