

# Reflections on chiral metal surfaces and their potential for catalysis

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## Abstract

Principal possibilities for imparting chirality to a metal surface are surveyed and an attempt is made to assess their potential for heterogeneous asymmetric catalysis. Most possible strategies for creating catalytically active enantiodifferentiating sites on metal surfaces possess inherent limitations concerning potential application in practical asymmetric catalysis. Among the various possibilities known today for bestowing chirality to a metal surface only chiral modification by adsorbed chiral organic molecules (chiral modifiers) has gained practical relevance in catalysis, though its application range is still relatively narrow, confined to asymmetric hydrogenation of C=O and C=C bonds in specific substrates. Opportunities and limitations of this approach are discussed using the enantioselective hydrogenation of ketopantolactone over cinchona-modified platinum as an example.

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## 1. Introduction

The increasing demand of the chemical and pharmaceutical industry for enantiomerically pure compounds has spurred research concerned with their production. A survey by Frost and Sullivan estimates that in 2002 of the \$7 billion in revenues of the global chiral technology market, 55% was generated by traditional technologies (chiral pool and separation), 35% by chemocatalysis, and 10% by biocatalysis. In 2005, the worldwide revenues are projected to increase to \$9.5 billion, indicating the fast growth of this market [1]. Among the various methods applied for production of pure enantiomers [2], catalysis is unique in the sense that with a small amount of optically active catalyst a large quantity of chiral product can be synthesized. In the past years, we have witnessed tremendous progress in homogeneous enantioselective catalysis, culminating in the Nobel Prizes in Chemistry of 2002 awarded to Knowles [3] and Noyori [4] for their work on enantioselective hydrogenation reactions and Sharpless for his work on enantioselective oxidation reactions [5]. A variety of transition metal complexes with chiral ligands have been synthesized

that are powerful working horses in asymmetric synthesis [6].

A comparable development has not taken place in chiral heterogeneous catalysis due to various reasons, the most important being the difficulty to create well-defined catalytically active and stable chiral sites on a solid surface. The creation or preparation of chiral surface structures that combine high catalytic activity and stereochemical control is often biased by geometrical constraints and the intrinsic heterogeneity of surfaces. Nevertheless, the inherent technical advantages connected with catalyst separation, reuse and regeneration, are fostering research in this area. Several comprehensive reviews [7–12] discuss possible strategies for the preparation of heterogeneous enantioselective catalysts. The most obvious strategy is the immobilization of effective chiral transition metal complexes on a suitable support material. Using this “heterogenization” strategy researchers try to merge the advantages of homogeneous with that of heterogeneous catalysis. Various immobilization techniques have been applied embracing simple impregnation, grafting, tethering, and encapsulation. Although these methods have led to remarkable success in some cases, the catalytic performance of the immobilized chiral transition metal complexes is often biased by several factors, such as surface heterogeneity,

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leaching of the active complex, sterical constraints imposed by the surface, and side reactions occurring on the support.

Another strategy that has been pursued is molecular chiral imprinting. Work on imprinted materials such as polymers, amorphous metal oxides and zeolites has been covered in recent reviews [13,14]. However, the practical implementation of catalysts based on molecular chiral imprinting has been hindered by their severe limitations imposed by the intrinsically low number density of active sites, site heterogeneity and possible surface reconstruction under reaction conditions.

Less attention has been devoted so far to the creation of chiral sites on metal surfaces. Here, I consider possible strategies for creating catalytically active enantiodifferentiating sites on metal surfaces and make an attempt to assess their potential for asymmetric catalysis. This assessment is certainly subjective and by no means all-inclusive. In the first part, I will discuss principal possibilities for imparting chirality to metal surfaces. Then the focus is laid on the most successful approach to induce enantiodifferentiation on catalytically active metal surfaces, namely, the chiral modification of metals by adsorbed chiral organic compounds (modifiers). Some characteristic features, opportunities and limitations will be discussed using the enantioselective reduction of ketopantolactone to (*R*)-pantolactone over cinchona-modified platinum as an example.

## 2. Principle possibilities for inducing chirality on metal surface

### 2.1. Chiral metal surfaces that are chiral due to their surface structure

Metals have achiral bulk structures. Supported polycrystalline metal particles, as used in heterogeneous catalysis are normally not perfectly symmetric structures, they contain defects such as kinks, some of which may be chiral. However, in the absence of additional chiral information the number of left- and right-handed kink sites or other chiral structures is equal and consequently the surfaces of such catalyst particles are achiral and do not yield enantiomeric excess.

However, metal surfaces exposing chiral sites of one handedness can be created by cutting metal single crystals along specific planes. McFadden et al. [15] have shown in their pioneering work on silver single crystal surfaces that high Miller index surfaces that expose kinked steps are chiral. They oriented and cut a silver single crystal to expose the Ag(643) on one side and the Ag( $\bar{6}\bar{4}\bar{3}$ ) surface on the other side. The authors proposed a system for naming these surfaces as Ag(643)<sup>R</sup> and Ag(643)<sup>S</sup>, respectively, in analogy with the Cahn–Ingold–Prelog rules used in the nomenclature of organic stereoisomers. Fig. 1a shows how the chirality of this type of surfaces arises from the chiral structure of the

steps and kinks on the example of fcc(643) and fcc( $\bar{6}\bar{4}\bar{3}$ ) surfaces [16]. These surfaces are non-superimposable mirror images of one another and are therefore chiral [17,18].

The chirality of this type was evidenced by the direction of the splitting of the low energy electron diffraction (LEED) spots. In principle, it could be expected that such chiral surfaces exhibit enantiospecific properties in the sense that they interact differently with the two enantiomers of a chiral molecule. Interestingly, in their original work McFadden et al. [15] could not observe any enantiospecificity in the desorption kinetics of the enantiomers of a chiral alcohol ((*R*)-2-butanol and (*S*)-2-butanol) on chiral silver single crystal surfaces by means of TPD. The first indication of enantiospecific properties of chiral single crystal surfaces was provided by Sholl [19] via molecular simulation of the adsorption of chiral hydrocarbons on chiral Pt surfaces. First experimental observations came from electrochemical studies by Attard and co-workers [20,21] who showed that the electro-oxidation of D- and L-glucose on achiral Pt(111) and Pt(211) surfaces did not reveal any enantioselectivity, whereas the chiral Pt(643) and Pt(531) surfaces indicated enantiospecificity in the electro-oxidation kinetics of glucose. More recently, Gellmann et al. [22] added further examples to the growing list of observation of enantiospecificity.

The study of as-prepared chiral surfaces and their interaction with chiral probe molecules is doubtless extremely gratifying because fundamental insight into chiral recognition on a metal surface can be gained that is hardly accessible by any other approach. However, there are a number of arguments, which renders these chiral surface sites probably not applicable to real catalysis. First of all, the population of chiral kinks, which can be created by this method, is far too low for efficient asymmetric catalysis. Consequently, the major part of the metal surface is achiral favoring the corresponding competing racemic reaction. An open question is also the stability of the chiral kinks under real reaction conditions, as used in asymmetric catalysis on metals. It is likely that under such conditions the chiral kinks will reconstruct and lose the chiral information. Finally, another problem that may impede practical application of this approach is the “size mismatch” between the chiral centers and the organic molecules, which may bias chiral recognition.

### 2.2. Selective poisoning of chiral surface sites of specific handedness

Another possibility to impart chiral recognition to an achiral metal surface is the selective poisoning by a strongly adsorbed chiral organic molecule. Such a chiral modifier may interact differently with chiral metal sites of opposite handedness. As a consequence chiral sites of one handedness can be poisoned selectively, leaving the sites with the opposite handedness exposed for the interaction with a reactant. This scenario is illustrated in Fig. 1b [23].

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