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Enantioselective Chemisorption on a Chirally Modified Surface in Ultrahigh Vacuum: Adsorption of Propylene Oxide on 2-Butoxide-Covered Palladium(111)

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Abstract: The enantioselective chemisorption of (*S*)- and (*R*)-propylene oxide is measured on a Pd(111) surface chirally modified using (*S*)- and (*R*)-2-butanol. Reflection–absorption infrared spectroscopic (RAIRS) data suggest that adsorbed 2-butanol forms 2-butoxide species when heated to ~150 K and converts to a ketone with a concomitant loss in chirality at 200 K. Methyl ethyl ketone, ethylene, methane, CO, and hydrogen are found as products in temperature-programmed desorption (TPD). Propylene oxide adsorbs reversibly on Pd(111) at 80 K without undergoing any thermal decomposition, thus providing an ideal probe of surface chirality. The coverage of (*R*)-propylene oxide adsorbing on an (*R*)-2-butoxide-covered surface, ratioed to that on one covered by (*S*)-2-butoxide, reaches a maximum value of ~2 at a relative 2-butoxide coverage of ~25% of saturation and decreases to unity at a coverage of ~50% of saturation. This implies that the enantioselectivity depends critically on coverage and arises due to chiral “pockets” formed on the surface.

Introduction

In contrast to work in the homogeneous phase, success in developing heterogeneous enantioselective catalysts has been limited to the hydrogenation of α -ketoesters on chinchona-alkaloid-modified platinum and the hydrogenation of methyl-acetoacetate on tartaric acid-modified nickel.^{1–4} Work to understand these reactions at the molecular level on planar substrates has focused on exploring the surface chemistry of these chiral modifiers, tartaric acid on Cu(110) and Ni(110)^{5–8} and chinchinodine on platinum.^{9,10} Chiral modifiers adsorbed on metallic palladium have also resulted in the formation of enantioselective hydrogenation catalysts.¹¹ A significant amount of work has been carried out to explore the alkyne and alkene hydrogenation pathway on Pd(111), where ethylene hydrogenation takes place on a surface that is covered by ethyldiyne species.¹² In addition, the presence of coadsorbed atomic hydrogen on the surface causes the ethylene to be π -bonded,

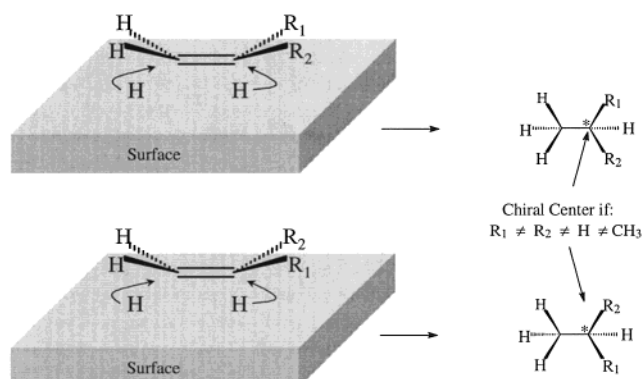


Figure 1. Schematic diagram illustrating how different adsorption geometries of $\text{CH}_2=\text{CHR}_1\text{R}_2$ lead to the formation of chiral hydrogenation products.

while it is di- σ -bonded on clean Pd(111).¹³ In both cases, ethylene adsorbs with the carbon–carbon bond parallel to the surface and bonds via its π orbitals. If the surface is modified by chiral molecules, enantiospecific catalysis could be induced by influencing the reactant adsorption configuration. This is illustrated in Figure 1, which shows the two possible adsorption configurations of a simple alkene with $\text{R}_1 \neq \text{R}_2 \neq \text{CH}_3$ or H on a clean surface and their reaction pathways to yield different chiral products. In the following, we use chiral molecules to probe the possibility of enantiospecific adsorption onto a chirally templated Pd(111) surface. The fundamental requirements for surface chiral template molecules are currently not well understood, although the minimal requirements are that they

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- (1) Orito, Y.; Imai, S.; Niwa, S.; Nguyen, G. H. *J. Synth. Org. Chem. Jpn.* **1979**, *37*, 173.
- (2) Izumi, Y. *Adv. Catal.* **1985**, *32*, 215.
- (3) Webb, G.; Wells, P. B. *Catal. Today* **1992**, *319*, 12.
- (4) Baiker, A.; Blaser, H. V. In *Handbook of Heterogeneous Catalysis*; Ertl, G.; Knözinger, H.; Weitkamp, J., Eds.; VCH: Weinheim, 1997; Vol. 5, p 2422.
- (5) Ortega, M.; Haq, S.; Bertrams, T.; Murray, P.; Raval, R.; Baddeley, C. J. *J. Phys. Chem. B* **1999**, *103*, 10661.
- (6) Humbolt, V.; Haq, S.; Muryn, C.; Hofer, W. A.; Raval, R. *J. Am. Chem. Soc.* **2002**, *124*, 503.
- (7) Barlow, S. M.; Haq, S.; Raval, R. *Langmuir* **2001**, *17*, 3292.
- (8) Raval, R. *CATECH* **2001**, *5*, 12.
- (9) Bonello, J. M.; Lambert, R. M.; Künzle, N.; Barker, A. *J. Am. Chem. Soc.* **2000**, *122*, 9864.
- (10) Kubota, J.; Zaera, F. *J. Am. Chem. Soc.* **2001**, *123*, 11115.
- (11) Tungler, A.; Fogassy, G. *J. Mol. Catal. A* **2001**, *173*, 231.
- (12) Kaltchev, M.; Thompson, A.; Tysoe, W. T. *Surf. Sci.* **1997**, *391*, 345.

- (13) Stacchiola, D.; Azad, S.; Burkholder, L.; Tysoe, W. T. *J. Phys. Chem. B* **2001**, *105*, 11233.

should possess (a) a chiral center and (b) a functionality that allows bonding to the surface, so that the general organic architecture should be $AC^*R_1R_2R_3$, where A is a surface anchoring group and $R_1 \neq R_2 \neq R_3 \neq A$ to yield a chiral carbon center C^* . Previous studies of small alcohols on Pd(111)^{14,15} reveal that they react to form alkoxide species. In the case of secondary alcohols, the β -hydrogen is eliminated on heating to form the corresponding ketone with a resulting loss of the chiral center. We have thus elected to use an alcohol of the form $HOC^*HR_1R_2$ as a chiral modifying species. Initial experiments are carried out using the smallest chiral hydrocarbon template molecule of this type, 2-butanol ($R_1 = CH_3$, $R_2 = C_2H_5$). The alkyl groups could subsequently be modified in a systematic way to explore the relationship between the structures of the chiral templating and probe molecules.

(S)- or (R)-propylene oxide is adsorbed onto the chirally modified surface to investigate how the presence of the template affects subsequent chemisorption. Propylene oxide is selected as a chiral probe since, as demonstrated below, it adsorbs on Pd(111) without undergoing thermal decomposition, and the overlayer can easily be distinguished from the multilayer using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). A similar approach, using the desorption temperature measured in TPD experiments, has been used to study chiral single-crystal surfaces.¹⁶ Furthermore, the functional groups on the epoxide ring can subsequently be varied in a systematic way to investigate how the relative structures of the modifying and probe molecules affect enantioselectivity.

Experimental Methods

Infrared data were collected using a system that has been described previously.¹² A palladium single crystal was mounted in a modified 2 $\frac{3}{4}$ in. six-way cross equipped with infrared-transparent KBr windows. It could be resistively heated to 1200 K, or cooled to 80 K using liquid nitrogen. Spectra were collected using a Bruker Equinox infrared spectrometer and a liquid nitrogen cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, CO₂-free air. Data were typically collected for 1000 scans at 4 cm⁻¹ resolution. Temperature-programmed desorption data were collected in another chamber that has been described in detail elsewhere.¹⁷ This consisted of a stainless steel chamber operating at a base pressure of 5×10^{-11} Torr following bakeout, and desorption spectra were detected using a Dycor quadrupole mass spectrometer interfaced to a computer that allowed up to five masses to be collected sequentially.

The Pd(111) sample was cleaned using a standard procedure, which consisted of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is insensitive to the presence of small amounts of surface carbon, which was instead detected by adsorbing oxygen onto the surface and carrying out a TPD experiment to monitor CO. The absence of CO desorption was taken to indicate a carbon-free surface.

2-Butanol (Acros, p.a.), (R)- and (S)-2-butanol (Acros, 98%), propylene oxide (Acros, p.a.), and (R)- and (S)-propylene oxide (Aldrich, 99%, Acros, 99% respectively) were transferred to glass bottles, attached to the gas-handling systems of the vacuum chambers, and further cleaned using repeated freeze-pump-thaw cycles. The cleanliness of all reactants was monitored by mass spectroscopy.

RAIRS of 2-Butanol / Pd(111)

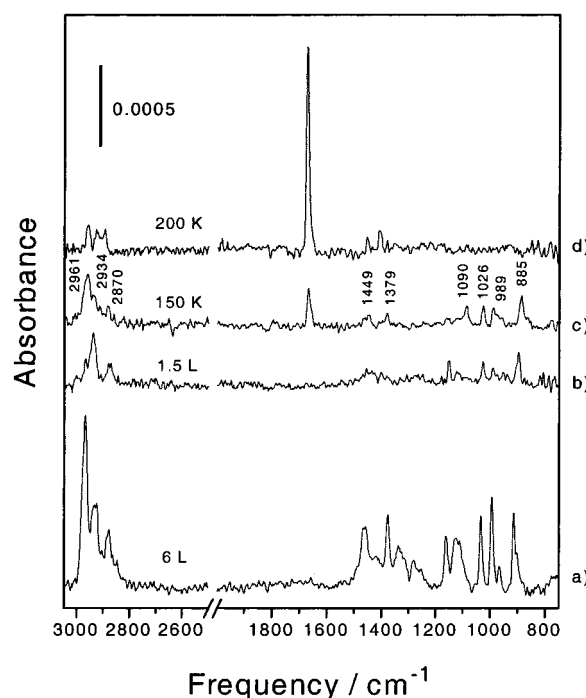


Figure 2. Reflection-adsorption infrared spectra of 2-butanol on Pd(111), (a) following a 6 L exposure to form a multilayer, (b) following a 1.5 L exposure, heating to (c) 150 K and subsequently to (d) 200 K.

Table 1. Vibrational Frequencies and Assignments for 2-Butanol Adsorbed on Pd(111)

assignment	frequency/cm ⁻¹		
	multilayer 2-butanol/Pd(111)	monolayer 2-butanol/Pd(111)	2-butoxide/Pd(111)
$\nu_a(CH_3)$	2968		2961
$2\delta_s(CH_3)$, $\nu_s(CH_3)$, $\nu(CH_2)$	2934, 2924	2937	2934
$\nu(CH)$	2878	2878, 2870	2870
$\delta_a(CH_3)$, $\delta_s(CH_2)$	1466, 1458, 1418	1452, 1400	1449
$\delta_s(CH_3)$	1375	1377	1379
$\rho(CH_2)$	1337, 1279		
$\rho(CH_3)$	1163	1153	
$\nu(CO)$	1128	1123	
$\delta(CH)$	1111		
$\nu(M-O-C)$			1090
$\nu(CC)$	1034	1026	1026
$\rho(CH_3)$, $\rho(CH_2)$	993, 966	989	989
$\rho(CH_3) + \nu(CO)$	914	897	885

Results

Adsorption of 2-Butanol on Pd(111). Figure 2a displays the infrared spectrum of multilayers of 2-butanol adsorbed on Pd(111) at 80 K (6 L exposure, 1 L = 1×10^{-6} Torr s). This spectrum exhibits features that are in excellent agreement with those of liquid 2-butanol,^{18,19} and their assignments are summarized in Table 1.

Displayed in Figure 2b is the corresponding infrared spectrum of a submonolayer coverage of 2-butanol (1.5 L exposure). The peak intensities are considerably attenuated compared to those of the multilayer. The majority of the vibrational frequencies

(14) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1987**, 387, 187.

(15) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1990**, 235, 235.

(16) Horvath, J. D.; Gellman, A. J. *J. Am. Chem. Soc.* **2001**, 123, 7953.

(17) Kaltchev, M.; Tysoe, W. T. *J. Catal.* **2000**, 193, 29.

(18) Quinan, J. R.; Wiberley, S. E. *Anal. Chem.* **1954**, 26, 1762.

(19) Saymanski, H. A. *Interpreted Infrared Spectra*; Plenum Press: New York, 1966.

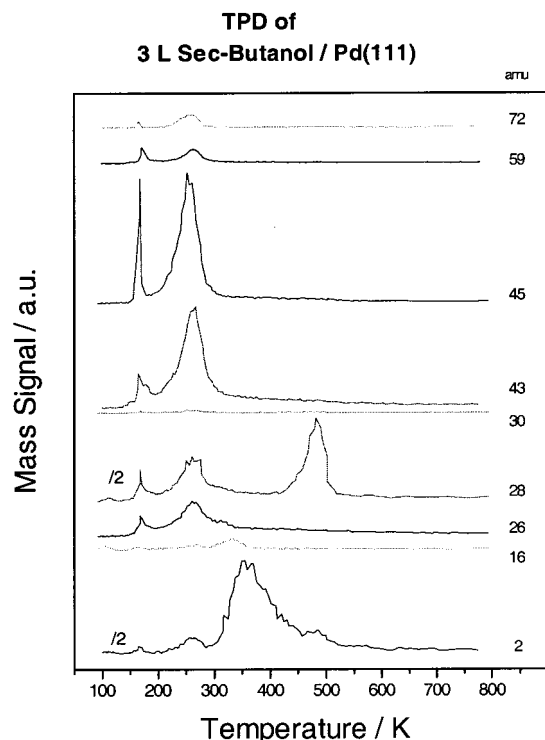


Figure 3. Temperature-programmed desorption spectra taken using a heating rate of 7 K/s following the adsorption of 3 L of 2-butanol on Pd(111) at 80 K monitored at various masses, where the masses are marked adjacent to the corresponding spectrum.

are close to those of the multilayer, and the assignments are also summarized in Table 1.

The major difference between the monolayer and multilayer spectra is the shift in the $\rho(\text{CH}_3) + \nu(\text{CO})$ mode from 914 cm^{-1} for the multilayer (Figure 2a) to 897 cm^{-1} for the monolayer (Figure 2b). A shoulder at this latter frequency is present on the 914 cm^{-1} feature in the multilayer spectrum, presumably due to 2-butanol adsorbed directly on the surface. Heating to 150 K causes further changes in the spectrum, most notably the shift of the $\rho(\text{CH}_3) + \nu(\text{CO})$ mode to 885 cm^{-1} , and the appearance of a new feature at $\sim 1090\text{ cm}^{-1}$. In addition, a sharp peak appears at $\sim 1670\text{ cm}^{-1}$, which continues to grow as the sample is heated to 200 K (Figure 2d), which is assigned to a C=O stretching mode due to the formation of a ketone adsorbed in an η^1 configuration.²⁰ The features at 2961, 2934, and 2870 cm^{-1} are assigned to C–H stretching, and those at 1449 and 1379 cm^{-1} , to asymmetric methyl deformation modes.

The corresponding temperature-programmed desorption spectra are displayed in Figure 3. Molecular 2-butanol desorption is detected at $\sim 170\text{ K}$ with peaks at 2, 26, 28, 43, 45, 59, and 72 amu, and the relative integrated desorption intensities at these masses agree well with the mass spectrometer ionizer fragmentation pattern of 2-butanol. A feature with a similar desorption temperature has been observed for smaller alcohols adsorbed on Pd(111) and assigned to the alcohol molecularly adsorbed on the metal surface.¹⁴ An additional relatively broad feature is evident at $\sim 260\text{ K}$, but with a mass spectrometer ionizer fragmentation pattern that is different from that of 2-butanol. Several reaction pathways have been identified for alcohols on Pd(111) including the formation of hydrocarbon fragments

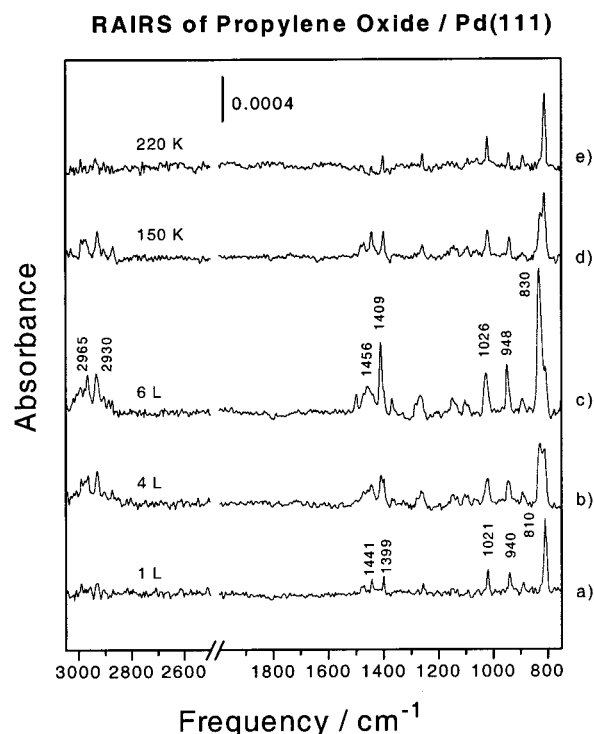


Figure 4. Reflection–adsorption infrared spectra of propylene oxide on Pd(111), (a) following a 1 L exposure, (b) a 4 L exposure, and (c) after a 6 L exposure, and subsequently after heating the sample to (d) 150 K and (e) 220 K.

Table 2. Vibrational Frequencies and Assignments for Propylene Oxide Adsorbed on Pd(111) (1 L) at 80 K

frequency/ cm^{-1}	assignment
$\text{C}_3\text{H}_6\text{O}/\text{Pd}(111)$, 1 L, 80 K	
810	ring deformation
940	methyl rock
1021	CH_3 wag
1399	CH_2 deformation
1441	CH_3 deformation

formed by cleavage of the α carbon–carbon bond and ketone formation. This feature is therefore assigned to a combination of ethylene (28, 26 amu) and ketone (72, 59, 45, and 43 amu) desorption from the surface. The desorption temperature of 260 K is in excellent agreement with the value for similar chemistry of 2-propanol on Pd(111).¹⁴ An additional feature is detected at $\sim 320\text{ K}$ at 16 amu due to methane desorption. A broad hydrogen desorption feature is seen between 310 and 450 K, consistent with that found following the adsorption of other alcohols on Pd(111), and finally, CO desorption is found at $\sim 470\text{ K}$.¹⁴

Adsorption of Propylene Oxide on Pd(111). The infrared spectrum of 1 L of propylene oxide adsorbed on Pd(111) at 80 K is displayed in Figure 4a and exhibits features at 810, 940, 1021, 1399, and 1441 cm^{-1} , with some slight intensity in the CH stretching region. The frequencies and assignments, based on the spectrum of liquid propylene oxide,²¹ are summarized in Table 2.

As the exposure increases to 4 L, the majority of these features grow and shift slightly to higher frequencies by 5–10 cm^{-1} , with the exception of the 810 cm^{-1} mode, which shifts

(20) Avery, N. R. *Surf. Sci.* **1983**, *125*, 771.

(21) Tobin, M. C. *Spectrochim. Acta* **1960**, *16*, 1108.

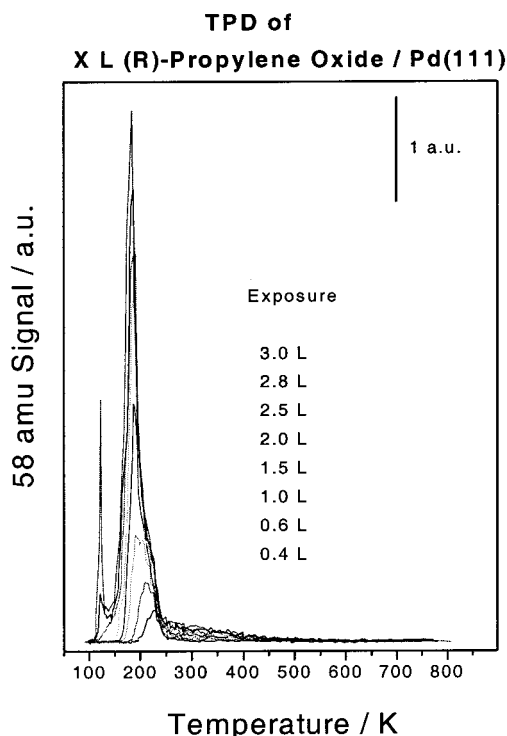


Figure 5. Temperature-programmed desorption spectra taken using a heating rate of 7 K/s following the adsorption of (*R*)-propylene oxide on Pd(111) at 80 K, monitored at 58 amu as a function of exposure, where the exposures are marked adjacent to the corresponding spectrum.

to 830 cm^{-1} . In addition, features at 2965 and 2930 cm^{-1} become evident in the CH stretching region. All the peaks, and in particular that at 830 cm^{-1} , continue to grow as the exposure increases to 6 L. As the surface is heated to 150 K, the peaks decrease in intensity, with the exception of the 810 cm^{-1} mode, while the mode at 830 cm^{-1} is significantly attenuated. Any residual 830 cm^{-1} intensity is completely absent after the surface is heated to 220 K.

The corresponding temperature-programmed desorption spectra are displayed in Figure 5, monitored at 58 amu. Measuring the desorption profile at other masses confirms that this is due to the desorption of molecular propylene oxide. No other desorption products are detected, indicating that propylene oxide adsorbs reversibly on Pd(111). The desorption profile consists of a sharp feature that shifts from ~ 230 K at low exposures to ~ 190 K as the coverage reaches saturation, indicating the existence of repulsive lateral interactions between adjacent adsorbed propylene oxide molecules. A sharp feature appears at ~ 120 K for propylene oxide exposures larger than 2.5 L and is assigned to adsorption into second and subsequent layers.

On the basis of these observations, the vibrational feature at 810 cm^{-1} in Figure 4e and d is assigned to propylene oxide adsorbed directly on the palladium surface. Thus, both infrared spectroscopy and temperature-programmed desorption can be used to monitor the coverage of propylene oxide adsorbed on the metal surface, by following the intensity of the 810 cm^{-1} feature in RAIRS and by temperature-programmed desorption from the integrated desorption yield between 150 and 250 K.

Adsorption of Propylene Oxide on 2-Butanol-Modified Pd(111). The study of enantioselective chemisorption of propylene oxide on a surface modified by 2-butanol is carried out

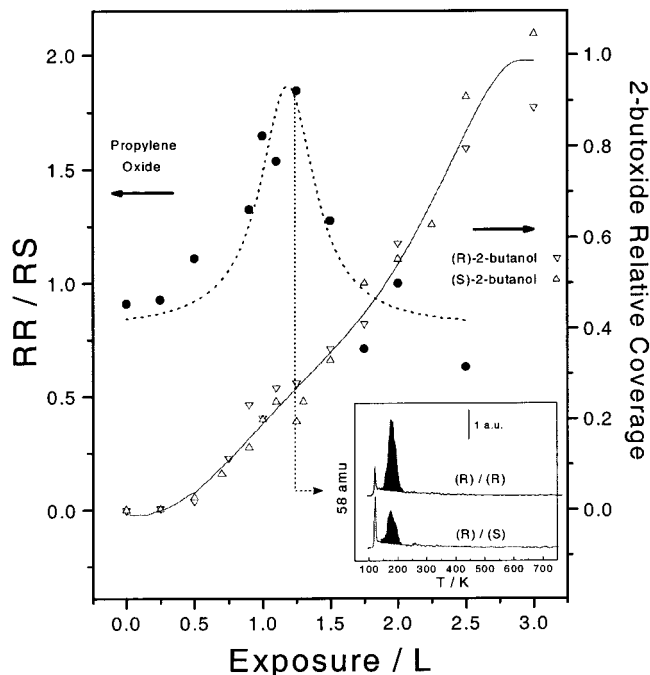


Figure 6. Plot of the relative coverage of (*S*)-2-butoxide (Δ) and (*R*)-2-butoxide (∇) as a function of exposure on Pd(111) (right axis), along with a plot of the ratio of the coverage of (*R*)-propylene oxide adsorbed on (*R*)-2-butoxide-covered Pd(111) (*RR*) to the saturation coverage of (*R*)-propylene oxide adsorbed on (*S*)-2-butoxide (*RR/RS*) (\bullet) (left axis), as a function of 2-butanol exposure. Shown as an inset are typical desorption spectra of propylene oxide from 2-butoxide-covered Pd(111).

using both temperature-programmed desorption and infrared spectroscopy.

In the case of temperature-programmed desorption experiments, the surface is exposed to a measured amount (in langmuirs) of either (*R*)- or (*S*)-2-butanol, and the surface heated to 150 K to form 2-butoxide species (see below). From the RAIRS data of Figure 2, by 150 K a small percentage of methyl ethyl ketone has already been formed, which is taken as an indication that the formation of 2-butoxide is complete. The surface is then allowed to cool to 80 K and exposed to 3 L of propylene oxide. The propylene oxide temperature-programmed desorption (Figure 5) and infrared (Figure 4) data indicate that multilayers of propylene oxide will form. These can, however, be easily distinguished from first-layer propylene oxide by their peak desorption temperatures, as exemplified by a typical coadsorption experiment shown as an inset in Figure 6. The results are summarized in Figure 6. The coverages of (*R*)-2-butoxide (∇) and (*S*)-2-butoxide (Δ), measured using temperature-programmed desorption, change in an identical fashion as a function of exposure and saturate at an exposure of ~ 3 L. The coverage of (*R*)-propylene oxide adsorbing on an (*R*)-2-butoxide-covered surface, ratioed to the coverage on an (*S*)-2-butoxide-covered surface (designated (*RR/RS*)), is also plotted versus 2-butanol exposure (\bullet). As expected, on the clean Pd(111) surface (2-butanol exposure = 0.0), this ratio is unity. As the 2-butoxide coverage increases to 25% of saturation (following an exposure of ~ 1.2 L), this ratio increases to 1.9 ± 0.2 , indicating enantioselective chemisorption of propylene oxide onto the surface. A further increase in 2-butoxide coverage to $\sim 50\%$ of saturation (at an exposure of ~ 1.8 L) causes the ratio to decrease once again to unity.

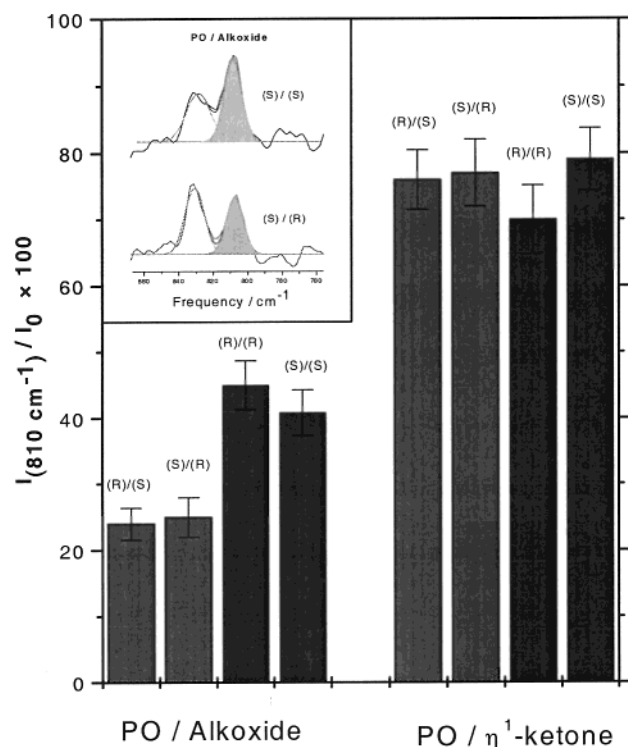


Figure 7. Histograms showing the relative amounts of propylene oxide adsorbed on a surface prepared by adsorbing 2-butanol on Pd(111) at 80 K and heating to 150 K. This is indicated as PO/Alkoxide. Each histogram is marked (X)/(Y) where X (=R or S) indicates the chirality of the propylene oxide, and Y (=R or S) indicates the chirality of the 2-butanol. Propylene oxide coverages are measured from the integrated intensity of the 810 cm^{-1} feature, where 100% represents the propylene oxide coverage on clean Pd(111). The data marked PO/ η^1 -ketone correspond to a surface prepared by adsorbing 2-butanol at 80 K and heating to 200 K. Shown as an inset are typical RAIRS data for propylene oxide adsorbed on 2-butoxide-covered Pd(111).

An analogous series of experiments were carried out, but in this case, using infrared spectroscopy to gauge the coverage of propylene oxide on the 2-butoxide-covered Pd(111) surface. These were carried out by exposing Pd(111) to 1.2 L of 2-butanol (so that the coverage is $\sim 25\%$ of saturation) at 80 K and heating to 150 K, as above. After the sample had cooled to 80 K, it was then exposed to 3 L of propylene oxide (which also leads to some multilayer formation), and the coverage of propylene oxide on the metal surface measured from the integrated area under the 810 cm^{-1} RAIRS feature. Typical RAIRS spectra of propylene oxide adsorbed on 2-butoxide-covered Pd(111) are shown as an inset in Figure 7. Note that the 2-butoxide-covered surface was used as a background spectrum for these data. The results are summarized in Figure 7 by the histograms indicated by PO/Alkoxide. The height of the histogram represents the coverage of propylene oxide relative to that required to saturate the clean surface (set to 100%). Each of the histograms is labeled (X)/(Y) where X, Y = R or S. X indicates the chirality of the propylene oxide and Y that of the 2-butanol. The ratios of the heights of these histograms are ~ 2 , in accord with results from temperature-programmed desorption data (Figure 6).

The effect of heating the 2-butoxide-covered surface to 200 K to form the ketone (Figure 2) is indicated by the data labeled PO/ η^1 -ketone. Evidently this reaction forms a more open surface, since now about 75% of the coverage of propylene oxide that

can be adsorbed on the clean surface is accommodated on this surface.

Discussion

Molecular multilayers of 2-butanol adsorb on Pd(111) at 80 K (Figure 2a). The peak assignments are summarized in Table 1.^{18,19} Submonolayer coverages of 2-butanol adsorbed on Pd(111) at 80 K (Figure 2b) exhibit similar peak positions except for the shift in the 897 cm^{-1} ($\rho(\text{CH}_3) + \nu(\text{CO})$) feature from 914 cm^{-1} for the multilayer. Heating to 150 K (Figure 2c) causes this feature to shift further to 885 cm^{-1} and a new peak to appear at 1090 cm^{-1} . Intense features due to the $\nu(\text{CO})$ mode at low frequencies have been associated with the formation of surface alkoxide species.^{22,23} Infrared spectroscopic studies of aluminum alkoxides assigned a strong feature at $\sim 1058 \text{ cm}^{-1}$ to the Al–O–C linkage in aluminum *sec*-butoxide.²⁴ The feature at 1090 cm^{-1} in Figure 2c is therefore assigned to the metal–O–C vibration of 2-butoxide. The 2-butoxide formation temperature found here is within the range of those found for methanol, ethanol, and propanol on Pd(111).^{14,15} An additional feature is evident at $\sim 1670 \text{ cm}^{-1}$, and this feature increases in intensity as the sample is heated to 200 K (Figure 2d). This peak is assigned to a C=O stretching mode of an η^1 -ketone formed via a β -hydride elimination reaction from the adsorbed 2-butoxide, providing further evidence for 2-butoxide formation. The ketone desorbs at $\sim 260 \text{ K}$ in temperature-programmed desorption (Figure 3), along with ethylene. In addition, some methane, hydrogen and carbon monoxide are detected, so that the decomposition pathway of 2-butoxide on palladium is completely analogous to that found for other alcohols on this surface.^{14,15}

Propylene oxide adsorbs molecularly on Pd(111) (Figure 4a and Table 2). The spectrum shows a substantial shift in the ring deformation mode from 830 cm^{-1} for the multilayer to 810 cm^{-1} for the monolayer, implying that propylene oxide adsorbs to palladium via the oxygen atom in a manner similar to that found on Pt(111).²⁵ However, unlike the decomposition of propylene oxide found on Pt(111), propylene oxide undergoes no thermal decomposition on Pd(111) and merely desorbs molecularly between 150 and 250 K, depending on coverage (Figure 5), similar to the behavior found on copper.¹⁶ This renders it an ideal chiral probe molecule on Pd(111) since it adsorbs without decomposition, and adsorption onto the metal surface can be simply distinguished from the multilayer by the shift in the ring deformation mode frequency in infrared spectroscopy (Figure 4) or by the desorption temperature in temperature-programmed desorption (Figure 5). These properties are used to probe enantioselective chemisorption on Pd(111) surfaces chirally modified using 2-butanol.

The results of Figure 6 indicate that, at low exposures (below $\sim 0.7 \text{ L}$), the 2-butoxide-covered surface exhibits no chemisorptive enantioselectivity ($(RR/RS) \sim 1$). The enantioselectivity then increases with increasing coverage until (RR/RS) reaches a maximum value of ~ 2 at a 2-butoxide coverage that is $\sim 25\%$ of saturation and then decreases to unity once again. This indicates that the 2-butoxide-covered surface is enantioselective

(22) Weldon, M. K.; Friend, C. M. *Chem. Rev.* **1996**, 96, 1391.

(23) Shorhouse, L. J.; Roberts, A. J.; Raval, R. *Surf. Sci.* **2001**, 480, 97.

(24) Guertin, D. L.; Wiberley, S. E.; Bauer, W. H.; Goldenson, J. J. *Phys. Chem.* **1956**, 60, 1018.

(25) Dinger, A.; Lutterlof, C.; Biener, J.; Küppers, J. *Surf. Sci.* **2000**, 449, 1.

over a rather narrow coverage range and implies that careful control of conditions during catalysis are required to ensure that the chiral modifying molecules are present at the correct coverage. Analogous behavior has been found in catalytic reactions where the most enantioselective catalysts have been found at relatively low loads of the chiral modifier.^{2,26} The above results suggest that enantioselectivity is induced by a cooperative effect between adsorbed 2-butoxide species formed on the surface; otherwise the enantioselectivity would increase linearly at low 2-butoxide coverages. The decrease in enantioselectivity for 2-butoxide coverages between ~25 and ~50% of saturation may be caused by the chiral "pockets" present in the 2-butoxide overlayer being filled by additional 2-butanol. Propylene oxide adsorption is almost completely suppressed when the 2-butoxide coverage exceeds 50% of saturation.

Infrared experiments (Figure 7) confirm the temperature-programmed desorption data. These results further show that the chirality of the modified surface is induced by the presence of the 2-butoxide species on the surface and is symmetrical in the sense that (*R*)-2-butoxide species inhibit (*S*)-propylene oxide adsorption to exactly the same extent as (*S*)-2-butoxide species inhibit (*R*)-propylene oxide adsorption. The enantioselectivity disappears completely when 2-butoxide species are heated to 200 K to form an η^1 -ketone, where the chiral center is lost, as indicated by the histograms labeled PO/ η^1 -ketone in Figure 7.

It is clear, however, that significant (*S*)-propylene oxide can still adsorb onto a surface modified by (*R*)-2-butoxide and vice versa (Figure 7), resulting in a maximum (*RR/RS*) ratio of ~2 (Figure 6). This could be due to several effects. It may be that the pockets themselves are not completely stereoselective and that the steric hindrance provided during chiral docking is not sufficiently strong to fully inhibit the adsorption of the "wrong" chirality. It may also be due to the presence of larger, achiral regions at boundaries between domains of 2-butoxide species or due to the adsorption at other defects in the structure. The observation that propylene oxide adsorption is almost completely suppressed by increasing the 2-butoxide coverage from ~25%

to ~50% of saturation suggests that this is not the case. Further characterization of the structure of the 2-butoxide overlayer, and measurements of its order, will help to clarify these issues. Moreover, measuring the stereoselective chemisorption of other chiral epoxides, $\text{CH}_2\text{OCR}_1\text{R}_2$, will allow the relationship between the chiral template and the probe molecule to be explored in a systematic way. Thus, the use of simple model systems, such as the one reported here, will allow us to gain insights into the fundamental molecular requirements for inducing enantioselective adsorption by chiral modification. If this is the step in which chirality is introduced into the final product as suggested in Figure 1, it may ultimately lead to the design of a wide variety of effective heterogeneous catalytic systems.

Conclusions

A method for probing the enantioselectivity of a chiral overlayer, in this case synthesized using 2-butanol, toward chemisorption on a Pd(111) surface is illustrated using propylene oxide as a chiral probe. Propylene oxide provides an ideal probe molecule on Pd(111) since it does not thermally decompose on the surface and the monolayer can easily be distinguished from the multilayer both by infrared spectroscopy and by temperature-programmed desorption. It is shown that enantioselectivity is only expressed over a narrow range of 2-butoxide coverage, reaching a maximum value of (*RR/RS*) ~ 2 at a relative 2-butoxide coverage of 25% of saturation. This is suggested to be due to the formation of chiral "pockets" in the 2-butoxide overlayer that are filled by further 2-butanol at higher coverages, almost completely suppressing propylene oxide adsorption.

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