

Probing enantioselective chemisorption in ultrahigh vacuum

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Abstract

A chiral overlayer was deposited on Pd(1 1 1) in ultrahigh vacuum by the adsorption of either *R*- or *S*-2-butanol. Enantioselective chemisorption onto this surface was explored by adsorption of a chiral probe, propylene oxide. It was found that the coverage of *R*-propylene oxide adsorbing on an *R*-2-butoxide-covered surface, ratioed to that on one covered by *S*-2-butoxide, reached a maximum value of ~ 2 at a relative 2-butoxide coverage of $\sim 25\%$ of saturation, and decreases to unity at a coverage of $\sim 50\%$ of saturation. This implies that the enantioselectivity depends critically on coverage and arises due to chiral “pockets” formed on the surface.

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1. 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 methylacetoacetate 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(1 1 0) and Ni(1 1 0) [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 substantial amount of work has also been carried out to explore the enantioselectivity of metal surfaces that have been cut so that they exhibit chiral faces [12–15]. Experiments to explore the alkyne and alkene hydrogenation pathway on Pd(1 1 1) have shown that ethylene hydrogenation takes place on a surface that is covered by ethynyl species [16]. In addition, the presence of co-adsorbed, sub-surface atomic hydrogen on Pd(1 1 1) causes the ethylene to be π -bonded, while it is di- σ -bonded on the clean surface [17]. In both cases, ethylene adsorbs with the carbon-carbon bond parallel to the surface. If the surface is modified by chiral molecules, enantiospe-

cific catalysis could be induced by influencing the reactant adsorption configuration. This is illustrated in Fig. 1, which shows the two possible adsorption configurations of a simple prochiral alkene (with $R_1 \neq R_2 \neq \text{CH}_3$ 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(1 1 1) surface. The fundamental requirements for surface chiral template molecules are currently not well understood, although the minimal requirements are that they should possess: (a) a chiral center and (b) a functional group that allows bonding to the surface, so that the general organic architecture should be $\text{AC}^*\text{R}_1\text{R}_2\text{R}_3$, where A is a surface anchoring group and $R_1 \neq R_2 \neq R_3 \neq \text{A}$ to yield a chiral carbon center C^* . Previous studies of small alcohols on Pd(1 1 1) [18,19] demonstrate 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 $\text{HOC}^*\text{HR}_1\text{R}_2$ as a chiral modifying species. Initial experiments are carried out using the smallest chiral hydrocarbon template molecule of this type, 2-butanol ($R_1 = \text{CH}_3$, $R_2 = \text{C}_2\text{H}_5$). The alkyl groups can 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 ox-

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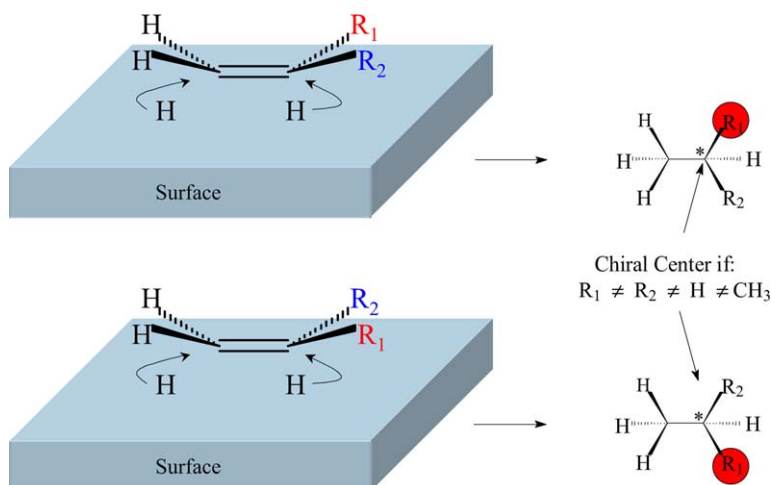


Fig. 1. Schematic diagram illustrating how different adsorption geometries of $CH_2=CHR_1R_2$ lead to the formation of chiral hydrogenation products.

ide is selected as a chiral probe since, as is 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) or 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 [13]. Furthermore, the functional groups on the epoxide ring as well as the template can subsequently be varied in a systematic way to investigate how the relative structures of the modifying and probe molecules affect enantioselectivity.

2. Experimental methods

Infrared data were collected using a system that has been described previously [16]. Temperature-programmed desorption data were collected in another chamber that has been described in detail elsewhere [20].

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.

3. Results

3.1. Adsorption of 2-butanol on Pd(111)

Fig. 2a shows the infrared spectrum of multilayers of 2-butanol adsorbed on Pd(111) at 80 K (61 exposure, $11 = 1 \times 10^{-6}$ Torr s). This spectrum exhibits features that are in excellent agreement with those of liquid 2-butanol [21,22]

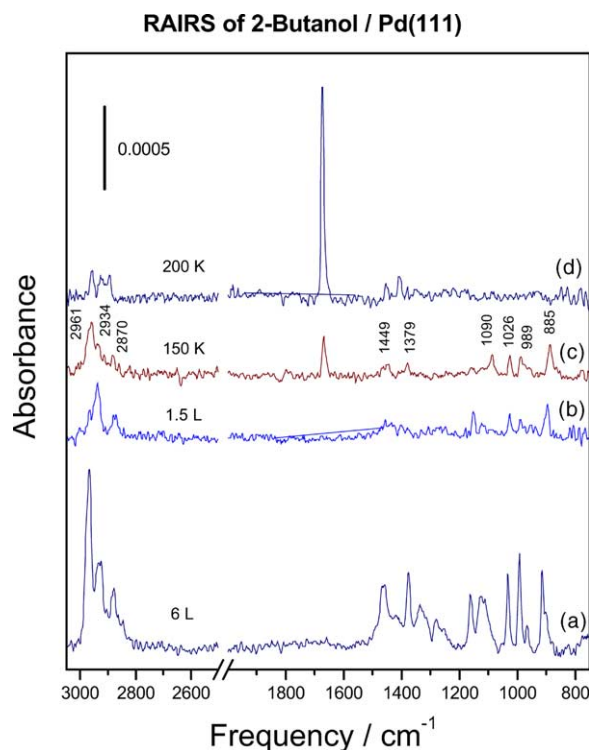


Fig. 2. Reflection-adsorption infrared spectra of 2-butanol on Pd(111): (a) following a 61 exposure to form a multilayer, (b) following a 1.51 exposure, heating to (c) 150 K and subsequently to (d) 200 K.

Table 1
Vibrational frequencies and assignments for 2-butanol adsorbed on Pd(1 1 1)

Assignment	Frequencies (cm ⁻¹)		
	Multilayer 2-butanol/ Pd(1 1 1)	Monolayer 2-butanol/ Pd(1 1 1)	2-Butoxide/ Pd(1 1 1)
$\nu_a(\text{CH}_3)$	2968	–	2961
$2\delta_s(\text{CH}_3)$, $\nu_s(\text{CH}_3)$, $\nu(\text{CH}_2)$	2934, 2924	2937	2934
$\nu(\text{CH})$	2878	2878, 2870	2870
$\delta_a(\text{CH}_3)$, $\delta_s(\text{CH}_2)$	1466, 1458, 1418	1452, 1400	1449
$\delta_s(\text{CH}_3)$	1375	1377	1379
$\rho(\text{CH}_2)$	1337, 1279	–	–
$\rho(\text{CH}_3)$	1163	1153	–
$\nu(\text{CO})$	1128	1123	–
$\delta(\text{CH})$	1111	–	–
$\nu(\text{M-O-C})$	–	–	1090
$\nu(\text{CC})$	1034	1026	1026
$\rho(\text{CH}_3)$, $\rho(\text{CH}_2)$	993, 966	989	989
$\rho(\text{CH}_3) + \nu(\text{CO})$	914	897	885

and their assignments are summarized in Table 1. Displayed in Fig. 2b is the corresponding infrared spectrum of a sub-monolayer coverage of 2-butanol (1.5 l exposure). The peak intensities are considerably attenuated compared to those of the multilayer where the majority of the vibrational frequencies 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 (Fig. 2a) to 897 cm⁻¹ for the monolayer (Fig. 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 ~1090 cm⁻¹. In addition, a sharp peak appears at ~1670 cm⁻¹, which continues to grow as the sample is heated to 200 K (Fig. 2d). This is assigned to a C=O stretching mode due to the formation of a ketone adsorbed in an η^1 configuration [23]. 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 shown in Fig. 3. Molecular 2-butanol desorption is detected at ~170 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(1 1 1) and assigned to desorption of the alcohol molecularly adsorbed on the metal surface [18]. An additional relatively broad feature is evident at ~260 K, but with a mass spectrometer ionizer fragmentation pattern that is different from that of 2-butanol. Several reaction pathways

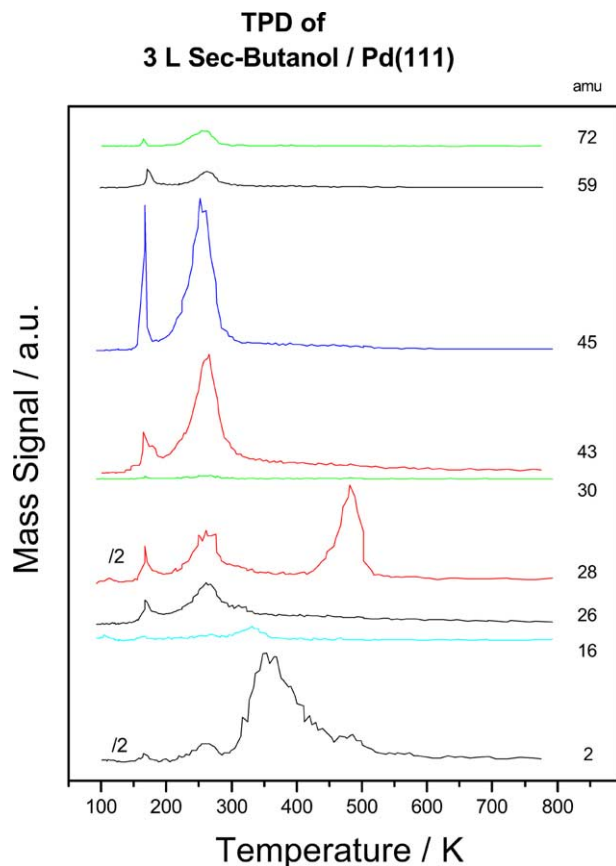


Fig. 3. Temperature-programmed desorption spectra taken using a heating rate of 7 K/s following the adsorption of 31 of 2-butanol on Pd(1 1 1) at 80 K monitored at various masses, where the masses are marked adjacent to the corresponding spectrum.

have been identified for alcohols on Pd(1 1 1) including the formation of hydrocarbon fragments formed by cleavage of the α carbon–carbon bond, and ketone formation. This feature is therefore assigned to a combination of ethylene (28 and 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(1 1 1) [14]. An additional feature is detected at ~320 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(1 1 1) and finally, CO desorption is found at ~470 K [18].

3.2. Adsorption of propylene oxide on Pd(1 1 1)

The infrared spectrum of 1 l of propylene oxide adsorbed on Pd(1 1 1) at 80 K is displayed in Fig. 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 [24], are summarized in Table 2. As the exposure increases to 4 l, the majority of these features grow and shift

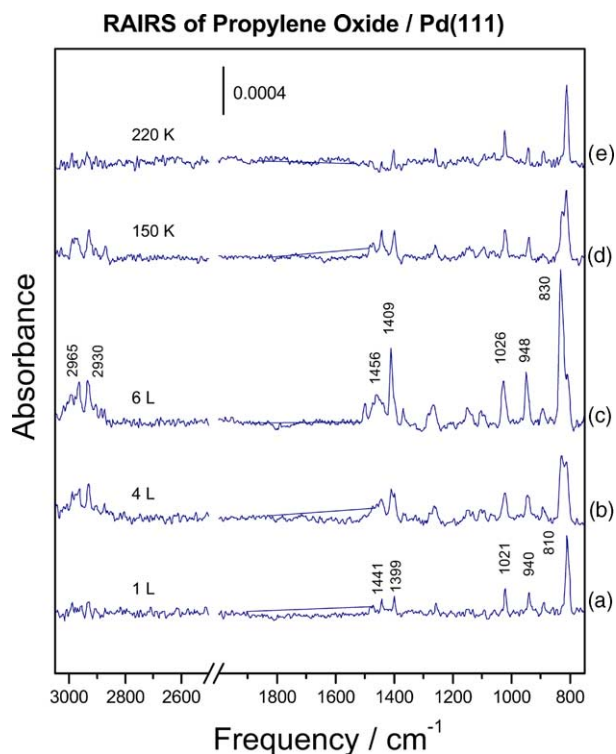


Fig. 4. Reflection-adsorption infrared spectra of propylene oxide on Pd(111): (a) following a 1 l exposure, (b) a 4 l exposure and (c) after a 61 l exposure, and subsequently after heating the sample to (d) 150 K and (e) 220 K.

slightly to higher frequencies by 5–10 cm^{-1} , with the exception of the 810 cm^{-1} mode, which shifts 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 61. 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 Fig. 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

TPD of X L (R)-Propylene Oxide / Pd(111)

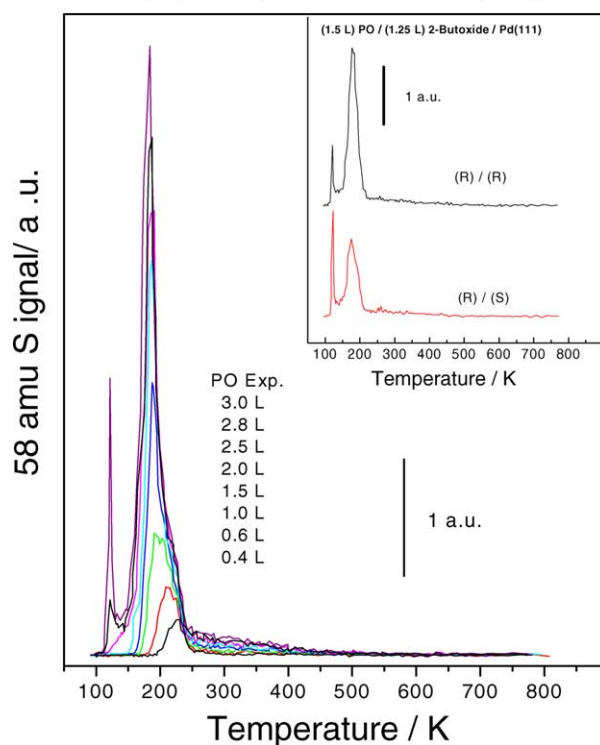


Fig. 5. Temperature-programmed desorption spectra taken using a heating rate of 7 K/s following the adsorption of R-propylene oxide on Pd(111) at 80 K, monitored at 58 amu as a function of exposure, where the exposures are marked adjacent to the corresponding spectrum.

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 2.51 and is assigned to adsorption into second and subsequent layers.

On the basis of these observations, the vibrational feature at 810 cm^{-1} in Fig. 4d and e 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 either the intensity of the 810 cm^{-1} feature in RAIRS, or by temperature-programmed desorption from the integrated desorption yield between 150 and 250 K.

3.3. 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 using both temperature-programmed desorption and infrared spectroscopy. In the case of temperature-programmed desorption experiments, the surface is exposed to a measured amount

Table 2

Vibrational frequencies and assignments for propylene oxide adsorbed on Pd(111) (11) at 80 K

Frequency (cm^{-1}) [$\text{C}_3\text{H}_6\text{O}/\text{Pd}(111)$, 11, 80 K]	Assignment
810	Ring deformation
940	Methyl rock
1021	CH_3 wag
1399	CH_2 deformation
1441	CH_3 deformation

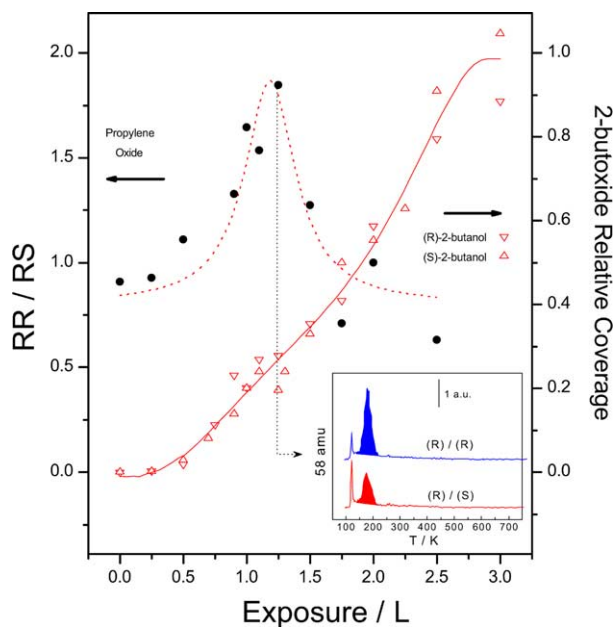


Fig. 6. Plot of the relative coverage of *S*-2-butoxide (Δ) and *R*-2-butoxide (∇) as a function of exposure on Pd(111) (right axis), along with a plot of the ratio of the coverage of *R*-propylene oxide adsorbed on *R*-2-butoxide-covered Pd(111) (RR) to the saturation coverage of *R*-propylene oxide 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).

(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 Fig. 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 31 of propylene oxide. The propylene oxide temperature-programmed desorption (Fig. 5) and infrared (Fig. 4) spectra show 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 co-adsorption experiment shown as an inset in Fig. 6. The results are summarized in Fig. 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 ~ 31 . 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 ~ 1.21), 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 ~ 1.81) causes the ratio to decrease once again to unity.

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 1.21 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 31 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 Fig. 7. Note that the 2-butoxide-covered surface was used as a background spectrum for these data. The results are summarized in Fig. 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* where 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 (Fig. 6).

The effect of heating the 2-butoxide-covered surface to 200 K to form the ketone (Fig. 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.

4. Discussion

Molecular multilayers of 2-butanol adsorb on Pd(111) at 80 K (Fig. 2a) where the peak assignments are summarized in Table 1 [21,22]. Submonolayer coverages of 2-butanol adsorbed on Pd(111) at 80 K (Fig. 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 (Fig. 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 [25,26]. 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 [27]. The feature at 1090 cm^{-1} in Fig. 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) [18,19]. An additional feature is evident at $\sim 1670\text{ cm}^{-1}$, which increases in intensity as the sample is heated to 200 K (Fig. 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 (Fig. 3), along with

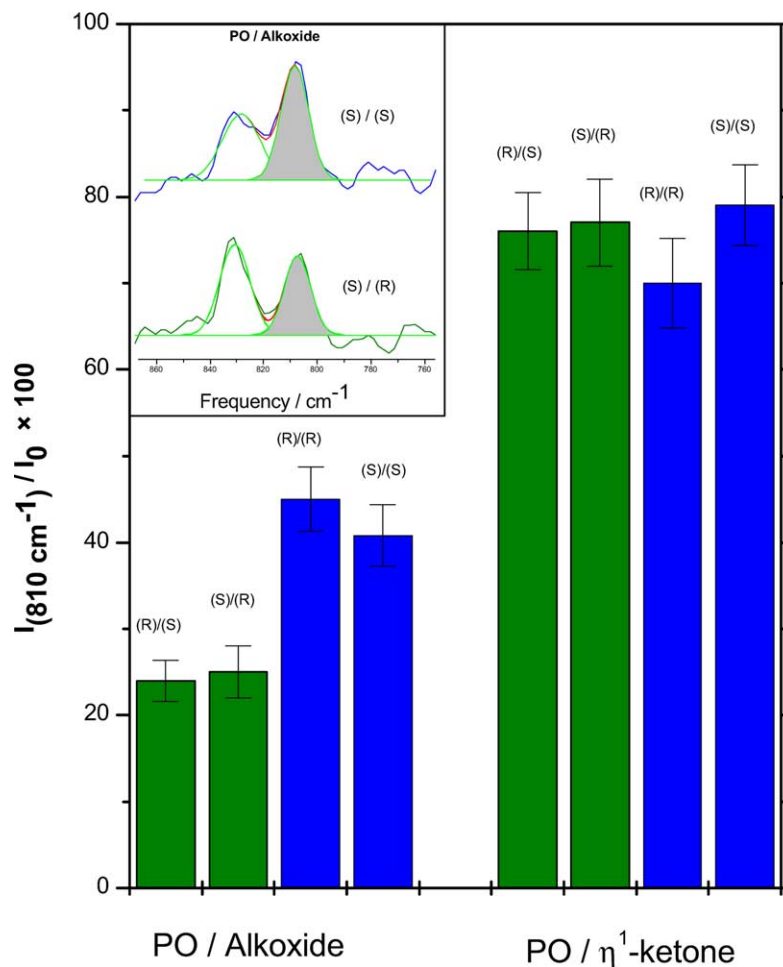


Fig. 7. Histograms showing the relative amounts of propylene oxide adsorbed on a surface prepared by adsorbing 2-butanol on Pd(111) at 80 K, and heating to 150 K. This is indicated as PO/alkoxide. Each histogram is marked by X/Y where X (=R or S) indicates the chirality of the propylene oxide, and Y (=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).

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 [18,19].

Propylene oxide adsorbs molecularly on Pd(111) (Fig. 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 similar manner to that found on Pt(111) [28]. However, unlike the decomposition of propylene oxide found on Pt(111), propylene oxide undergoes no thermal decomposition on Pd(111) and merely desorbs molecularly at between 150 and 250 K, depending on coverage (Fig. 5), similar to the behavior found on copper [20]. 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 (Fig. 4), or by the

desorption temperature in temperature-programmed desorption (Fig. 5). These properties are used to probe enantioselective chemisorption on Pd(111) surfaces chirally modified using 2-butanol.

The results of Fig. 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 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 [2,29]. 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. The evolution of the number of ensembles of adsorbates has been calculated analytically or by using Monte Carlo simulations [30]. It is found that the number of some of these surface ensembles varies as a function of adsorbate coverage in a similar manner to the enantioselectivity of the chiral modifier (Fig. 6). While this does not prove that the observed variation in chemisorptive enantioselectivity is due to the formation of such ensembles, this approach does provide a theoretical framework for analyzing these data.

Infrared experiments (Fig. 7) confirm the temperature-programmed desorption results. These further demonstrate 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, coincident with the loss of the chiral center, as indicated by the histograms labeled PO/ η^1 -ketone in Fig. 7. Thus, the use of simple model systems, such as the one reported here, will allow insights into the fundamental molecular requirements for inducing enantioselective adsorption by chiral modification to be gained. If this is the step in which chirality is introduced into the final product as suggested in Fig. 1, it may ultimately lead to the design of a wide variety of effective heterogeneous catalytic systems.

5. 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 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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