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Enantiospecific Desorption of *R*- and *S*-Propylene Oxide from a Chiral Cu(643) Surface

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The creation or preparation of surfaces with chiral structures offers opportunities for enantioselective heterogeneous chemical processing such as catalysis or adsorption. Although such heterogeneous processes may have advantages over their homogeneous counterparts, the development of enantioselective surfaces lags far behind developments in enantioselective homogeneous chemistry. One approach to the preparation of a chiral surfaces is the irreversible adsorption of a chiral molecule on a substrate.[1−3] Such templated surfaces do exhibit enantiospecific properties. This communication describes a type of naturally chiral surface formed by cutting a single crystal, face-centered cubic metal to expose a surface with periodic steps with kinks. We demonstrate enantiospecificity in the kinetics of a well-defined elementary reaction step from such naturally chiral surfaces: molecular desorption of a chiral adsorbate.

Although the bulk face-centered cubic structure has high symmetry and is not chiral, it has been pointed out that that such high Miller index planes do expose chiral surfaces.[4−6] One example is the naturally chiral Cu(643) surface shown in Figure 1. The Cu(643) and Cu(−6,−4,−3) surfaces are nonsuperimposable mirror images of one another and are therefore chiral. These surfaces are denoted Cu(643)^S and Cu(643)^R on the basis of the orientations of the microfacets that comprise the kinks on the surface.[5,7,8] The chirality of this type of surface can be demonstrated using low-energy electron diffraction (LEED) and is described in more detail elsewhere.[4,5] This handedness implies that the two enantiomers of a chiral compound should interact enantiospecifically with such surfaces. We have demonstrated such enantiospecificity by measuring the desorption kinetics of *R*- and *S*-propylene oxide from Cu(643)^R and Cu(643)^S using temperature-programmed desorption (TPD).

The first attempt to observe enantiospecific effects on naturally chiral, high Miller index metal surfaces examined the desorption energies of *R*- and *S*-butan-2-ol from the Ag(643)^R and Ag(643)^S surfaces and the activation barriers to β-hydride elimination for *R*- and *S*-butan-2-oxide on the Ag(643)^R and Ag(643)^S surfaces.[4,5] No enantiospecific differences in kinetics were detected for either of these reactions. If the adsorption of these molecules is influenced by the chirality of the surface, the differences in the desorption energies and the activation barriers must be less than the experimental resolution of ∼0.1 kcal/mol. Later experiments by Attard et al. investigated the electro-oxidation of the D- and L-glucose and other molecules at chiral platinum electrodes.[7−9] Pt(643) and Pt(531) electrodes do exhibit enantiospecific oxidation kinetics for the two enantiomers of glucose. Glucose is a fairly complex molecule with five chiral carbon atoms, and its electrooxidation is a multistep reaction. The experiments described in this communication have made use of a simpler chiral molecule, propylene oxide, with a single chiral center and have focused on the kinetics of a simple elementary reaction step, the desorption of propylene oxides from the Cu(643) surfaces.

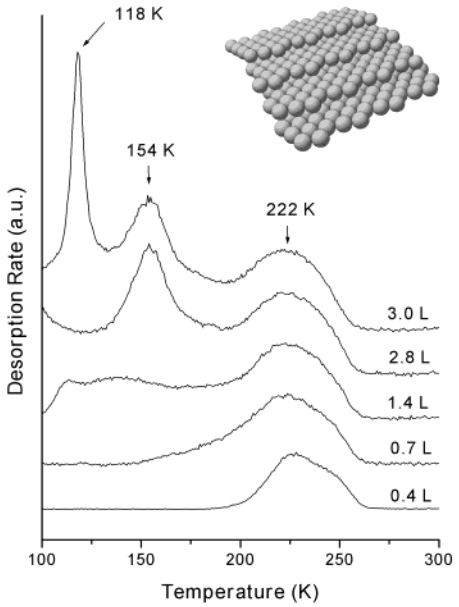

Figure 1. Series of TPD spectra taken following increasing exposures of *R*-propylene oxide to the Cu(643)^R surface. The two highest-temperature peaks (∼222, ∼154 K) correspond to different adsorption states for *R*-propylene oxide on the Cu(643)^R surface, while the low-temperature peak (118 K) corresponds to multilayer desorption. The inset shows the Cu(643)^R surface. The spectra were obtained by monitoring the signal at $m/q = 27$ while heating at 1 K/s.

The experiments were performed in an ultrahigh vacuum chamber in which the surfaces of the Cu single-crystal sample were cleaned and characterized. The Cu(643)^R and Cu(643)^S surfaces were cleaned by cycles of Ar^+ sputtering followed by annealing to 1000 K. The cleanliness of the surfaces was determined by Auger electron spectroscopy and the observation of sharp low-energy electron diffraction patterns.[4−6] The temperature-programmed desorption (TPD) experiment is performed in several steps. Once the surfaces were clean, the propylene oxide was adsorbed by exposure to its vapor with the surface at a temperature of 125 K. A mass spectrometer was then used to measure the rate of desorption during heating at 1 K/s. The mass spectrometer housing is designed to sample desorption from one face of the crystal only. The result of such a TPD experiment is a plot of the propylene oxide desorption rate as a function of temperature.

TPD spectra were acquired for both *R*- and *S*-propylene oxide adsorbed on both Cu(643)^R and Cu(643)^S surfaces. These experiments revealed that the propylene oxide adsorbs and desorbs from the surface reversibly. Figure 1 shows TPD spectra for *R*-propylene oxide on Cu(643)^R following exposures in the range 0.4−3.0 L ($1\ \text{L} = 1.0 \times 10^{-6}$ Torr·sec). As the exposures increased, desorption peaks appeared at 222, 154, and 118 K, sequentially. The lowest-temperature peak did not saturate with

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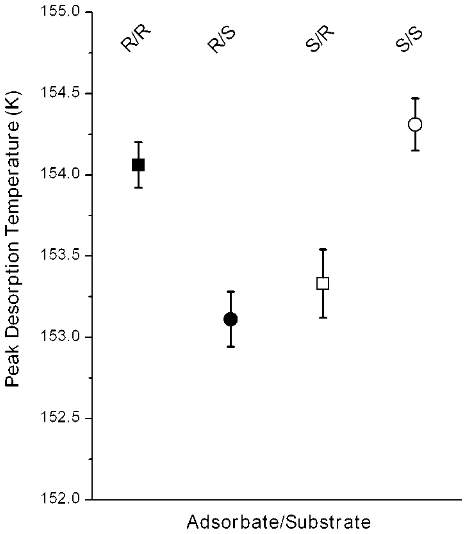

Figure 2. Plot of the average peak desorption temperatures of *R*- and *S*-propylene oxide desorbing from the Cu(643)^R and the Cu(643)^S surfaces. Peak desorption temperatures for *R*-propylene oxide are 1 K higher on the Cu(643)^R surface than on the Cu(643)^S surface. Peak desorption temperatures for *S*-propylene oxide are 1 K lower on the Cu(643)^R surface than on the Cu(643)^S surface. Error bars are given as ± one standard deviation and come from six repetitions of each measurement.

increasing coverage and is due to multilayer desorption. The two higher-temperature peaks became saturated at high exposures and are due to desorption of the monolayer directly bonded to the Cu(643)^R surface. The origin of the difference between the two monolayer peaks is not known at this time; however, the peaks must correspond to different adsorption states on the Cu(643)^R surface. TPD spectra obtained for *R*-propylene oxide on Cu(643)^S and *S*-propylene oxide on Cu(643)^R and Cu(643)^S were similar to those shown in Figure 1.

The TPD experiments were repeated six times for each adsorbate/substrate combination, using coverages of approximately 1 monolayer adsorbed on the Cu(643) surface at 125 K. This adsorption temperature is above the multilayer desorption temperature of 118 K and prevents multilayer adsorption. To determine the peak temperatures most accurately, the maxima have been determined by fitting a Gaussian function through the points lying ±12.5 K from the maximum. Using this approach we have been able to reproduce peak desorption temperatures, T_p, to an accuracy of better than ±0.2 K during six repetitions on each surface. The values of T_p on the Cu(643) surfaces were calculated and averaged for the experiments using each adsorbate/substrate combination. Figure 2 shows the average values of T_p for *R*- and *S*-propylene oxide on Cu(643)^R and Cu(643)^S for each adsorbate/substrate combination. This analysis only considers the mid-temperature peak (~154 K) in the TPD spectra for propylene oxide on the Cu(643) surfaces. *R*-propylene oxide has average values of T_p that are approximately 1 K higher on the Cu(643)^R surface than the Cu(643)^S surface. In contrast, the values of T_p for *S*-propylene oxide are 1 K higher on the Cu(643)^S surface than on the Cu(643)^R surface. The T_p of *R*-propylene oxide on Cu(643)^R match the T_p of *S*-propylene oxide on Cu(643)^S and T_p of *S*-propylene oxide on Cu(643)^R match the T_p of *R*-propylene oxide on Cu(643)^S. These results reveal a true diastereomeric effect and clearly indicate that the desorption of enantiomerically pure propylene oxide from the Cu(643) surface is influenced by the chirality of the surface. These results represent the first observation of molecular desorption kinetics on naturally chiral surfaces that exhibit a diastereomeric effect.

The origin of the two desorption features of the adsorbed monolayer of propylene oxide on the Cu(643) surfaces is not clear at this point. Low-energy electron diffraction did not reveal any ordered superstructures for the propylene oxides on the Cu(643) surfaces. Examination of the structure of the surfaces suggests that the two binding states for the adsorbed molecules might correspond to one species adsorbed at the edge of the step and one that is adsorbed on the (111) terrace. It is tempting to suggest that the state that is occupied at lowest coverage and has T_p = 222 K corresponds to adsorption at the step edge. The less highly coordinated adsorption state is on the (111) terrace and thus has a lower desorption energy and T_p = 154 K. Preliminary experiments on the Cu(111) surface bear out this interpretation. Within the context of this model one would expect the higher-temperature desorption peak to exhibit the greater enantiospecificity. Unfortunately, because of the breadth of this peak it is not possible to measure the peak temperature accurately enough to resolve enantiospecific differences, although we do believe that they exist. One might not expect enantiospecific differences to be observed for desorption from the (111) terraces of the Cu(643) surface; however, it is important to remember that if the molecules desorbing in the peak at 154 K are indeed adsorbed on the terraces, they are adjacent to those molecules already adsorbed at the step edge. The fact that we observe enantiospecificity in the T_p of the desorption feature at ~154 K suggests that the chirality of the steps on the Cu(643) surfaces can be transmitted through the molecules adsorbed at the step edge out to those adsorbed on the (111) terrace.

Finally, the desorption energies of propylene oxide adsorbed on the Cu(643) surface can be estimated from the values of T_p using the Redhead equation.[10] The assumption is that the desorption process is first-order in coverage and that the pre-exponent of the desorption rate constant is $\upsilon = 10^{13}$ sec^{-1}. The desorption energies of the states with T_p of 222 K and 154 K are 58.8 and 40.4 kJ/mol, respectively. More importantly the enantiospecificity in the desorption energies of the two enantiomers desorbing at 154 K is $\Delta\Delta E_{des} = 0.27 \pm 0.06$ kJ/mol. This corresponds to a difference in desorption rates of ~10% at room temperature. Although the desorption energy differences are small for this system, enantioselective processes can be designed to exploit small differences in enantiospecific behavior.

This communication presents the first observation of a true diastereomeric effect in the molecular desorption of a chiral molecule from naturally chiral single-crystal surfaces. Such a result supports previous predictions of such effects based on theory.[11,12] Furthermore, its adds to the existing experimental evidence of enantiospecificity on such surfaces that has been obtained from electrochemical measurements and from measurements of adsorbate orientation using infrared absorption.[6,9]

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