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Probing Enantioselectivity on Chirally Modified Cu(110), Cu(100), and Cu(111) Surfaces†

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Temperature programmed desorption methods have been used to probe the enantioselectivity of achiral Cu(100), Cu(110), and Cu(111) single crystal surfaces modified by chiral organic molecules including amino acids, alcohols, alkoxides, and amino-alcohols. The following combinations of chiral probes and chiral modifiers on Cu surfaces were included in this study: propylene oxide (PO) on L-alanine modified Cu(110), PO on L-alaninol modified Cu(111), PO on 2-butanol modified Cu(111), PO on 2-butoxide modified Cu(100), PO on 2-butoxide modified Cu(111), *R*-3-methylcyclohexanone (*R*-3-MCHO) on 2-butoxide modified Cu(100), and *R*-3-MCHO on 2-butoxide modified Cu(111). In contrast with the fact that these and other chiral probe/modifier systems have exhibited enantioselectivity on Pd(111) and Pt(111) surfaces, none of these probe/modifier/Cu systems exhibit enantioselectivity at either low or high modifier coverages. The nature of the underlying substrate plays a significant role in the mechanism of hydrogen-bonding interactions and could be critical to observing enantioselectivity. While hydrogen-bonding interactions between modifier and probe molecule are believed to induce enantioselectivity on Pd surfaces (Gao, F.; Wang, Y.; Burkholder, L.; Tysoe, W. T. *J. Am. Chem. Soc.* **2007**, *129*, 15240−15249), such critical interactions may be missing on Cu surfaces where hydrogen-bonding interactions are believed to occur between adjacent modifier molecules, enabling them to form clusters or islands.

1. Introduction

There is a tremendous demand for enantiomerically pure chiral compounds in the pharmaceutical and agrochemical industries. Single-enantiomer drugs had worldwide sales of more than $225 billion in 2005 and were poised for further market growth.[1] Because enantiomers have identical physical properties, for example, solubility and boiling point, most synthesis and/or separation processes produce racemic (equimolar) mixtures of the two. The difficulty in producing enantiomerically pure compounds and the fact that enantiomers can exhibit vastly different effects in living organisms have fueled research into the development of chiral surfaces for enantioselective chemical processing such as catalysis and adsorption.

One approach to fabricating chiral surfaces for the production of pure enantiomers is through the adsorption of enantiomerically pure chiral molecules onto achiral surfaces. These chiral modifiers can impart chirality to the achiral surface by a number of means. First, the adsorbed modifiers can self-assemble into an ordered layer to form a "templated chiral surface". For example, adsorption of *R*,*R*-tartaric acid or L-alanine on Cu(110) results in several well-ordered, overlayer structures stabilized by hydrogen bonding and imparting long-range chirality to the achiral Cu(110) surfaces.[2] These supramolecular adlayer structures were reported to contain nanosized chiral spaces at which the underlying metal is exposed. These nanosized chiral spaces are believed to be enantioselective sites at which the reactant molecules can adsorb in a specific asymmetric orientation, forcing subsequent reactions to occur enantioselectively. Even without the long-range chirality imparted by the formation of an ordered modifier overlayer, chirality can be conferred to the surface by the intrinsic chirality of the adsorbed modifier and the consequent asymmetry of adsorption sites in its immediate vicinity. In this case, enantioselectivity arises from the chiral-directing interaction between the adsorbed modifier(s) and an adsorbed reactant molecule. For example, such a one-to-one interaction between methyl pyruvate (reactant) and cinchonidine (modifier) on Pt is one of the possible mechanisms underlying the enantioselective hydrogenation of methyl pyruvate over cinchonidine modified Pt catalysts.[3,4] Adsorption of chiral organic species can also imprint chirality onto an achiral surface by inducing reconstruction of the achiral surface into a naturally chiral structure which exposes kinked step edges. Such an adsorbate-induced reconstruction of achiral surfaces results in the creation of chiral $Cu(3,1,17)^R$ facets by adsorption of L-lysine on Cu(100).[5−7]

The Cu(110) surface modified by adsorbed L-alanine, $CH_3-CH(NH_2)-CO_2H$, is one of the most extensively studied templated chiral surfaces. The local and supramolecular adsorption structures of L-alanine on Cu(110) have been studied by various methods and described in detail in several papers and review articles.[2,8−16] Alanine is found to exist in its anionic form,

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(1) Erb, S. *Pharm. Technol.* **2006**, 14–18.
(2) Raval, R. *CATTECH* **2001**, *5*(1), 12–28.
(3) Baddeley, C. J. *Top. Catal.* **2003**, *25*, 17–28.
(4) Zaera, F. *J. Phys. Chem. C* **2008**, *112*(42), 16196–16203.
(5) Chen, Q.; Richardson, N. V. *Prog. Surf. Sci.* **2003**, *73*, 59–77.
(6) Zhao, X.; Zhao, R. G.; Yang, W. S. *Langmuir* **2000**, *16*, 9812–9818.
(7) Zhao, X. *J. Am. Chem. Soc.* **2000**, *122*, 12584–12585.
(8) Barlow, S. M.; Raval, R. *Surf. Sci. Rep.* **2003**, *50*, 201–341.
(9) Barlow, S. M.; Louafi, S.; Le Roux, D.; Williams, J.; Muryn, C.; Haq, S.; Raval, R. *Langmuir* **2004**, *20*, 7171–7176.
(10) Barlow, S. M.; Louafi, S.; Le Roux, D.; Williams, J.; Muryn, C.; Haq, S.; Raval, R. *Surf. Sci.* **2005**, *590*, 243–263.
(11) Haq, S.; Massey, A.; Moslemzadeh, N.; Robin, A.; Barlow, S. M.; Raval, R. *Langmuir* **2007**, *23*, 10694–10700.
(12) Jones, G.; Jones, L. B.; Thibault-Starzyk, F.; Seddon, E. A.; Raval, R.; Jenkins, S. J.; Held, G. *Surf. Sci.* **2006**, *600*, 1924–1935.
(13) Rankin, R. B.; Sholl, D. S. *Surf. Sci.* **2005**, *574*, L1–L8.
(14) Rankin, R. B.; Sholl, D. S. *J. Phys. Chem. B* **2005**, *109*, 16764–16773.
(15) Sayago, D. I.; Polcik, M.; Nisbet, G.; Lamont, C. L. A.; Woodruff, D. P. *Surf. Sci.* **2005**, *590*, 76–87.
(16) Williams, J.; Haq, S.; Raval, R. *Surf. Sci.* **1996**, *368*, 303–309.

$CH_3-CH(NH_2)-CO_2^-$, and retain its chirality upon adsorption on Cu(110). Depending on coverage, L-alanine is bonded to the surface through the amino N atom and through one or both of its carboxylate O atoms. Annealing the high coverage phase at 430 K leads to a (2,$\bar{2}$;5,3) structure in which clusters of six or eight alanine molecules interact through a network of hydrogen bonding between the N−H and O groups as well as between the C−H and O groups. These alanine clusters are aligned along a low symmetry direction of the Cu(110) surface; thus, they exhibit both local and global chirality. In spite of these extensive studies of the L-alanine modified Cu(110) surface, no one has explored its enantioselective interactions with chiral probe molecules. Hence, in the first part of this paper, we aim to find direct experimental evidence of enantioselective adsorption of a chiral probe molecule on the L-alanine templated Cu(110) surface.

As the alcohol analogue of alanine, the molecule L-alaninol, $CH_3CH(NH_2)CH_2OH$, has also been selected to chirally modify the Cu(111) surface. L-Alaninol is an amino-alcohol with $-NH_2$ and $-OH$ functional groups which are responsible for the bonding to Cu surfaces.[17,18] Similar to the adsorption of L-alanine on Cu(110), L-alaninol has been shown to form two-dimensional homochiral domains on Cu single crystal surfaces.[19,20] The work presented here adds to that work the study of enantioselective adsorption on the L-alaninol modified Cu(111) surface.

The latter part of this paper is motivated by the observation of enantioselective adsorption reported on chirally modified Pd(111) and Pt(111) surfaces.[21−23] Tysoe et al. have used propylene oxide (PO) as a chiral probe molecule to investigate the enantioselectivity of a Pd(111) surface chirally modified by adsorbed *R*- and *S*-butanol and *R*- and *S*-butoxide.[21,22] In this system, some of the 2-butanol molecules convert to 2-butoxide upon heating the Pd sample to 150 K. It has been shown that for a given exposure of *R*-PO to the surface, the coverage of *R*-PO that adsorbs on an *R*-2-butoxide modified surface is higher than that on an *S*-2-butoxide modified surface. This enantioselectivity is only expressed over a narrow range of 2-butoxide coverages, reaching a maximum at a 2-butoxide coverage of 25% of its saturation value on Pd(111). Tysoe et al. previously attributed the observed enantioselective adsorption of PO to chiral "pockets" in the 2-butoxide overlayer on Pd(111). However, they have since reported experimental evidence that the true enantioselective modifier on Pd(111) is 2-butanol with the measured enantioselectivity decreasing with increasing proportion of 2-butoxide on the surface.[24] The observed enantioselectivity was ascribed to the hydrogen-bonding interaction between PO and the −OH group in 2-butanol. Enantioselective adsorption of PO has also been reported on Pd(111) chirally modified by 2-aminobutanoate but it is not observed on a 2-methylbutanoate modified Pd(111) surface.[25] Similar work has also been performed on Pt(111).

Table 1. Matrix of Probe/Modifier/Substrate Used to Study Enantioselective Adsorption on Cu Single Crystal Surfaces

	chiral probe	
chiral modifier	PO	*R*-3-MCHO
L-alanine	(110)	
L-alaninol	(111)	
2-butanol	(111)	
2-butoxide	(100)	(100)
2-butoxide	(111)	(111)

Zaera and Lee[23] have detected enantioselective adsorption of PO on Pt(111) modified by the adsorption of 2-butanol, but to a lesser degree than was found on the modified Pd(111) surface. A similar degree of enantioselectivity was also reported on Pt(111) modified by *S*-2-methylbutanoic acid.[26] The findings on these modifier/metal systems indicate that enantioselectivity depends upon the type of underlying metal substrate.

This paper focuses on assessing the enantioselective properties of several achiral Cu single crystal surfaces modified by different chiral organic molecules in order to provide insight into the roles of the substrate and the modifier in determining enantioselectivity. Temperature programmed desorption (TPD) has been employed successfully to study both the surface chemistry and also the enantioselectivity of chiral surfaces. This can be done, for example, by demonstrating differences in desorption kinetics between *R*- and *S*-enantiomers of a chiral probe molecule from a chiral surface. Equally, TPD can be used to demonstrate enantiospecific differences in the coverages of chiral probe molecules exposed to chirally modified surfaces. The chiral probe molecules used in this work are pure *R*-PO, *S*-PO, and *R*-3-methylcyclohexanone (*R*-3-MCHO). As summarized in Table 1, the following Cu-based systems are included in this study of enantioselective adsorption: PO on L-alanine modified Cu(110), PO on L-alaninol modified Cu(111), PO on 2-butanol modified Cu(111), PO on 2-butoxide modified Cu(100), PO on 2-butoxide modified Cu(111), *R*-3-MCHO on 2-butoxide modified Cu(100), and *R*-3-MCHO on 2-butoxide modified Cu(111).

2. Experimental Section

The experiments were performed in two stainless steel ultrahigh vacuum (UHV) systems with a base pressure of 2×10^{-10} Torr. The chambers were equipped with quadrupole mass spectrometers used to conduct the TPD measurements, ion sputter guns to clean the sample by Ar^+ bombardment, leak valves to admit gases into the chambers, and low energy electron diffraction (LEED) optics to study the structure of clean surfaces and adsorbate overlayers.

L-Alanine (Sigma-Aldrich, $CH_3-CH(NH_2)-CO_2H$, ≥98% purity) was deposited onto the Cu surfaces from an evaporative source consisting of a glass vial which contains the L-alanine powder and is resistively heated by nichrome wire. The deposition rate was controlled by the sublimation temperature which was measured and controlled by a chromel-alumel thermocouple connected to a digital PID-temperature controller (Micromega). Vapors of the other adsorbates were introduced into the UHV chambers through leak valves. Enantiomerically pure and racemic PO (Alfa Aesar, C_3H_6O, 99%), L-alaninol (Sigma-Aldrich, $CH_3-CH(NH_2)-CH_2-OH$, 98%), *R*-3-MCHO (Sigma-Aldrich, $CH_3-C_6H_9=O$, 98%), and *S*- and *R*-2-butanol (Sigma-Aldrich, $C_4H_{10}O$, 99%) were first transferred to clean glass vials and subjected to multiple freeze−pump−thaw cycles to remove air, water vapor, and other high vapor pressure impurities. The purity of each chemical was verified by mass spectrometry before use. The relatively high vapor pressure of these chemicals at room

(17) Gori, P.; Contini, G.; Prosperi, T.; Catone, D.; Turchini, S.; Zema, N.; Palma, A. *J. Phys. Chem. B* **2008**, *112*, 3963–3970.
(18) Gori, P.; Contini, G.; Prosperi, T.; Ronci, F.; Colonna, S.; Zema, N.; Turchini, S.; Catone, D.; Cricenti, A.; Palma, A. *Superlattices Microstruct.* **2009**, *46*, 52–58.
(19) Irrera, S.; Contini, G.; Zema, N.; Turchini, S.; Sanna, S.; Moras, P.; Crotti, C.; Prosperi, T. *Surf. Sci.* **2007**, *601*, 2562–2565.
(20) Irrera, S.; Contini, G.; Zema, N.; Turchini, S.; Fujii, J.; Sanna, S.; Prosperi, T. *J. Phys. Chem. B* **2007**, *111*, 7478–7480.
(21) Stacchiola, D.; Burkholder, L.; Tysoe, W. T. *J. Mol. Catal. A: Chem.* **2004**, *216*, 215–221.
(22) Stacchiola, D.; Burkholder, L.; Tysoe, W. T. *J. Am. Chem. Soc.* **2002**, *124*, 8984–8989.
(23) Lee, I.; Zaera, F. *J. Phys. Chem. B* **2005**, *109*, 12920–12926.
(24) Gao, F.; Wang, Y.; Burkholder, L.; Tysoe, W. T. *J. Am. Chem. Soc.* **2007**, *129*, 15240–15249.
(25) Stacchiola, D.; Burkholder, L.; Zheng, T.; Weinert, M.; Tysoe, W. T. *J. Phys. Chem. B* **2005**, *109*, 851–856.
(26) Lee, I.; Zaera, F. *J. Am. Chem. Soc.* **2006**, *128*, 8890–8898.

temperature allowed exposure of the Cu sample surface to each chemical by admitting its vapor into the UHV chamber through a leak valve while measuring the pressure with the ion gauge. Background exposures were done when the sample was placed in a position that had no line of sight to the leak valve. Direct exposures were done with the use of a dosing tube inside the chamber connected to the leak valve. The sample could be placed ~5 mm away from the end of this dosing tube to achieve higher coverages for any given pressure−time exposure. The dosing tubes provided an enhancement factor of 50 times the background exposure. Exposures are reported in units of Langmuirs (L) where $1\ L = 10^{-6}$ Torr·s.

The Cu(110), Cu(111), and Cu(100) single crystal disks of approximately 1 cm diameter were used as substrates for adsorption of modifier molecules followed by coadsorption of chiral probes. Each Cu sample was spot-welded between two Ta wires mounted to a sample holder at the bottom of a manipulator, and could be resistively heated to >1000 K and cooled to <100 K using liquid nitrogen. The sample temperature was measured with a chromel-alumel thermocouple, spot-welded to the edge of the Cu sample via a thin strip of Ni foil.

Each Cu sample was cleaned by repeated cycles of 1 keV Ar^+ ion sputtering while annealing at 750 K for 500 s. The sample was then cooled at a controlled rate of −1 K/s, until the clean surface yielded a sharp LEED pattern. Following adsorption of the desired compound(s) at an appropriate adsorption temperature, TPD measurements were performed by heating the sample at a constant heating rate while the species desorbing from the surface were monitored using the mass spectrometer. TPD spectra were obtained by positioning the samples within ~5 mm of the aperture to a Feulner cap that shrouded the mass spectrometers. Desorption peak temperatures were obtained directly from the TPD spectra, while desorption yields were measured from the integrated desorption peak areas. The long-range order of the L-alanine overlayer was monitored using LEED after exposing the clean Cu(110) surface to L-alanine for the required exposure time and annealing to a desired temperature.

Argon gas (Matheson, 99.995% purity) and oxygen gas (Linde, 99.995% purity) were taken from high pressure lecture bottles. The purity of each gas was verified by mass spectrometry before use.

3. Results

3.1. Enantioselective Adsorption of PO on L-Alanine Modified Cu(110). *3.1.1. Adsorption of L-Alanine on Cu(110).* Prior to studying enantioselectivity, it was necessary to characterize the adsorption of the L-alanine modifier on the achiral Cu(110) surface. The desorption and decomposition of L-alanine on the Cu(110) surface were studied by TPD. To prepare for the TPD experiments, the clean Cu(110) surface was cooled to 180 K and then exposed to L-alanine vapor sublimed at 348 K. The signals at various mass-to-charge ratios (m/q = 15, 18, 27, 28, 42, 43, 44, and 74) were monitored with the mass spectrometer while the sample was heated at 1 K/s. These m/q ratios were selected based on the result of a TPD experiment in which signals at all m/q values from 1 to 90 were monitored during L-alanine desorption from Cu(110). Figure 1A shows the TPD spectrum recorded following an exposure of the Cu(110) surface to L-alanine for 1000 s. Displayed adjacent to the desorption peaks in Figure 1A are the two insets which capture the change in each desorption feature with L-alanine exposure times ranging from 20 to 1000 s. Only the signal at m/q = 44 is shown in these plots, as it has the highest intensity in the fragmentation pattern of L-alanine. Note that the fragmentation pattern of L-alanine was determined by desorption of thick multilayers (>20 monolayers) at a low heating rate of 0.5 K/s (data not shown). After the highest L-alanine exposure, desorption peaks were observed at 307, 327, and 519 K in Figure 1A. As shown in the high temperature inset, at the lowest L-alanine coverage, there is a single desorption feature at ~491 K which grows in intensity and shifts to higher temperature as the exposure increases. The peak saturates at an exposure of 300 s, before the appearance of desorption peaks at 307 K at higher exposure time (>300 s) and then at 327 K at even higher exposures (>500 s) as shown in the low temperature inset. The peak at 327 K did not saturate with increasing exposures and hence was attributed to desorption of L-alanine multilayers.

As mentioned above, the desorption peak at 519 K shown in the high temperature inset of Figure 1A saturates at L-alanine exposures >300 s and is, therefore, attributed to desorption from the first L-alanine layer on Cu(110) and is a result of either L-alanine desorption or thermal decomposition. In this regard, we found that the fragmentation pattern of the peak at 519 K did not match that of L-alanine, indicating that this peak is not attributable to desorption of intact L-alanine. This suggests that the L-alanine molecules are stable to temperatures up to 470 K before undergoing thermal decomposition on the surface and desorbing as decomposition products. In addition, it is evident from the high temperature inset of Figure 1A that small changes in exposure lead to significant shifts of ~30 K in the decomposition temperature over exposure times ranging from 50 to 200 s.

After sputtering and prior to adsorption, the surface ordering of the Cu sample was examined by LEED. The Cu(110) lattice consists of a rectangular array of atoms and gives a rectangular LEED pattern. Following exposure to L-alanine for 300 s to form a saturated monolayer, the Cu(110) surface was positioned in front of the LEED optics. During adsorption, L-alanine was sublimed at 348 K while the Cu(110) surface was held at 180 K. Immediately after adsorption, a LEED image of an L-alanine saturated Cu(110) surface was taken without annealing the surface. No new spots were observed in the LEED image obtained for this unannealed system, indicating a lack of long-range order in the overlayer as deposited at 180 K.

When the LEED experiment was conducted after annealing the L-alanine saturated Cu(110) surface at 400 K for 5 min, the LEED image shown in Figure 2A with a real space unit cell of $(2,\bar{2};5,3)$. Annealing this $(2,\bar{2};5,3)$ overlayer at 460 K for 5−10 min changed the LEED pattern into a (3×2) structure (Figure 2B). These results are consistent with those reported by Raval et al.[9,10] We then repeated the experiments in reverse order by first annealing the L-alanine-saturated Cu(110) surface at 460 K and then at 400 K. As expected, the (3×2) phase appeared after the surface was annealed at 460 K for 5−10 min; however, the $(2,\bar{2};5,3)$ homochiral phase did not reappear after the surface was annealed at 400 K. Instead, the (3×2) phase remained on the surface. These results are consistent with the L-alanine in its ionic form being stable on the Cu(110) surface to temperatures of 460 K.

LEED experiments were also conducted on Cu(110) with lower than saturation L-alanine coverages. No additional spots apart from the Cu(110) substrate unit cell were observed in the LEED image taken after exposing the clean surface to L-alanine for 125 s and annealing at 460 K. When the surface was annealed at 400 K instead, the LEED image in Figure 2C was observed showing faint and diffuse but visible additional spots which were similar to those in the $(2,\bar{2};5,3)$ structure observed in Figure 2A.

3.1.2. Adsorption of PO on Cu(110) and on L-Alanine Modified Cu(110). Each of the L-alanine/Cu(110) phases described above was exposed to *S*- and *R*-PO in order to probe their enantioselectivity for PO adsorption. The TPD spectra of PO on clean Cu(110) shown in Figure 1B reveal that the saturated PO monolayer on Cu(110) desorbs with a peak temperature of 159 K, whereas the PO multilayer desorbs with a peak

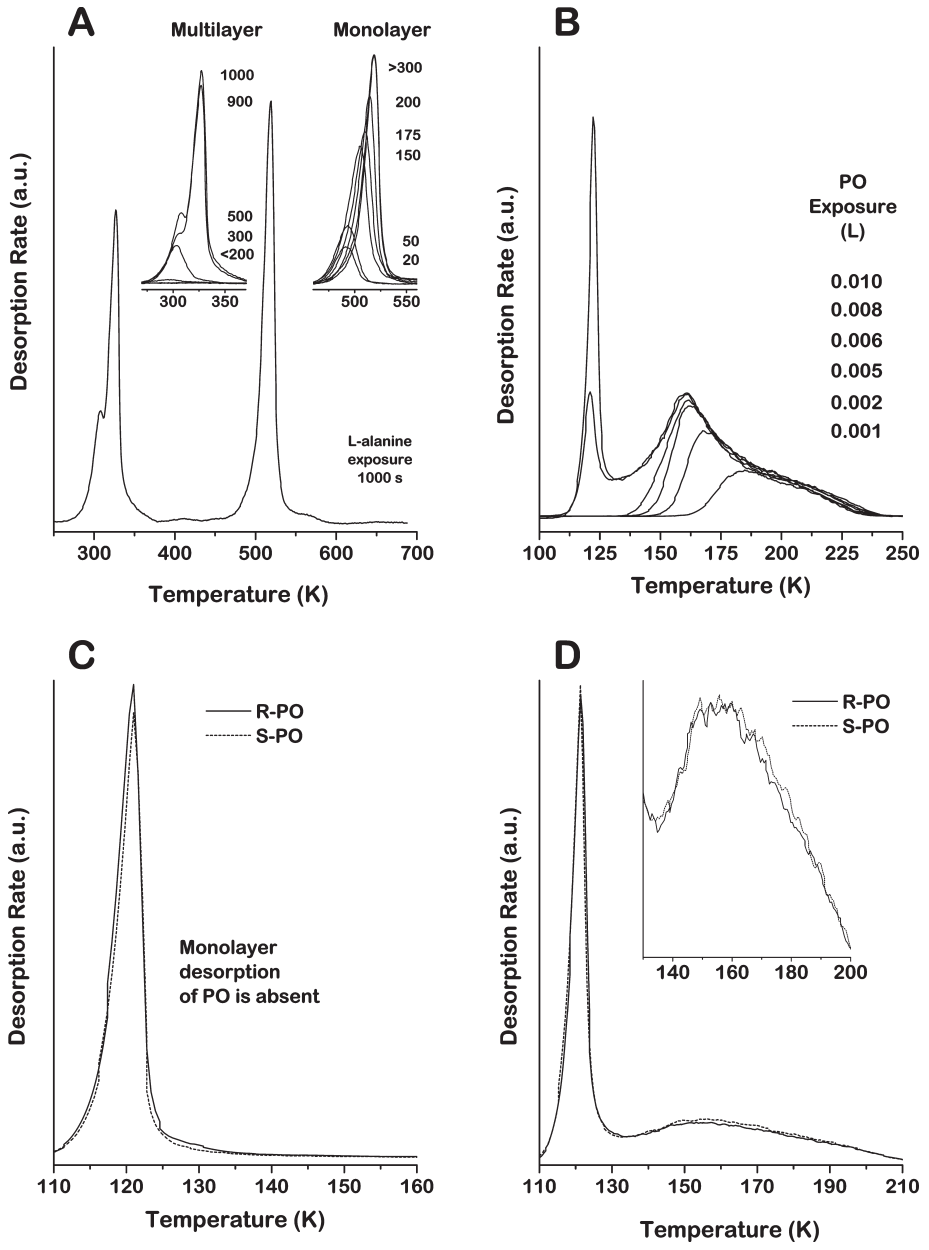

Figure 1. TPD measurements on the L-alanine modified Cu(110) surface. (A) TPD spectra of L-alanine from the Cu(110) surface following exposure to L-alanine at 180 K for 1000 s using the evaporative doser. The insets show the monolayer and multilayer growth of L-alanine on the Cu(110) surface for exposure times from 20 to 1000 s. The desorption features at 490−520 K arise from decomposition of the L-alanine monolayer. The monolayer saturates in coverage at an exposure of 300 s. The features at 300−330 K arise from molecular desorption of L-alanine from the multilayer and do not saturate with increasing exposure. Signal was collected at $m/q = 44$ using a heating rate of 1 K/s. (B) TPD of PO from clean Cu(110) following increasing exposures to PO from 0.001 to 0.01 L using a doser. Monolayer desorption occurs over the temperature range 160−210 K. Multilayer desorption occurs at 121 K. The monolayer saturates in coverage at an exposure of 0.006 L. No decomposition of PO was observed. (C) TPD of PO from the chiral (2,$\bar{2}$;5,3) phase of L-alanine/Cu(110) following a 0.006 L exposure to *R*- or *S*-PO at 95 K. Desorption occurred at the multilayer desorption temperature of 121 K for both *R*- and *S*-PO. The yield of both enantiomers was identical. (D) TPD of PO from the Cu(110) surface annealed at 400 K for 5 min following exposure to L-alanine for 125 s (yielding a submonolayer coverage) and a 0.006 L exposure to *R*- or *S*-PO. PO desorbs from the bare regions of the Cu(110) surface at 160 K and from the L-alanine layer at 121 K. The inset shows only the monolayer desorption of *R*- and *S*-PO from this L-alanine/Cu(110) surface. The two TPD traces overlap one another, indicating that there is no enantiospecificity to the adsorption of PO. TPD spectra of PO were collected at a heating rate of 1 K/s while monitoring the signal at $m/q = 58$.

temperature of 121 K. No decomposition of PO was observed as a result of heating during TPD experiments. Using the doser, a PO exposure of 0.006 L was sufficient to saturate the clean Cu(110) surface with a monolayer of PO. In order to study PO desorption from the L-alanine modified Cu(110) surface, the (2,$\bar{2}$;5,3) phase was prepared at 400 K. The surface was then cooled to 95 K, followed by exposure to 0.006 L PO and a TPD experiment. Figure 1C shows that the peak associated with desorption of PO from the underlying Cu surface was absent in the TPD spectrum. The presence of the high alanine coverage needed to create the globally chiral (2,$\bar{2}$;5,3) phase on Cu(110) leaves no spaces for PO to adsorb directly onto the Cu surface. The single peak at 121 K in the TPD spectra of Figure 1C which corresponds to the desorption of *S*- and *R*-PO multilayers does not show any enantiospecific difference in their desorption temperatures. The amount of *R*-PO desorbing from the (2,$\bar{2}$;5,3) phase is also equal to the

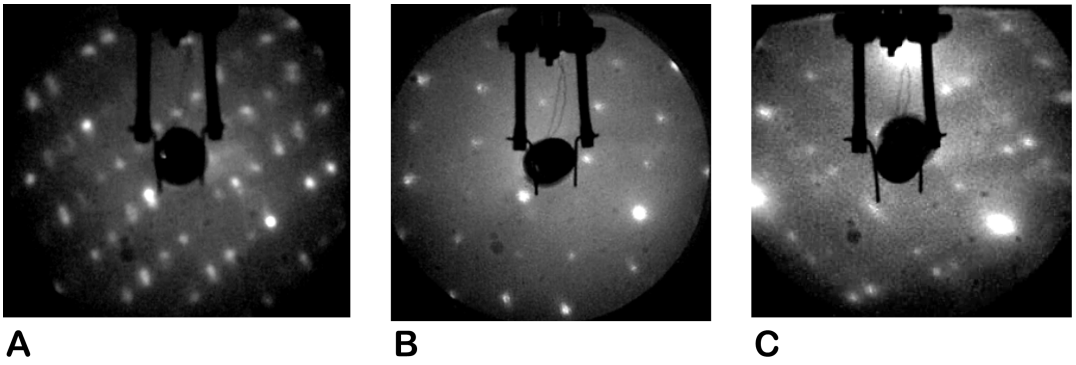

Figure 2. LEED patterns obtained for L-alanine/Cu(110) at different exposures and annealing temperatures (beam energy = 52 eV). (A) LEED pattern of the homochiral (2,$\bar{2}$;5,3) phase, created by exposing the Cu(110) surface to L-alanine for 400 s and annealing the overlayer at 400 K for 5 min. (B) LEED pattern of the (3 × 2) phase, created with an L-alanine exposure time of 400 s and an annealing temperature of 460 K for 5 min. This phase also appeared when the surface in (A) was subsequently annealed at 460 K for 5 min. (C) LEED pattern obtained after exposing the Cu(110) surface to L-alanine for 125 s followed by annealing at 400 K for 5 min. This LEED image showed weak but visible additional spots which were strikingly similar to that in the (2,$\bar{2}$;5,3) structure in (A). This result suggests that, upon annealing this lower-coverage phase at 400 K, the L-alanine molecules adsorb on Cu(110) in clusters or islands in which the L-alanine molecules adopt the same arrangement as in the (2,$\bar{2}$;5,3) phase.

amount of *S*-PO desorbing. Therefore, PO exhibits no sign of enantiospecific behavior on the (2,$\bar{2}$;5,3) homochiral phase of the L-alanine/Cu(110) system. Similar observations were made when *S*- and *R*-PO were adsorbed onto the stable (3 × 2) phase created by annealing the L-alanine saturated Cu(110) system at 460 K. The structure of the (3 × 2) phase does not allow interaction of adsorbed PO with the Cu substrate and does not interact enantiospecifically with either *R*- or *S*-PO.

The enantioselectivity of the PO/L-alanine/Cu(110) system was probed further by using lower L-alanine coverages. The exposure of Cu(110) to L-alanine was decreased to 125 s such that the monolayer desorption peak of PO became observable. This L-alanine covered Cu(110) surface was annealed at 400 K, followed by the adsorption of enantiomerically pure PO. Figure 1D shows the TPD spectra of *R*- and *S*-PO from this alanine modified Cu(110) surface. It is obvious from these TPD spectra that the desorption temperatures and the desorption yields of *R*- and *S*-PO from the underlying Cu atoms are identical. The coverage of *R*-PO adsorbing on this L-alanine covered surface was identical to that of *S*-PO adsorbing on the same surface. This again indicates that there is no experimentally detectable enantioselectivity in the adsorption of PO on alanine modified Cu(110) surfaces. Likewise, enantioselectivity was not detected on the modified surfaces created using a subsaturation L-alanine exposure of 125 s followed by annealing at 460 K or by using an L-alanine exposure of 175 s followed by annealing at 400 K.

3.2. Enantioselective Adsorption of PO on L-Alaninol Modified Cu(111). *3.2.1. Adsorption of L-Alaninol on Cu(111).* Adsorption of the alcohol analogue of alanine, alaninol, was studied on Cu(111). The surface was first cooled to < 100 K and then exposed to L-alaninol using the leak valve to introduce the vapor into the chamber. The desorption of L-alaninol was then studied using TPD experiments. Such an experiment was repeated for background exposures to L-alaninol vapor varying from 0.05 to 1.5 L. Shown in Figure 3A are the coverage dependent TPD spectra of L-alaninol obtained from Cu(111) by monitoring the signal at $m/q = 44$. A large desorption peak was detected at ~260 K. The intensity of this peak increases with exposure without a significant shift in its maximum and nearly saturates at an exposure of ~1.5 L, at which point another narrow peak at ~200 K becomes dominant and does not saturate with increasing exposures. Based on the shape and behavior of these peaks, the peak at 260 K is attributed to desorption of L-alaninol from the first monolayer while the zero-order desorption feature at 200 K is typical of multilayer desorption. In addition, a higher-temperature desorption peak is present at ~380 K. This peak saturates at an exposure of ~0.9 L and is likely due to desorption of decomposition products of an irreversibly adsorbed fraction of the adsorbed L-alaninol.

3.2.2. Adsorption of PO on L-Alaninol Modified Cu(111). The desorption of *R*- and *S*-PO from the L-alaninol modified Cu(111) surface was studied to probe enantioselectivity over a range of modifier coverages. Note that the desorption of PO from clean Cu(111) is similar to that from Cu(110) (shown in Figure 1B) except that the monolayer desorption temperature is 140 K on Cu(111) as opposed to 159 K on Cu(110). TPD measurements were obtained after coadsorption of enantiomerically pure PO and L-alaninol on the Cu(111) surface. Figure 3B presents the TPD spectra of *R*-PO desorbing from Cu(111) modified with varying coverages of L-alaninol. Similar TPD spectra were obtained for the desorption of *S*-PO from L-alaninol covered Cu(111). As the L-alaninol modifier coverage is increased, PO is displaced from the Cu surface and desorbs at a temperature similar to that of the PO multilayer desorption. The available sites for adsorption of PO on the Cu(111) surfaces are blocked as the surface is modified by increasing coverages of L-alaninol modifier. At an L-alaninol exposure of 0.45 L, desorption of PO from the exposed Cu(111) surface becomes undetectable.

From the integrated desorption peak areas in the TPD spectra of Figure 3B, one can measure the coverages of *R*- or *S*-PO adsorbed in the monolayer on the L-alaninol modified Cu(111) surface. These amounts are denoted as θ_L^R and θ_L^S, where the superscript represents the handedness of the PO probe molecule and the subscript represents the handedness of the L-alaninol modifier. The enantioselectivity ratio, $ER = \theta_L^R/\theta_L^S$, is a measure of enantioselectivity on chirally modified surfaces, and it has been used successfully in previous studies of enantioselective adsorption.[21−26] When ER is different from unity, the chirally modified surface can be said to exhibit enantioselectivity. Enantioselectivity does not exist when ER = 1. On the L-alaninol/Cu(111) surface, the integrated monolayer desorption peak areas of *R*-PO (θ_L^R) and *S*-PO (θ_L^S) were calculated over a range of L-alaninol coverages. The ER is plotted in Figure 3C as a function of L-alaninol coverage on Cu(111). It is evident that the values of ER, as shown in Figure 3C, are constant and are close to ER = 1 over the range of L-alaninol coverages studied. In addition, the desorption peak

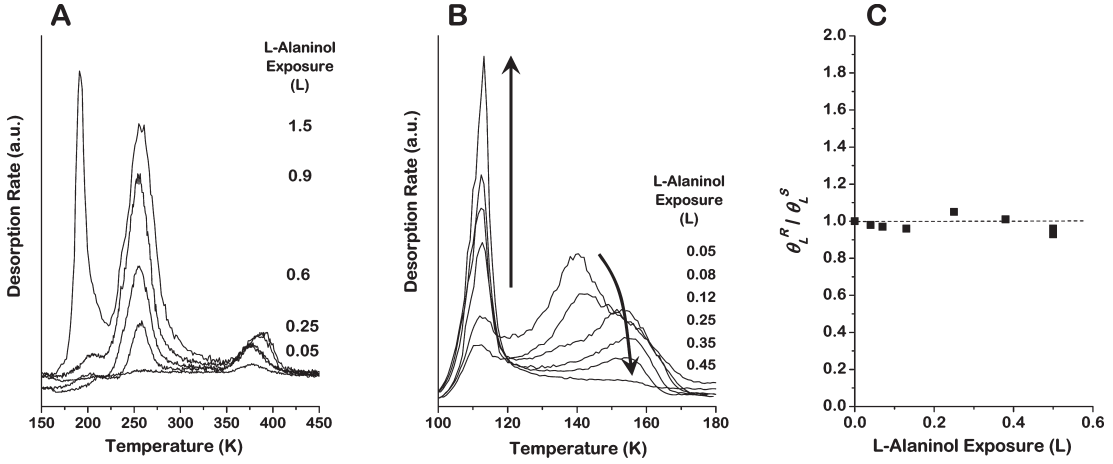

Figure 3. TPD measurements on the L-alaninol modified Cu(111) surface. (A) Desorption of L-alaninol from the Cu(111) surface at various exposures. The L-alaninol monolayer desorbs at 260 K and saturates at an exposure of ~1.5 L. Multilayer desorption occurs at 200 K. The small peak at 380 K is attributed to the product of alaninoxide decomposition by β-hydride elimination on Cu(111). Signal was collected at $m/q = 44$ using a heating rate of 2 K/s. (B) TPD spectra of *R*-PO from the Cu(111) surface chirally modified by various L-alaninol coverages. The *R*-PO exposure of 0.5 L at 95 K was sufficient to saturate the monolayer on the clean Cu(111) surface. As the modifier coverage is increased, the peak associated with monolayer desorption of *R*-PO (140−160 K) decreases in intensity while the peak associated with multilayer desorption (110 K) increases. L-Alaninol blocks sites for PO adsorption. Virtually no PO adsorbs in the monolayer at an L-alaninol exposure of 0.45 L. TPD spectra were collected while monitoring the signal at $m/q = 58$ while heating the surface at 2 K/s. (C) Enantioselectivity ratio of *R*-PO to *S*-PO coverage in the monolayer, ER = θ_L^R/θ_L^S, when adsorbed on L-alaninol modified Cu(111) versus L-alaninol exposure. The ER was found to be unity at all modifier exposures, indicating no enantioselective adsorption.

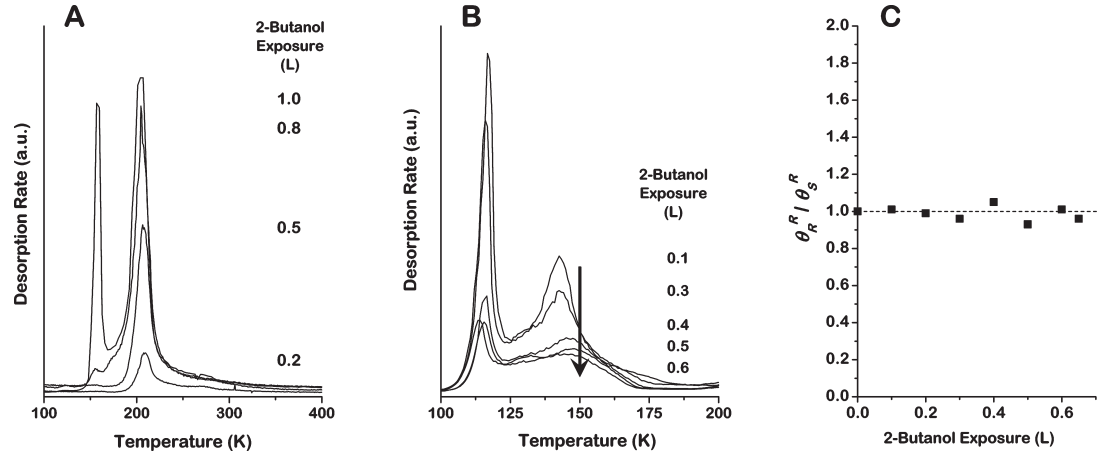

Figure 4. TPD measurements on the 2-butanol modified Cu(111) surface. (A) TPD spectra of *S*-2-butanol on the achiral Cu(111) following increasing exposure to *S*-2-butanol from 0.2 to 1.0 L. The desorption peaks at 160 and 205 K are assigned to the multilayer and monolayer desorption of *S*-2-butanol, respectively. Signal was collected at $m/q = 45$ using a heating rate of 2 K/s. (B) Desorption of *R*-PO from the Cu(111) surface chirally modified by various coverages of *S*-2-butanol. The peak associated with desorption of the *R*-PO monolayer (140 K) decreases in intensity with increasing 2-butanol coverage. In these experiments, a range of PO exposures from 0.4 to 1.0 L was used as the PO exposure was decreased for each increased *S*-2-butanol exposure such that the monolayer desorption peak of PO would not be overwhelmed by the strong signal of multilayer desorption peak. (C) Enantioselectivity ratio of the *R*-PO coverages on *R*- or *S*-2-butanol modified Cu(111), ER = θ_R^R/θ_S^R, versus the initial 2-butanol exposure. No enantioselective adsorption was observed as ER $\approx$ 1 at any modifier exposure.

temperatures of the *R*-PO and *S*-PO monolayers are the same at all coverages of L-alaninol on Cu(111). Similar to the L-alanine templated Cu(110) surface, no enantioselective adsorption of PO was found for the L-alaninol/Cu(111) system.

3.3. Enantioselective Adsorption of PO on 2-Butanol Modified Cu(111). *3.3.1. Adsorption of 2-Butanol on Cu(111).* The adsorption of *R*- and *S*-2-butanol on surfaces such as Pd(111) and Pt(111) has been shown to yield chirally modified surfaces that exhibit enantioselective adsorption of *R*- and *S*-PO.[21−24] Here, the surface chemistry of 2-butanol was studied on the clean Cu(111) surface. Various background exposures of 2-butanol (0.2−1.0 L) were used to modify the Cu(111) surface at an adsorption temperature of < 100 K. Figure 4A displays the TPD spectra of *S*-2-butanol on the clean Cu(111) surface obtained for various initial coverages. The major peak at ~205 K can be easily identified as the monolayer desorption peak of 2-butanol molecules from Cu(111), while the narrow peak at ~160 K is due to the desorption of 2-butanol multilayers. On the clean Cu(111) surface, the alcohol monolayer desorbs reversibly. No decomposition of 2-butanol was found on this surface.

3.3.2. Adsorption of PO on 2-Butanol Modified Cu(111). To probe enantioselectivity, enantiomerically pure PO was adsorbed on Cu(111) modified with varying coverages of *R*- or *S*-2-butanol. Figure 4B shows the TPD spectra of *R*-PO desorbing from Cu(111) modified by different coverages of *S*-2-butanol. The monolayer desorption temperature of *R*-PO from the

S-2-butanol/Cu(111) surface remains identical to that from the clean Cu(111) surface, ~140 K. As expected, one can see from Figure 4B that the amount of PO adsorbed in the monolayer decreases with increasing coverage of *S*-2-butanol on the Cu(111) surface. Similar TPD spectra were also obtained for desorption of *R*-PO from Cu(111) modified by different coverages of *R*-2-butanol.

The ratio of the monolayer desorption yield of *R*-PO from *R*-2-butanol/Cu(111) to that from *S*-2-butanol/Cu(111) was calculated and denoted as the enantioselective ratio ER = θ_R^R/θ_S^R. Figure 4C shows ER plotted against the 2-butanol exposure. The values of the ER, as shown in Figure 4C, do not differ significantly from unity regardless of the 2-butanol modifier coverage. This indicates no enantioselective adsorption of PO on the 2-butanol modified Cu(111) surface.

3.4. Enantioselective Adsorption of PO on 2-Butoxide Modified Cu(100) and Cu(111). *3.4.1. Adsorption of 2-Butoxide on Cu(100).* Before creating 2-butoxide species as the modifier, adsorption of 2-butanol was first studied on the clean Cu(100) surface. The 2-butanol desorption features from Cu(100) are very similar to those from Cu(111) shown in Figure 4A except that the monolayer desorbs at 220 K on Cu(100) and that an additional small peak is present at ~360 K which is attributed to the desorption of methylethyl ketone arising from β-hydride elimination of a 2-butoxide species. A desorption peak similar to this peak at 360 K was also observed for the L-alaninol/Cu(111) surface at 380 K, as shown in Figure 3A. This result is in good agreement with prior studies of short chain alcohols on clean Cu(100), Cu(110), and Cu(111) surfaces.[27−30] Hence, on the clean Cu(100) surface, the major fraction of the alcohol monolayer desorbs reversibly. A small fraction of the adsorbed alcohol deprotonates to yield alkoxide species that decompose by β-hydride elimination to yield aldehydes or ketones at higher temperatures. If the surface is preoxidized prior to adsorption of the alcohol, then all of the alcohol is deprotonated on the surface to yield alkoxides.

In order to create a Cu(100) surface with a high coverage of 2-butoxide species, we first preoxidized the surface. It is known that adsorption of small alcohols on an oxygen covered Cu(100) or Cu(110) surface results in the formation of alkoxides and water.[27−30] For 2-butanol reacting on an oxygen covered Cu(100) surface, a preadsorbed O atom on the surface first attacks the hydroxyl proton of 2-butanol and generates 2-butoxide and a OH group. The OH group reacts with another 2-butanol to generate another 2-butoxide and water. Water then desorbs from the Cu surface at temperatures in the range 150−180 K while the 2-butoxide species remains on the surface and is stable to ~360 K.

Based on this mechanism, the experiments to create 2-butoxide species on Cu(100) were designed as follows. First, the Cu(100) surface was exposed to varying amounts of oxygen at 470 K.[28] After cooling the surface to 100 K, 2-butanol was then adsorbed in an amount greater the stoichiometric amount needed to react with the oxygen atoms on the surface. During heating, the adsorbed oxygen and 2-butanol generate 2-butoxide species. The surface was then heated to 300 K to desorb the water and excess 2-butanol to ensure that 2-butoxide species were the only species remaining on the surface. Figure 5A shows the set of TPD spectra collected for the desorption of methylethyl ketone generated by 2-butoxide decomposition on Cu(100) covered with different initial amounts of adsorbed oxygen. From Figure 5A, one can see that the amount of oxygen initially adsorbed on Cu(100) determines the amount of 2-butoxide created on the surface. An O_2 exposure of 3 L at 470 K is sufficient to maximize the coverage of 2-butoxide on the Cu(100) surface.

3.4.2. Adsorption of PO on 2-Butoxide Modified Cu(100). Enantioselective adsorption of pure *R*- or *S*-PO was studied on the 2-butoxide modified Cu(100) surface. *R*-PO was allowed to adsorb on the Cu(100) surface modified with various coverages of *R*- or *S*-2-butoxide. Figure 5B shows the TPD spectra of *R*-PO desorbing from Cu(100) modified by different coverages of *S*-2-butoxide. These various coverages of *S*-2-butoxide species were generated by exposing *S*-2-butanol to the Cu(100) surface covered by different amounts of preadsorbed oxygen and subsequently heating the surface at 300 K to desorb excess 2-butanol and water. The monolayer desorption temperature of *R*-PO from the 2-butoxide/Cu(100) surface is almost the same as that from the clean Cu(100) surface, that is, at 150 K. As expected, the amount of PO adsorbed in the monolayer decreases with increasing coverage of 2-butoxide on the Cu(100) surface. The TPD spectra acquired for desorption of *R*-PO from Cu(100) modified by different coverages of *R*-2-butoxide species were qualitatively similar to those in Figure 5B.

The TPD spectra of *R*-PO from 2-butoxide/Cu(100) were used to estimate the monolayer desorption yields of *R*-PO from both the *S*-2-butoxide and *R*-2-butoxide modified Cu(100) surfaces. The ratio ER = θ_R^R/θ_S^R was then plotted for each *R*- or *S*-2-butoxide coverage as shown in Figure 5C. The coverage of 2-butoxide generated on the surface is roughly proportional to the amount of preadsorbed oxygen on the Cu(100) surface prior to 2-butanol exposure. The amount of 2-butoxide species on Cu(100) saturates at an oxygen exposure of 3 L, indicating that the maximum amount of 2-butoxide that can be created on the surface has been reached. Most importantly, Figure 5C shows that ER = 1, regardless of the 2-butoxide modifier coverage. The same observations were made for *S*-PO on the *R*- and *S*-2-butoxide modified Cu(100) surfaces (data not shown). Once again, we noticed that ER = θ_R^S/θ_S^S = 1 over the entire range of 2-butoxide coverages on the surface. Furthermore, there were no observable enantiospecific differences in the PO desorption temperatures. The finding that $\theta_R^R/\theta_S^R = \theta_R^S/\theta_S^S$ = 1 indicates that there is no enantioselective adsorption of PO on the 2-butoxide modified Cu(100) surface.

3.4.3. Adsorption of PO on 2-Butoxide Modified Cu(111). For comparison with prior observations of enantiospecific adsorption on Pt(111) and Pd(111),[21−23] we turned our investigation to study the 2-butoxide modified Cu(111) surface, thereby exploring the role of substrate structure on enantioselective adsorption. The procedure for creating 2-butoxide on Cu(111) was almost identical to that for creating 2-butoxide on Cu(100) except that the temperature for preoxidizing the surface was 600 K on Cu(111), higher than the temperature of 470 K used on Cu(100).[29,30] The decomposition of the 2-butoxide modifier on Cu(111) is very similar to that on Cu(100) shown in Figure 5A, except that methylethyl ketone desorbs from Cu(111) at slightly lower temperature of ~340 K. Following preparation of *R*-2-butoxide modifier layers at different coverages on Cu(111), enantiomerically pure *R*- or *S*-PO was adsorbed on the surface at low temperature and PO TPD spectra were obtained. The desorption yields of *R*- and *S*-PO adsorbed on the *R*-2-butoxide/Cu(111) surface were used to calculate ER = θ_R^R/θ_R^S for PO on the *R*-2-butoxide/Cu(111) system. Figure 5D shows that the values of ER did not deviate from unity over

(27) Bowker, M.; Madix, R. J. *Surf. Sci.* **1982**, *116*, 549–572.
(28) Dai, Q.; Gellman, A. J. *J. Phys. Chem.* **1993**, *97*, 10783–10789.
(29) Gellman, A. J.; Buelow, M. T.; Street, S. C.; Morton, T. H. *J. Phys. Chem. A* **2000**, *104*(11), 2476–2485.
(30) Gellman, A. J.; Dai, Q. *J. Am. Chem. Soc.* **1993**, *115*(2), 714–722.

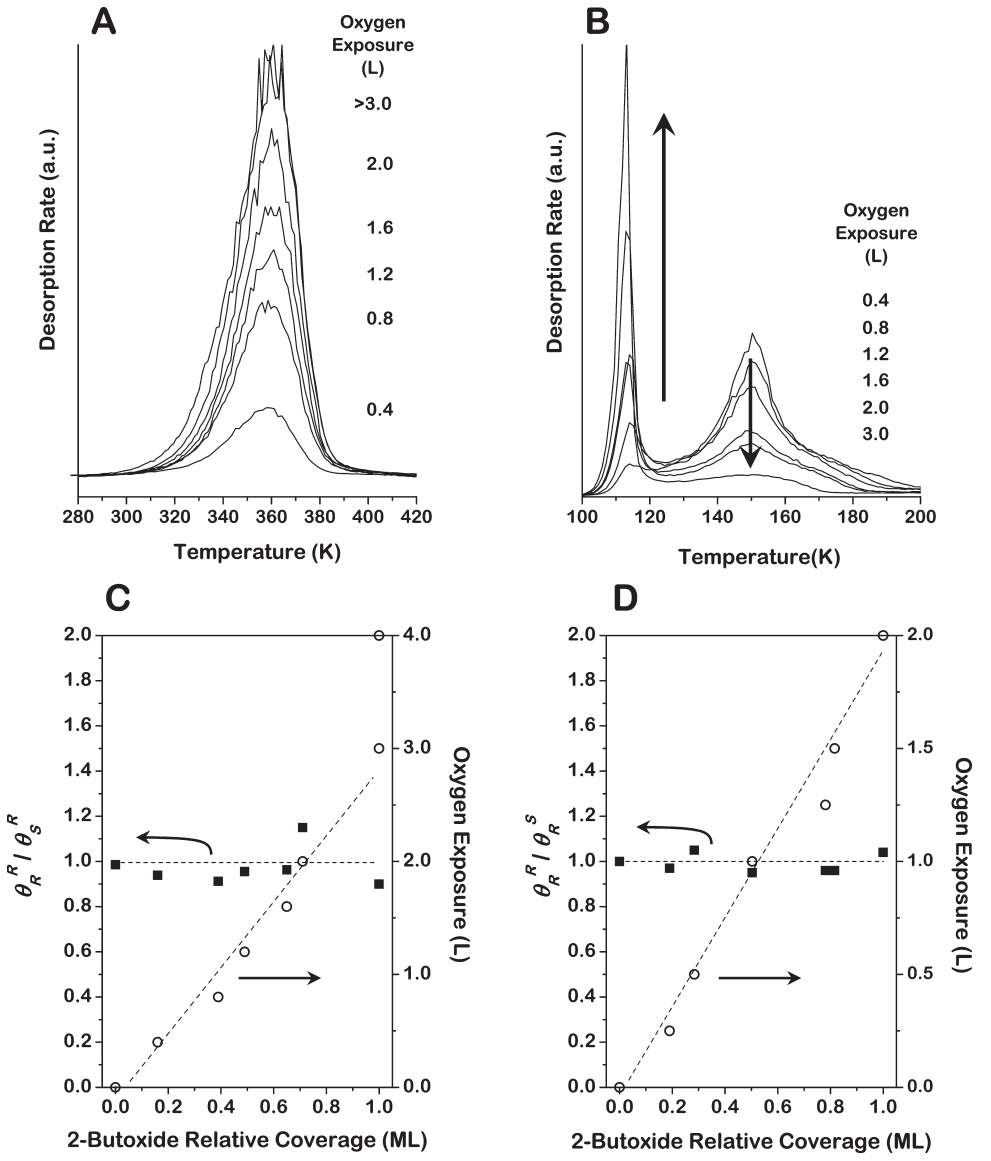

Figure 5. TPD measurements of the 2-butoxide modified Cu(100) surface using PO as the chiral probe. (A) TPD spectra of methylethyl ketone produced by β-hydride elimination of *S*-2-butoxide species on the Cu(100) surface. The initial coverage of the *S*-2-butoxide species was varied by preoxidizing the Cu(100) surface at 470 K with varying exposures to O_2 followed by a saturation exposure of *S*-2-butanol. An O_2 exposure of 3 L at 470 K is sufficient to saturate the Cu(100) surface with *S*-2-butoxide. TPD spectra were collected by monitoring the signal at $m/q = 43$ while heating the surface at 2 K/s. (B) TPD spectra of *R*-PO after an exposure of 0.5 L from the Cu(100) surface chirally modified by various coverages of *S*-2-butoxide. The Cu(100) surface was preoxidized with different amounts of oxygen and then exposed to *S*-2-butanol to generate *S*-2-butoxide species. The peak associated with desorption of the *R*-PO monolayer (150 K) decreases in intensity with increasing 2-butoxide coverage. The intensity of the peak associated with multilayer PO desorption increases with increasing 2-butoxide coverage. Desorption of PO from the monolayer is completely blocked at an *S*-2-butoxide coverage corresponding to a 3 L exposure of oxygen. The signal at $m/q = 58$ was monitored and a heating rate of 2 K/s was used during the TPD experiments. (C) Plot of ER (■, left axis) and oxygen exposure (○, right axis) versus 2-butoxide relative coverage in monolayer (ML), using PO as the probe molecule on the 2-butoxide modified Cu(100) surface. θ_R^R/θ_S^R is the ratio of the amounts of *R*-PO monolayer desorbed from the *R*-2-butoxide and *S*-2-butoxide modified Cu(100) surface. (D) Same plot as (C) but using the Cu(111) surface as the underlying substrate. The 2-butoxide coverage is proportional to the oxygen exposure prior to saturation of 2-butoxide. The value of ER = 1 on both surfaces indicates that there is no enantioselective adsorption of PO on either surface.

the range of *R*-2-butoxide coverages investigated. No enantioselective adsorption of PO was detected in the PO/2-butoxide/Cu(111) system.

3.5. Enantioselective Adsorption of *R*-3-MCHO on 2-Butoxide Modified Cu(100) and Cu(111). *3.5.1. Adsorption of R-3-MCHO on Cu(100).* Selection of the chiral probe molecule has been proven to be critical to the experimental observation of enantioselective adsorption on chiral surfaces.[31,32] This is especially true for chirally modified surfaces on which the chiral probe interacts with both the substrate and the adsorbed modifier. To extend the effort to observe enantioselective adsorption on Cu surfaces, *R*-3-MCHO was also used as a chiral probe in our search for enantioselective adsorption on the 2-butoxide modified Cu surfaces. More importantly, *R*-3-MCHO was chosen for our study because it has a higher adsorption energy than PO on Cu and was found to exhibit higher enantiospecificity than PO on the naturally chiral Cu(643) surface.[31]

(31) Horvath, J. D.; Gellman, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 2384–2392.
(32) Horvath, J. D.; Gellman, A. J. *Top. Catal.* **2003**, *25*(1−4), 9–15.

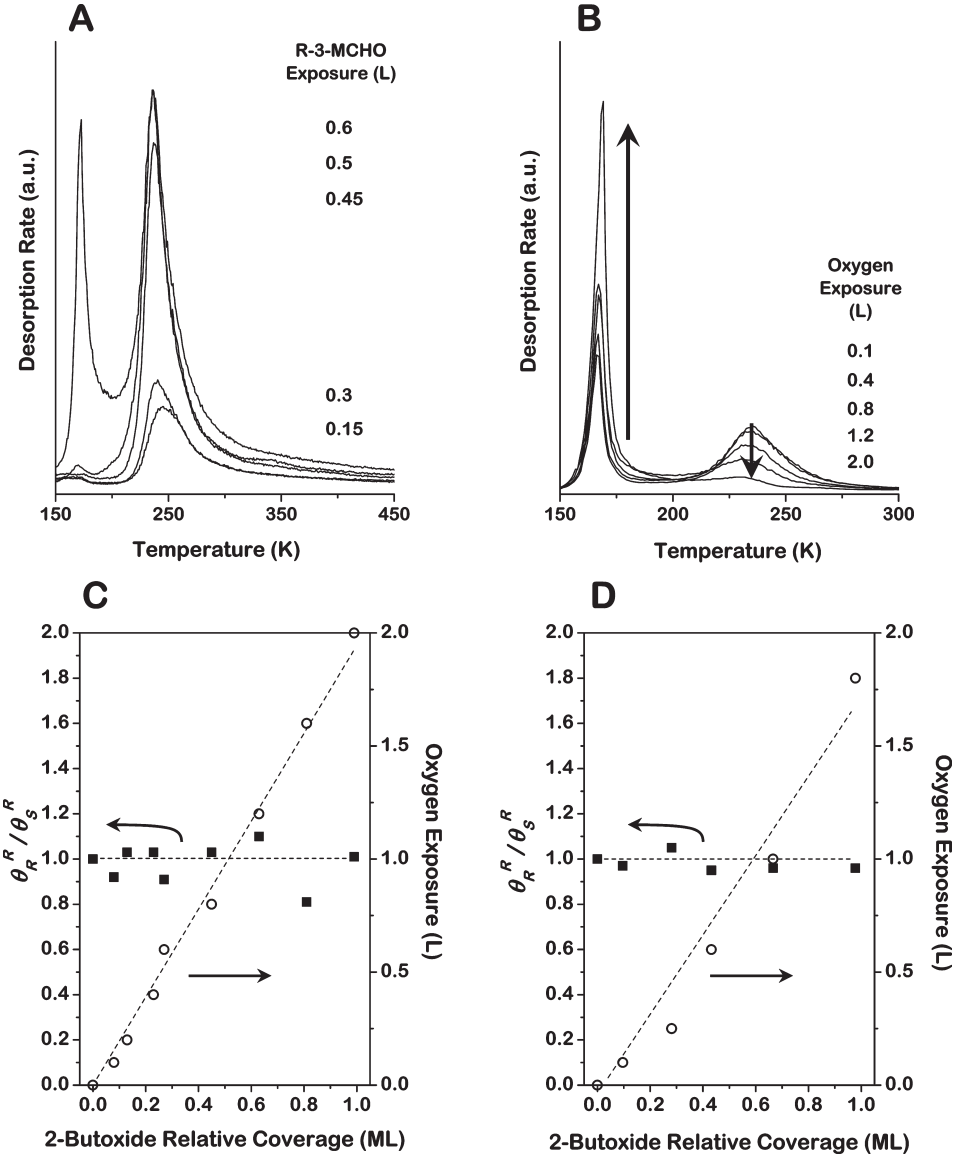

Figure 6. TPD measurements of the 2-butoxide modified Cu(100) surface using *R*-3-MCHO as the chiral probe. (A) TPD spectra of *R*-3-MCHO from the clean Cu(100) surface at varying initial coverages of *R*-3-MCHO. The peaks at 170 and 240 K are assigned to multilayer and monolayer desorption of *R*-3-MCHO, respectively. The signal at $m/q = 55$ was monitored while heating at a rate of 2 K/s. (B) TPD spectra of *R*-3-MCHO from the *R*-2-butoxide modified Cu(100) surface following an *R*-3-MCHO exposure of 0.6 L. The amount of *R*-3-MCHO desorbing from the monolayer decreases with increasing initial coverage of *R*-2-butoxide. At the saturation *R*-2-butoxide coverage generated by preoxidation of the Cu(100) surface with a 2 L exposure of O_2 at 470 K, all of the *R*-3MCHO desorbs from the multilayer. (C) Plot of ER (■, left axis) and oxygen exposure (○, right axis) versus 2-butoxide relative coverage. ER $= \theta_R^R/\theta_S^R$ is the ratio of the amount of *R*-3-MCHO monolayer desorbed from the *R*- and *S*-2-butoxide modified Cu(100) surfaces. (D) Plot of ER and oxygen exposure versus 2-butoxide relative coverage, using *R*-3-MCHO as the probe molecule on the 2-butoxide modified Cu(111) surface. The value of ER = 1 on both surfaces indicates that there is no enantioselective adsorption of *R*-3-MCHO on either surface.

The adsorption of *R*-3-MCHO on the clean Cu(100) surface was studied before performing the coadsorption experiments of *R*-3-MCHO with 2-butoxide. Figure 6A displays the TPD spectra of *R*-3-MCHO on Cu(100) at various initial coverages. At low exposures, there is a single desorption peak of *R*-3-MCHO from the submonolayer at ~245 K. This peak shifts to slightly lower temperatures as the exposure increases. The *R*-3-MCHO monolayer then saturates at an exposure of about 0.5 L before the appearance of multilayer desorption at 170 K.

3.5.2. Adsorption of R-3-MCHO on 2-Butoxide Modified Cu(100). TPD spectra were obtained for *R*-3-MCHO on Cu(100) modified by varying coverages of *R*- or *S*-2-butoxide. The TPD results for *R*-3-MCHO desorbing from the *R*-2-butoxide/Cu(100) surface are shown in Figure 6B. As the coverage of the *R*-2-butoxide modifier increases, the coverage of *R*-3-MCHO in the monolayer decreases. From these spectra, we calculated the integrated yields for the *R*-3-MCHO monolayer desorption peak as a function of *R*-2-butoxide coverage. The same experiments were performed for *R*-3-MCHO desorbing from the *S*-2-butoxide/Cu(100) surface (data not shown). The enantioselective ratio ER $= \theta_R^R/\theta_S^R$ determined from the monolayer desorption yield of *R*-3-MCHO from *R*-2-butoxide/Cu(100) and *S*-2-butoxide/Cu(100) was calculated for each 2-butoxide coverage, and the results are plotted in Figure 6C. This plot clearly indicates that there is no observable enantioselective adsorption of *R*-3-MCHO on the 2-butoxide modified Cu(100) surface; the values of ER are approxiametly unity over the entire range of 2-butoxide coverages.

3.5.3. Adsorption of R-3-MCHO on 2-Butoxide Modified Cu(111). The enantioselective adsorption of *R*-3-MCHO was also studied on the 2-butoxide modified Cu(111) surface. TPD spectra of *R*-3-MCHO from the clean Cu(111) surface were obtained before the coadsorption experiments, and were found to resemble those obtained from the Cu(100) surface (Figure 6A) except that the *R*-3-MCHO monolayer desorbed at a lower temperature (~225 K) from Cu(111) than from Cu(100). This result was in very good agreement with prior studies of the desorption of *R*-3-MCHO from Cu(111).[31]

For a range of *R*- and *S*-2-butoxide coverages on Cu(111), TPD spectra of *R*-3-MCHO were collected and used to calculate the monolayer desorption yields of *R*-3-MCHO from the *R*-2-butoxide/Cu(111) surface (θ_R^R) and from the *S*-2-butoxide/Cu(111) surface (θ_S^R). The values of ER = θ_R^R/θ_S^R over the range of 2-butoxide coverages on Cu(111) are plotted in Figure 6D. This plot clearly shows that the values of ER do not differ significantly from unity over a range of 2-butoxide coverages. Therefore, the 2-butoxide modified Cu(111) surface does not exhibit enantioselective adsorption of *R*-3-MCHO.

4. Discussion

On Cu(110), the surface chemistry of L-alanine modifier molecules was studied by TPD. At temperatures below 470 K, alanine molecules remain intact on Cu(110) and are believed to be in the anionic form.[10,11,16] All adsorbed L-alanine molecules begin to decompose at 470 K, resulting in the formation of CO_2 as the major decomposition product. As shown in the enlarged plot of the monolayer decomposition peak in the high temperature inset of Figure 1A, this peak continuously shifts to higher temperatures with small changes in exposure time between 50 and 200 s. This is because, at low alanine coverages, the functional groups tend to interact directly with the surface. At higher coverage, the alanine molecules are more closely packed together, adopting a more upright stance with fewer functional groups bonded to the surface. This is consistent with the previous finding that at low coverage alanine is bonded to the surface with the two carboxylate O atoms and the amino N atom, but that at high coverage it is adsorbed with only one carboxylate O atom and the amino N atom.[8−12,16] Decomposition requires the presence of an empty site into which the initial decomposition fragment can bind prior to desorption. The shift of the monolayer decomposition peak in Figure 1A to high temperature with increasing L-alanine coverage is consistent with explosive decomposition kinetics which require the existence of empty sites in order for decomposition to be initiated.[33,34] In addition, the two lower-temperature desorption peaks (307 and 327 K in the low temperature inset of Figure 1A) were found to have fragmentation patterns identical to the fragmentation pattern of alanine, indicating that both desorption features in the multilayer regime indeed resulted from desorption of alanine and not from other species or any decomposed products. The origin of this two-peak feature in the multilayer desorption was not fully explored, because in this investigation of enantioselectivity the alanine modifier layers were created with exposure times of < 400 s and annealing temperatures of > 400 K at which alanine multilayers did not form. TPD results provided two important pieces of information that are useful to our subsequent LEED and enantioselectivity studies: the exposure time (~300 s) required to saturate the surface with L-alanine as well as the maximum temperature (~470 K) to which the sample could be annealed without desorbing and decomposing the adsorbed alanine.

Annealing the Cu(110) surface saturated with L-alanine at 400 K and at 460 K resulted in the formation of the (2,$\bar{2}$;5,3) and (3 × 2) phases, respectively (Figure 2A and B). Raval et al. reported a lower local coverage of L-alanine on the (3 × 2) phase than on the (2,$\bar{2}$;5,3) phase.[10] It was, therefore, very likely that some alanine molecules desorbed during the transformation from the (2,$\bar{2}$;5,3) to the (3 × 2) overlayer structures when the surface was heated from 400 to 460 K. This was supported by our observation that the formation of (2,$\bar{2}$;5,3) was irreversible as the (3 × 2) phase remained on the surface when we first annealed the L-alanine-saturated Cu(110) surface at 460 K and then at 400 K. Both of these ordered overlayer structures were then subjected to the adsorption of *S*- and *R*-PO to observe enantioselectivity. The absence of the monolayer desorption peak of PO in Figure 1C suggests that the chiral spaces observed by Raval et al.[9,10] in the (2,$\bar{2}$;5,3) superstructure are not large enough to accommodate adsorption of PO directly onto the Cu(110) surface. The slightly reduced local coverage of L-alanine molecules arranged in the (3 × 2) structure did not add sufficient void spaces to allow PO adsorption directly onto the Cu(110) surface. The (3 × 2) structure of L-alanine on the Cu(110) surface has been studied using density functional theory (DFT) modeling.[13,14] The alanine adsorbs in the deprotonated form with the carboxylate group interacting with two adjacent atoms in a close packed row on the Cu(110) surface and the amine interacting with a Cu atom in an adjacent parallel row. The (3 × 2) unit cell contains two alanine molecules, and visual inspection of the overlayer structures predicted by DFT suggests that there is insufficient room in the unit cell for adsorption of PO onto the Cu(110) substrate. This is entirely consistent with our observation that PO adsorbs only on the alanine overlayer, thus hindering our effort to probe enantioselectivity.

We did not detect any enantioselective difference in the desorption behavior of *S*- and *R*-PO from the Cu(110) with a low coverage of L-alanine created by adsorbing for 125 s and annealing the surface at 400 K (Figure 1D). In fact, the corresponding LEED image taken for this surface (Figure 2C) provided a rationale for the observed lack of enantioselectivity. The weak (2,$\bar{2}$;5,3) LEED pattern shown in Figure 2C suggested that at low coverage the L-alanine molecules were formed islands upon annealing at 400 K, and within the island the L-alanine molecules were arranged in the same way as they were in the (2,$\bar{2}$;5,3) homochiral phase. Hence, no adsorption of PO on the underlying Cu atoms was allowed within the island because the chiral spaces within the unit cell of the (2,$\bar{2}$;5,3) structure were found to be too small to accommodate any PO molecules. PO was therefore believed to adsorb on the bare Cu atoms exposed by the spaces between the islands where few or no L-alanine modifiers were present. Without the alanine modifier, no enantiospecific interaction was expected between the enantiomerically pure PO and the achiral Cu(110) surface. Therefore, the L-alanine/Cu(110) system did not reveal any enantioselective properties.

Enantioselective studies were extended to other achiral Cu surfaces modified by alkoxides and alcohols. Chiral 2-butoxide was used as the modifier on both Cu(100) and Cu(111) surfaces. The 2-butoxide species were created by adsorbing chiral 2-butanol onto the preoxidized Cu(100) and Cu(111) surfaces. Note that the structures of the substrate as well as the oxygen adsorption temperature have pronounced effects on the oxygen reactivity in the dehydrogenation of adsorbed alcohols. The optimum adsorption temperatures for oxygen found in our experiments were 600 K on Cu(111) but 470 K on Cu(100).[28−30] The 2-butoxide

(33) Bowker, M.; Morgan, C.; Zhdanov, V. P. *Phys. Chem. Chem. Phys.* **2007**, *9* (42), 5700–5703.
(34) Aas, N.; Bowker, M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*(8), 1249–1255.

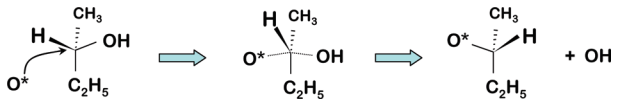

Figure 7. Schematic of an adsorbed oxygen atom (label O*) reaction with 2-butanol via the S_N2 mechanism. This reaction could invert the chirality of the resulting 2-butoxide when the O* atom replaces the original oxygen atom in the −OH group from the opposite site. If a subsequent 2-butanol were to then deprotonate by reaction with the OH group, this would effectively racemize the 2-butanol during formation of the 2-butoxide overlayer.

covered Cu(100) and Cu(111) surfaces were then subjected to adsorption of chiral PO to observe enantioselectivity. Neither plot of enantioselective ratios in Figure 5C and D manifests any enantioselective adsorption of PO on Cu(100) and Cu(111), over a range of 2-butoxide modifier coverages. Changing the chiral probe from PO to *R*-3-MCHO did not induce enantioselectivity on these surfaces, as shown in Figure 6C and D. Hence, no enantioselective behavior was found for the 2-butoxide modified Cu(100) and Cu(111) systems.

Enantiospecific interactions between PO and 2-butoxide have been observed on Pd(111) and Pt(111) surfaces.[22−24] One obvious difference between those experiments and ours conducted on Cu surfaces is the need for preadsorbed oxygen atoms on Cu to deprotonate adsorbed 2-butanol. It is possible that the reaction between adsorbed oxygen atoms and 2-butanol molecules to form the 2-butoxide may eliminate the intrinsic chirality of the 2-butanol molecule, if the reaction follows a S_N2 mechanism illustrated in Figure 7. In Figure 7, if the adsorbed oxygen atom (labelled O*) replaces the original oxygen atom in the 2-butanol hydroxyl group from the opposite site, the handedness of the 2-butanol molecule may be inverted. The first step of the overall reaction, in which an *R*-2-butanol molecule reacts with an adsorbed oxygen atom and forms an *S*-2-butoxide plus an OH^- group, is presented as

$$R^ROH + O^* \rightarrow R^SO^* + OH^-$$

In the second step of the reaction, the OH^- group generated in step 1 will react with another *R*-2-butanol molecule to form an *R*-2-butoxide and water:

$$R^ROH + OH^- \rightarrow R^RO + H_2O$$

The net reaction is

$$2R^ROH + O^* \rightarrow R^RO + R^SO^* + H_2O$$

One can clearly see from the net reaction that if the adsorbed *R*-2-butanol reacts with adsorbed oxygen via the S_N2 mechanism, a mixture consisting of equal amounts of *R*-2-butoxide and *S*-2-butoxide will be formed. This would effectively racemize the surface modifier species, which could explain the observed lack of enantioselectivity when using 2-butoxide as the chiral modifier.

In order to determine whether the reaction between adsorbed oxygen and 2-butanol molecules occurs by the S_N2 mechanism, $^{18}O_2$ was adsorbed onto the Cu(111) surface to react with 2-butanol. If the reaction occurs by the S_N2 mechanism, the water desorbing from Cu(111) would be $H_2{}^{16}O$. However, our TPD measurements (data not shown) indicated that the desorbing water was indeed $H_2{}^{18}O$. This suggested that the reaction did not follow the S_N2 mechanism and that the chirality of the 2-butoxide species was not lost. This result is consistent with prior studies of the mechanism of oxygen induced deprotonation of smaller alcohols on Ag and Cu surfaces.

Our study of the adsorption of PO on 2-butanol and 2-butoxide modified Cu(100) and Cu(111) surfaces reveals no enantioselectivity. From an experimental standpoint, the nice feature of the Cu surfaces is that they allow preparation of the overlayers such that one has either 2-butanol or 2-butoxide as the modifier. Prior studies of the adsorption of PO in 2-butanol modified Pd(111) are complicated by the fact that the modifier can exist in both 2-butanol and 2-butoxide forms simultaneously. Gao et al.[24] were able to eliminate the presence of the 2-butanol on Pd(111) and show that the enantioselectivity was not observed in the presence of just 2-butoxide. On the basis of this observation, they suggested that the presence of the −OH bonds in the 2-butanol is necessary for the enantioselective adsorption of PO. Of course, our observations indicate that the presence of the −OH group is not sufficient to yield enantioselective adsorption of PO on either the Cu(100) or Cu(111) surface. The origin of the difference must lie in the details of the structure and properties of the 2-butanol overlayer on Cu versus Pd(111) surfaces. It is important to note that, even in the case of 2-butanol on the Pd(111) surfaces, enantioselective adsorption of PO is only observed in a narrow coverage range about 0.25 of a monolayer (fraction of saturation coverage). Thus, even coverage dependent changes in the properties of 2-butanol modifiers are sufficient to eliminate their capacity for enantiospecific interaction with coadsorbed PO. It is possible that on the Cu surfaces the adsorbed 2-butanol overlayer coalesces into islands with local coverages that are sufficiently high that they cannot accommodate adsorption of PO within the island. Unfortunately, the differences between the properties of 2-butanol on Pd and Cu surfaces are not known with sufficient clarity to understand the origins of the differences in their enantiospecific properties.

Another chiral alcohol modifier used in our study is L-alaninol, the alcohol analogue of L-alanine. Besides the −OH group, this amino-alcohol molecule provides an extra hydrogen-bonding site at the $-NH_2$ group that might induce enantioselectivity. From the TPD spectra of L-alaninol from Cu(111) in Figure 3A, two desorbed species from the first layer were detected: L-alaninol which desorbed molecularly from the surface at ∼260 K and another unknown species desorbed from the surface at ∼380 K. This result is consistent with the desorption of other alcohols from Cu surfaces, such as the desorption of 2-butanol from Cu(100). A prior study of the adsorption of alaninol on Cu(100) reported the presence of alaninoxide on the surface.[35] Therefore, the desorption peak at ∼380 K most likely corresponds to desorption of the β-hydride elimination product of alaninoxide species on Cu(111). Yet again, the Cu(111) surface modified by adsorption of L-alaninol did not manifest any enantioselective adsorption of PO over the L-alaninol coverages explored.

Obviously, the nature of the underlying substrate plays a significant role in enantioselective adsorption of chiral molecules as enantioselectivity is successfully seen on chirally modified Pd(111) and Pt(111) but not on Cu(111) when using an alcohol modifier such as 2-butanol.[22−24] It is reasonable to expect some differences in the interaction between the alcohol modifier with the Cu surface and with the Pd surface. The alcohol modifier may adsorb on Pd in such a way that hydrogen-bonding interaction occurs between the alcohol modifier and the probe molecule. Instead, on Cu, it is highly possible that hydrogen-bonding interaction takes place between adjacent alcohol modifier molecules to form modifier clusters which may or may not develop

(35) Irrera, S.; Costa, D. *J. Chem. Phys.* **2008**, *128*, 1–10.

into an ordered structure across the surface. Although we were unable to obtain any LEED images of 2-butanol or L-alaninol on Cu(111) at the time we performed this study, previous literature has reported sharp ordered LEED pattern for L-alaninol on Cu(100).[19,20] In any case, the alcohol modifier clusters resulting from hydrogen bonding interactions on Cu(111) may not contain the spaces necessary to allow adsorbed PO to interact with the Cu substrate. We have learned this from the aforementioned L-alanine/Cu(110) system. If the hydrogen bonding between the alcohol modifier and the probe molecule is truly the origin of enantioselective adsorption of PO on 2-butanol modified Pd(111) as suggested by Gao et al.,[24] the absence of such interactions on Cu surfaces may result in the loss of enantioselectivity.

5. Conclusions

Using PO and *R*-3-MCHO as probe molecules, enantioselectivity was probed on the following chirally modified Cu-based systems using temperature programmed desorption: PO on L-alanine/Cu(110), PO on L-alaninol/Cu(111), PO on 2-butanol/Cu(111), PO on 2-butoxide/Cu(100), PO on 2-butoxide/Cu(111), *R*-3-MCHO on 2-butoxide/Cu(100), and *R*-3-MCHO on 2-butoxide/Cu(111). None of these probe/modifier/metal systems displayed any degree of enantioselectivity at either low or high modifier coverages. The availability of hydrogen-bonding interactions, which may depend on the nature of the underlying substrate, could be critical to observing enantioselectivity. The 2-butoxide species does not possess any functional group that could offer hydrogen-bonding interaction with the PO. While hydrogen-bonding interaction is possible for the amino acid (L-alanine) and alcohol (2-butanol and L-alaninol) modifiers, the available hydrogen donor groups may be involved in the interactions between adsorbed modifiers that form clusters or islands on Cu and, therefore, they are unavailable for enantiospecific interaction with chiral probe molecules. In such a case, achiral Cu surfaces may still be viable substrates for chiral modification and enantioselective adsorption of chiral molecules, if more suitable modifier candidates with additional hydrogen donor sites are identified and explored.

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