Monte Carlo modeling of the enantioselective adsorption of propylene oxide on 1-(1-naphthyl)ethylamine-modified Pt(1 1 1) surfaces

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Abstract

Molecular models are proposed to study the enantioselective adsorption of enantiopure propylene oxide (PO) species on platinum surfaces modified by preadsorption of enantiopure 1-(1-naphthyl)ethylamine (NEA) chiral species. This system has been studied experimentally recently[12], and has been found to present a very complex behavior. In this report we show that the observed behavior cannot be explained simply through pair-wise interactions between adsorbed molecules, but rather requires the consideration of cooperative effects arising in some particular local configurations. Starting from a very simple model, kinetic Monte Carlo simulations were used in order to predict the thermal programmed desorption spectra of PO from template surfaces with different NEA coverages. As these predictions were analyzed, more complex conditions were seen to be necessary for a satisfactory reproduction of experimental data. The final model developed in this work does account for many of the trends observed experimentally in the PO + NEA/Pt(1 1 1) system, but is intended to be only a first step toward the understanding of the complex behavior reported at a molecular level. Throughout the development of our model, it was possible to identify some basic necessary conditions in connection with cooperative effects required to reproduce the experimental data.

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1. Introduction

Chiral molecules are found in two enantiomeric forms, two mirror-image not superimposable structures. The two enantiomers, (R) and (S), of a chiral molecule often have identical chemical and physical properties, but they do display different chemistry when interacting with other chiral elements despite having the same chemical composition. This is of fundamental importance in drug design, since it has been found that, while one enantiomer of a drug may be completely effective for the treatment of a given disease, the other can be very harmful. During the last decade considerable effort has been directed toward developing new methods to obtain enantiomerically pure compounds. Special interest has been manifested in finding heterogeneous chiral catalysis methodology to replace existing homogeneous chiral catalysis processes. Thus, understanding enantioselective adsorption, the first step in heterogeneous chiral catalysis, may be of great relevance to the design of new drug synthesis, in particular if it can lead to selectively produce one of the two enantiomers of a chiral molecule.

There are currently thought to be two main mechanisms by which a chiral adsorbate may modify and impart enantioselectivity to a heterogeneous catalyst:

(a) One-to-one mechanism

One chiral modifier is anchored to a surface in such a way it modifies an adjacent site and imparts enantioselectivity to the adsorption of a reactant molecule via a direct one-to-one modifier–reactant interaction. This kind of mechanism may operate in the case of large chiral modifiers such as cinchonidine [1,2]. The effectiveness in chiral modification in this case is mostly dependent on the molecular characteristics of the individual modifier molecules [3,4].

(b) Template mechanism

In this case the substrate is partially covered by a modifier of a given chirality, say R, forming a structure that act as a “template” [5,6]. This template may present an extended chiral structure that may selectively affect the subsequent adsorption of other prochiral molecules. This kind of mechanism appears to apply to the systems studied in Refs.[7–11].

Given that the precise structural relationship between a templating overlayer and the probe molecules is not yet well understood, advances in the study of the problem can be made by taking
advantage of the fact that the two mechanisms described above should yield different dependencies of enantioselectivity as a function of coverage of the chiral one-to-one modifier or templating species. In particular, enantioselectivity based on the modification of the substrate by chemisorption of a templating chiral species is expected to yield a significant enantioselective excess only in a narrow range of coverage of the templating species [7–11]. There have been recent interesting lattice-gas studies in the literature [13–15] where it has been shown how enantioselectivity of a chiral probe molecule could arise on a substrate with a pattern of strong and weak adsorbing sites. This mechanism may certainly apply in many cases. However, there are other systems, especially those studied experimentally in Refs. [7,10,11], where the cause of enantioselectivity in adsorption cannot be due to a difference in adsorption energy of different sites. In those experiments, one enantiomer of a chiral probe molecule is adsorbed on a surface previously templated via preadsorption of a specific enantiomer, (R) or (S), of another chiral species until reaching saturation. The enantioselectivity of the templated surface in those systems is manifested by differences in yields of adsorption energetics between the two enantiomers, (R) vs. (S), of another chiral probe molecule. The ratio between the desorption yields, for instance \( \text{Yield}_{(R)/(R)} / \text{Yield}_{(R)/(S)} \), reflects the enantioselectivity of the template surface. In these circumstances, a difference in adsorption energy between the (R)/(R) and (R)/(S) pairings would perhaps affect the adsorption kinetics. However, since both enantiomers are adsorbed until saturation is reached, no measurable differences in yield would be expected. Therefore, the behavior of systems like those studied in Refs. [7,10,11] needs to be explained on the basis of a different mechanism.

In the present study we focus on the enantioselective adsorption of propylene oxide (PO) on Pt surfaces modified by the preadsorption of 1-(1-naphthyl)ethylamine (NEA) [12] and propose a number of increasingly more complex models that may serve as a starting point toward a better understanding of the experimental observations at a molecular level.

Some of the key experimental data from thermal programmed desorption (TPD) spectra obtained using both (R)- and (S)-PO, as a probe molecule on Pt(1 1 1) surfaces previously templated with different coverages of (S)-NEA, expressed in Langmuir units, are shown in Figs. 1 and 2 [12]. These include integrated coverages and enantioselectivity data. The behavior seen in these TPD spectra is quite complex: the desorption traces display two well-separated groups of peaks at temperatures around approximately 180 and 210 K, respectively, indicating the presence of two energetically distinct desorption states. One of the most surprising features of these TPD spectra is that, as the NEA coverage on the surface increases steadily, the PO coverage for one of the enantiomers does