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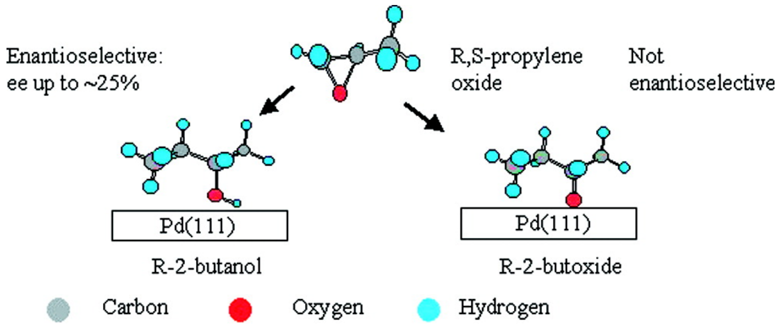

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Enantioselective Chemisorption of Propylene Oxide on a 2-Butanol Modified Pd(111) Surface: The Role of Hydrogen-Bonding Interactions

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Abstract: The enantioselective chemisorption of *R*- and *S*-propylene oxide has been measured either on clean Pd(111) that has been exposed to *S*-2-butanol at various temperatures to vary the proportion of 2-butanol and 2-butoxide species or by adsorbing *S*-2-butanol on oxygen-covered Pd(111) to form exclusively 2-butoxide. The results reveal that enantioselective chemisorption is only found when 2-butanol is present on the surface. This is ascribed to enantiospecific hydrogen-bonding interactions between 2-butanol and propylene oxide. Measurements of the variation in enantiospecificity with 2-butanol exposure suggest that propylene oxide can interact either with a single adsorbed 2-butanol molecule or, at higher coverages, with two adsorbed 2-butanol species to form enantioselective sites.

1. Introduction

The synthesis of chiral pharmaceuticals or agrochemicals often relies on enantioselective catalytic reactions. As part of an effort to understand heterogeneous chiral catalysis, we have previously measured enantioselective chemisorption on Pd(111) under ultrahigh vacuum (UHV) when the surface is chirally modified by *R*- or *S*-2-butanol, where enhanced chemisorption of propylene oxide (PO) of the same chirality as the modifier is found over a narrow 2-butanol coverage range.[1,2] More recently, similar behavior was found on Pt(111).[3] In both cases, the surface species that induce enantioselectivity (the modifier species) was ascribed to 2-butoxide generated by deprotonation of chemisorbed 2-butanol. Indeed, reflection−absorption infrared spectroscopic (RAIRS) measurements following 2-butanol adsorption at 80 K and annealing to 150 K detected a mode assigned to a Pd−O vibration indicating the formation of some 2-butoxide species.[1] The formation of 2-butanone, by β-hydride elimination from adsorbed 2-butoxide species at approximately the same temperature, confirms the formation of some 2-butoxide. However, the largest enantioselective ratio (defined as $(\Theta_{S-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})/(\Theta_{R-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}}))$ of ~1.8 is obtained by adsorbing chiral 2-butanol on Pd(111) at 80 K and subsequently annealing to 150 K.[1,2] In contrast, dosing chiral 2-butanol directly onto Pt(111) at 170 K yielded an enantioselective ratio of less than 1.4.[3] While it is possible that this difference could be due to different substrates, it may be that, by 150 K, the conversion from 2-butanol to 2-butoxide is not complete on Pd(111). Moreover, according to Barteau et al.'s studies of alcohols on Pd(111) using HREELS, a mixture of alcohol and alkoxide species coexists on the surface following alcohol adsorption at low temperatures and annealing to 170 K.[4] This immediately raises questions concerning which of the two species, 2-butanol or 2-butoxide, is the active chiral modifier. In order to address this issue, the following investigates 2-butanol as a chiral modifier by dosing 2-butanol at different temperatures to vary the extent of deprotonation. This effect is further explored by dosing 2-butanol on an oxygen-covered Pd(111) surface, where the presence of coadsorbed oxygen facilitates 2-butoxide formation.[5]

2. Experimental Section

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber operating at a base pressure of 8×10^{-11} Torr that has been described in detail elsewhere[6] where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample. The temperature ramp and data collection were controlled using LabView software. This chamber was also equipped with a double-pass cylindrical mirror analyzer for Auger spectroscopy measurements to gauge the cleanliness of the sample and an ion-sputtering gun for sample cleaning.

The Pd(111) substrate (1 cm diameter, 0.5 mm thick) was cleaned using a standard procedure, which consisted of cycles of argon ion bombardment (2 kV, 1 μA/cm^2) and annealing in 4×10^{-8} Torr of O_2 at 1000 K.[1] The cleanliness of the sample was judged using Auger spectroscopy and oxygen titration, where O_2 instead of CO desorbs following O_2 adsorption when the sample is carbon free. Following each TPD experiment, the surface is briefly annealed once again in O_2 to regain the cleanliness.

Enantiopure 2-butanol and propylene oxide (abbreviated as PO in the following) were obtained from Aldrich, and were purified by

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(1) Stacchiola, D.; Burkholder, L.; Tysoe, W. T. *J. Am. Chem. Soc.* **2002**, *124*, 8984.
(2) Stacchiola, D.; Burkholder, L.; Tysoe, W. T. *J. Mol. Catal. A: Chem.* **2004**, *216*, 215.
(3) Lee, I.; Zaera, F. *J. Phys. Chem. B* **2005**, *109*, 12920.
(4) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1990**, *235*, 235.
(5) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1988**, *197*, 123.
(6) Kaltchev, M. G.; Thompson, A.; Tysoe, W. T. *Surf. Sci.* **1997**, *391*, 145.

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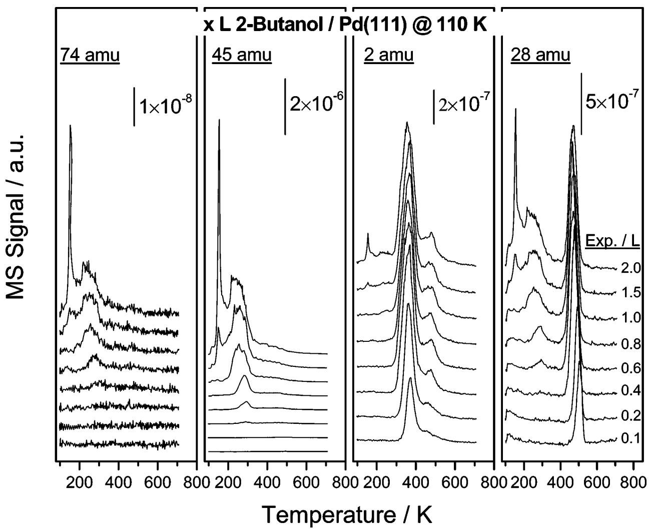

Figure 1. Temperature-programmed desorption profiles collected at 74, 45, 2, and 28 amu using a heating rate of 6.5 K/s following exposure of 2-butanol to clean Pd(111) at a sample temperature of 110 K, where the 2-butanol exposures are indicated adjacent to the corresponding spectrum.

multiple freeze−pump−thaw cycles before adsorption. ^{13}CO (ISOTEC, ≥99% ^{13}C) was used as received.

3. Results

3.1. 2-Butanol Adsorption at 110 K. Figure 1 displays a series of TPD profiles following various 2-butanol exposures at 110 K monitoring desorption at 74, 45, 2, and 28 amu. Both the 74 and 45 amu signals are due exclusively to 2-butanol, where the 74 amu profile is due to the parent mass and 45 amu is the most intense fragment.[7] Clearly, below an exposure of 0.4 L (1 L = 1 × 10^{-6} Torr s; exposures are not corrected for ionization gauge sensitivities), no molecular desorption is detected indicating complete dissociation of adsorbed 2-butanol. At an exposure of 0.6 L, however, a weak molecular desorption state is found at ~290 K, assigned to desorption from the monolayer. This feature shifts to lower temperatures with increasing exposure. At exposures of 1.5 L and above, this feature saturates and simultaneously a multilayer desorption state appears at ~155 K. Interestingly, starting from an exposure of 0.6 L, where molecular desorption becomes detectable, both the 2 (H_2) and 28 (CO) amu yields saturate. Note that the hydrogen desorption profiles contain a dominant feature centered at ~370 K and a much weaker shoulder at ~480 K suggesting multiple stages of dissociation of the surface species that decompose to release hydrogen. Furthermore, at the lowest 2-butanol exposures, CO desorbs at ~506 K, shifting to ~470 K at higher exposures. However, by comparing desorption lineshapes at 74 and 45 amu, the 28 amu signals detected below 400 K are due to fragmentation of 2-butanol.

Note that none of the above-mentioned masses provide a direct measurement of the coverage of 2-butanol. In order to directly measure the monolayer coverage, bare palladium sites are titrated using CO, where isotopically labeled ^{13}CO is used to distinguish it from decomposition products (Figure 1). Figure 2a plots the 29 amu desorption profiles (^{13}CO) using 10 L of ^{13}CO to saturate the (partially covered) surfaces, as a function of 2-butanol exposure where both molecules are adsorbed at 110 K. ^{13}CO desorbs from clean Pd(111) over a wide temperature range, where features below 400 K are assigned to desorption from atop sites, and desorption above 400 K to bridge and 3-fold hollow sites.[8] For 2-butanol exposures of 0.8 L and above, the low-temperature CO features disappear (Note that desorption intensity below 400 K is due predominately to fragmentation of 2-butanol). Even at a 2-butanol exposure of 2.0 L, where multilayer 2-butanol desorption is detected (Figure 1), some ^{13}CO desorption is still detectable at ~470 K and is assigned to a small amount of desorption from the back of the Pd sample and/or sample mounts. Figure 2b plots the integrated ^{13}CO desorption yield as a function of 2-butanol exposure. This shows a linear decrease versus 2-butanol exposure suggesting

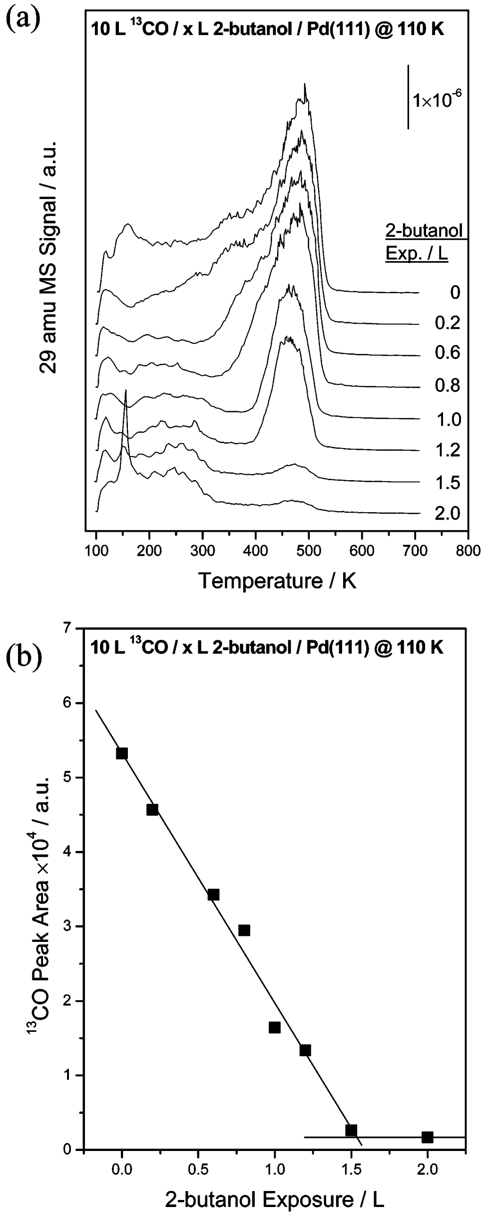

Figure 2. (a) Temperature-programmed desorption profiles collected at 29 amu after exposing 10 L of ^{13}CO to a Pd(111) surface exposed to 2-butanol at 110 K, where the 2-butanol exposures are displayed adjacent to the corresponding spectra. (b) Resulting plot of the integrated ^{13}CO desorption yield versus 2-butanol exposure.

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[7] NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/.

[8] Guo, X.; Yates, J. T., Jr. *J. Chem. Phys.* **1989**, *90*, 6761.

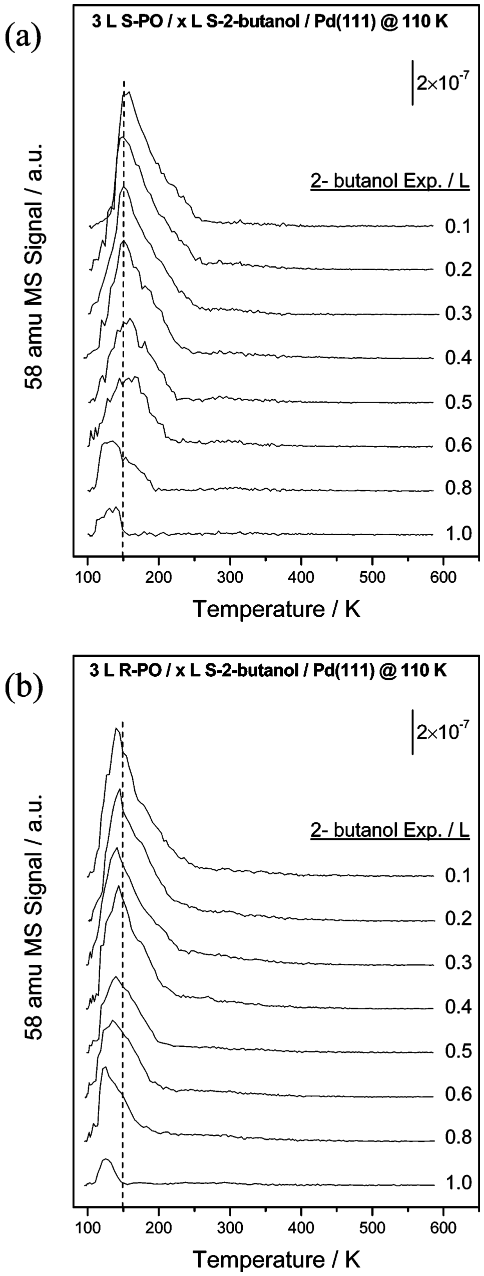

Figure 3. Temperature-programmed desorption profiles collected at 58 amu (propylene oxide) using a heating rate of 6.5 K/s following exposure of a Pd(111) surface covered by *S*-2-butanol at a sample temperature of 110 K and then exposure to (a) 3 L of *S*-propylene oxide and (b) 3 L of *R*-propylene oxide. The 2-butanol exposures are indicated adjacent to the corresponding spectrum.

a constant 2-butanol sticking probability over the whole coverage range.

The chemisorptive enantioselectivity of propylene oxide was explored on a surface modified by 2-butanol adsorbed at 110 K. Figure 3 presents the 58 amu (PO) desorption profiles as a function of *S*-2-butanol exposure, where Figure 3a shows the desorption of *S*-PO and Figure 3b shows the *R*-PO profiles. In these experiments the Pd(111) surface (always held at 110 K) is first exposed to various amounts of *S*-2-butanol and then 3 L of PO prior to TPD measurements. The data in Figure 3 reveal that the PO yield decreases with increasing *S*-2-butanol coverage, as expected from the CO titration results (Figure 2). Note that since PO is adsorbed at 110 K, propylene oxide does not adsorb extensively into the second layer. There are noticeable differences in the desorption temperatures for *R*- and *S*-propylene oxide on the *S*-2-butanol covered surfaces. This is highlighted by the dashed reference lines located at 150 K in each figure. At every *S*-2-butanol exposure, the desorption temperature of *S*-PO is ~5 K higher than that of the corresponding *R*-PO. This, in accord with previous studies,[9] emphasizes the fact that PO molecules interact more strongly with the templates that have the same chirality.

At the highest 2-butanol exposures, an additional propylene oxide feature appears at ~120 K. The data of Figure 2b indicate that at a 2-butanol exposure of ~1 L, for example, only a small portion of the surface is available for CO adsorption, implying that the 120 K propylene oxide feature arises due to adsorption on top of the 2-butanol overlayer. In order to exclude contributions from second-layer propylene oxide, only the desorption yield above 150 K is used to measure enantioselective adsorption onto the palladium surface. Figure 4a plots the integrated PO desorption areas as a function of *S*-2-butanol exposure, and Figure 4b displays the corresponding enantioselective ratios, where the enantioselective ratio of unity for the clean surface is measured by adsorbing *R*- and *S*-PO on clean Pd(111). The error in the measurement of the enantioselective ratio is estimated to be ±0.05. This demonstrates that indeed more *S*-PO adsorbs on the *S*-2-butanol/Pd(111) surface than *R*-PO, and the largest enantioselective ratio of 1.7 ± 0.05 occurs at an *S*-2-butanol exposure of 0.6 L.

3.2. 2-Butanol Adsorption at 130 and 150 K. In an attempt to avoid effects due to possible interference from second-layer propylene oxide adsorption, both 2-butanol and PO were dosed at 130 K. The surface chemistry of 2-butanol was again examined using TPD, and the coverage was measured using ^{13}CO titrations. These results are identical to those found following adsorption at 110 K outlined above and are therefore not shown. Figure 5a plots the desorption profiles of *S*-PO as a function of *S*-2-butanol exposure, and Figure 5b shows the corresponding results for *R*-PO, where again the PO desorption yield decreases with increasing *S*-2-butanol exposure. Figure 6 displays the resulting enantioselectivity ratios as a function of 2-butanol exposure, where the propylene oxide coverage is now obtained from the integrated areas of the whole peak. The enantioselectivity ratios of 1.6 ± 0.05 found for *S*-2-butanol exposures between 0.3 and 0.6 L agree very well with the data of Figure 4. These data again display two maxima in the plot of enantioselectivity versus 2-butanol exposure as found for adsorption at 110 K (Figure 4). The maximum enantioselectivity at low coverages for adsorption at 110 K (Figure 4) is lower than when 2-butanol is adsorbed at 130 K (Figure 6). It is not clear whether this difference is significant or whether it is an artifact that arises from the way in which the integration was carried out to attempt to exclude second-layer contributions. Note especially that, for *S*-2-butanol exposures below 0.3 L, the adsorption of *S*-PO is not blocked by *S*-2-butanol and may even increase slightly, while the coverage of *R*-PO decreases as a function of *S*-2-butanol exposure. This is in line with the higher desorption temperature of *S*-PO and further addresses the stronger interaction between *S*-PO and *S*-2-butanol.

Figure 7 plots the results of similar chemisorptive enantioselectivity measurements following S-2-butanol adsorption at

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[9] Lee, I.; Zaera, F. *J. Am. Chem. Soc.* **2006**, *128*, 8890.

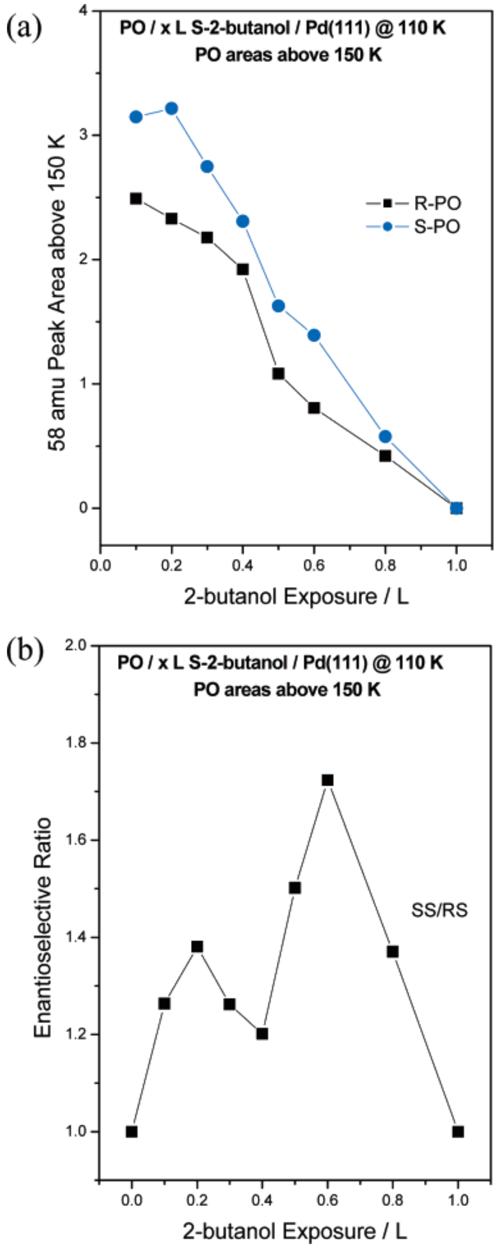

Figure 4. (a) Plot of the integrated propylene oxide desorption yield measured above 150 K to avoid inclusion of the desorption from multilayers, as a function of 2-butanol exposure at 110 K for *R*-propylene oxide (■) and *S*-propylene oxide (●). (b) Plot of the resulting enantioselective ratio (defined as $(\Theta_{S-PO}/\Theta_{S-2-butanol})/(\Theta_{R-PO}/\Theta_{S-2-butanol})$) versus *S*-2-butanol exposure.

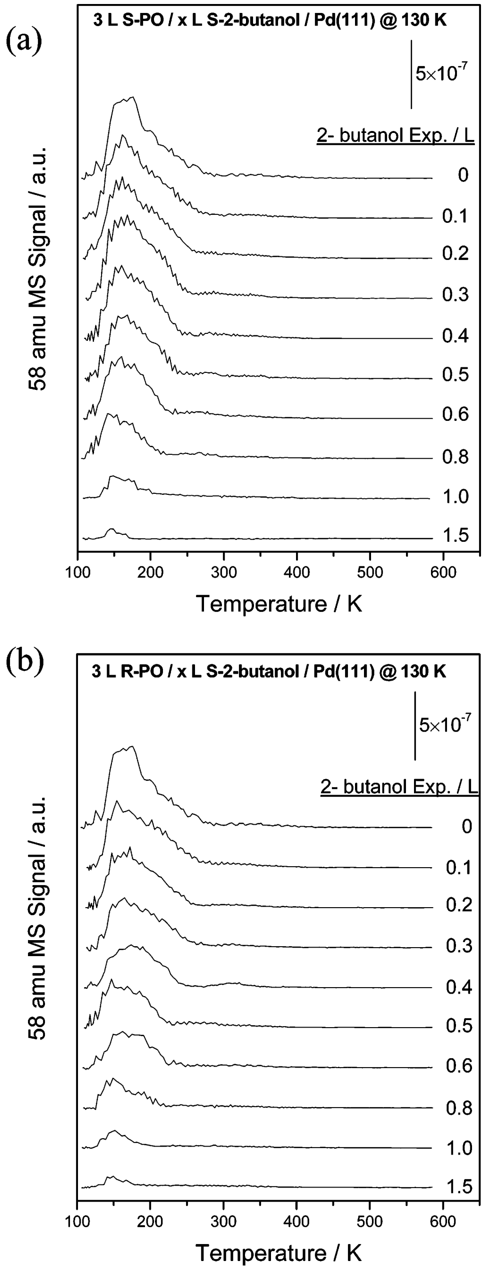

Figure 5. Temperature-programmed desorption profiles collected at 58 amu (propylene oxide) using a heating rate of 6.5 K/s following exposure of a Pd(111) surface covered by *S*-2-butanol at a sample temperature of 130 K and then exposure to (a) 3 L of *S*-propylene oxide and (b) 3 L of *R*-propylene oxide. The 2-butanol exposures are indicated adjacent to the corresponding spectrum.

150 K, followed by PO adsorption at 130 K. Prior to these measurements, the TPD profiles of 2-butanol alone were collected and ^{13}CO titration experiments were also performed to measure the coverage of the bare surface. Again these showed no significant differences from the data in Figures 1 and 2 and are therefore not displayed. As shown in Figure 7b, enantioselective chemisorption is still rather pronounced and the largest ratio of 1.6 ± 0.05 is found at an *S*-2-butanol exposure of ~0.6 L. Note that there are some differences between the adsorption of *S*-2-butanol at 130 and 150 K where the *S*-PO coverage remains constant for *S*-2-butanol exposures below 0.3 L in the former case (Figure 6a). This is not found for 2-butanol adsorption at 150 K (Figure 7a) resulting in a plot of enantioselective ratio versus 2-butanol exposure with a different shape from that found in Figures 4 and 6. It should also be mentioned that data shown in Figure 7 reproduce previous results.[1,2] In this case, in addition to measuring the enantioselectivity of *R*- and *S*-PO on *S*-2-butanol covered surfaces, experiments were also carried out on *R*-2-butanol covered surfaces, which showed enhanced adsorption of *R*-PO.[1,2]

3.3. 2-Butanol Adsorption at 200 K. As shown previously, 2-butanol starts to convert to 2-butoxide species at 150 K as demonstrated by the detection of a Pd−O vibrational mode and concomitant detection of η^1-2-butanone by reflection−absorption infrared spectroscopy.[1] While such reactions have occurred to some extent on heating to 150 K, a substantial portion of 2-butoxide species will only have formed by heating to ~200 K. To address the differences that might occur when 2-butanol

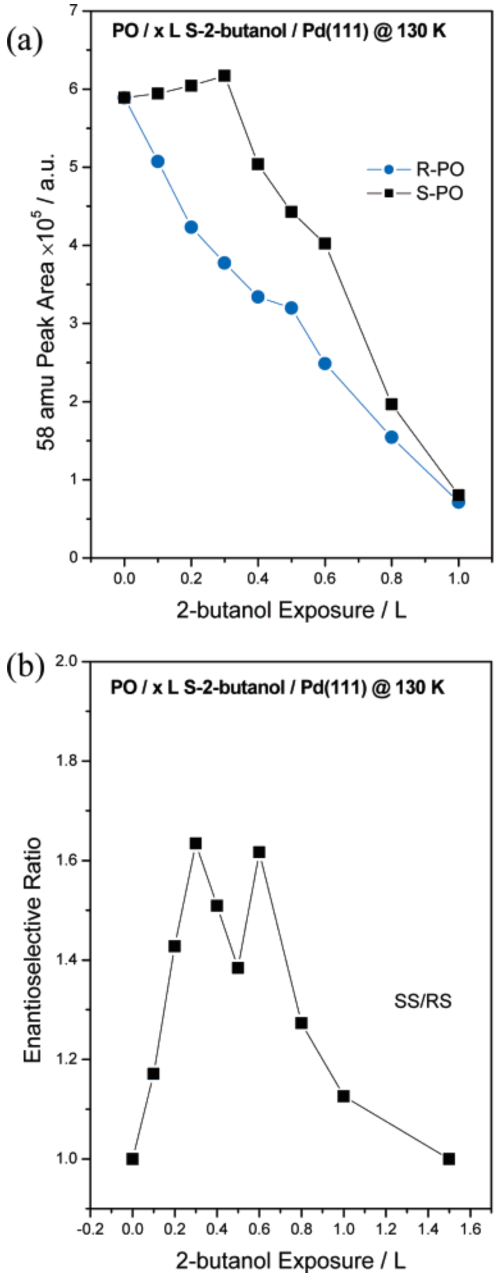

Figure 6. (a) Plot of the integrated propylene oxide desorption yield as a function of 2-butanol exposure at 130 K for *R*-propylene oxide (●) and *S*-propylene oxide (■). (b) Plot of the resulting enantioselective ratio (defined as $(\Theta_{S-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})/(\Theta_{R-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})$) versus *S*-2-butanol exposure.

is adsorbed at 200 K, TPD spectra of 2-butanol were collected and ^{13}CO titration experiments were performed.

Figure 8 plots a series of TPD profiles following various 2-butanol exposures at 200 K, monitoring desorption at 74, 45, 2, and 28 amu where, as expected, no multilayer desorption is detected. 2-Butanol desorbs at exposures of 0.4 L and greater and could originate either from intact 2-butanol desorbing from the surface or alternatively by hydrogenation of 2-butoxide species. The H_2 (2 amu) and CO (28 amu) desorption profiles do not change for a 2-butanol exposure of ~0.6 L and greater, where the maximum hydrogen desorption yield is only ~70% and the maximum CO yield is only ~60% of that found following adsorption at 110 K (Figure 1). Figure 9a plots the ^{13}CO desorption profiles as a function of 2-butanol exposure, and Figure 9b plots the corresponding integrated ^{13}CO desorption peak areas, where both 2-butanol and ^{13}CO were adsorbed at a sample temperature of 200 K. These data display markedly different behavior from that found following adsorption at 110 K (Figure 2) since only ~70% of the Pd surface is blocked, even at 2-butanol exposures of 4 L. This strongly indicates that some surface reaction products desorb easily at 200 K leaving a portion of the Pd(111) surface exposed.

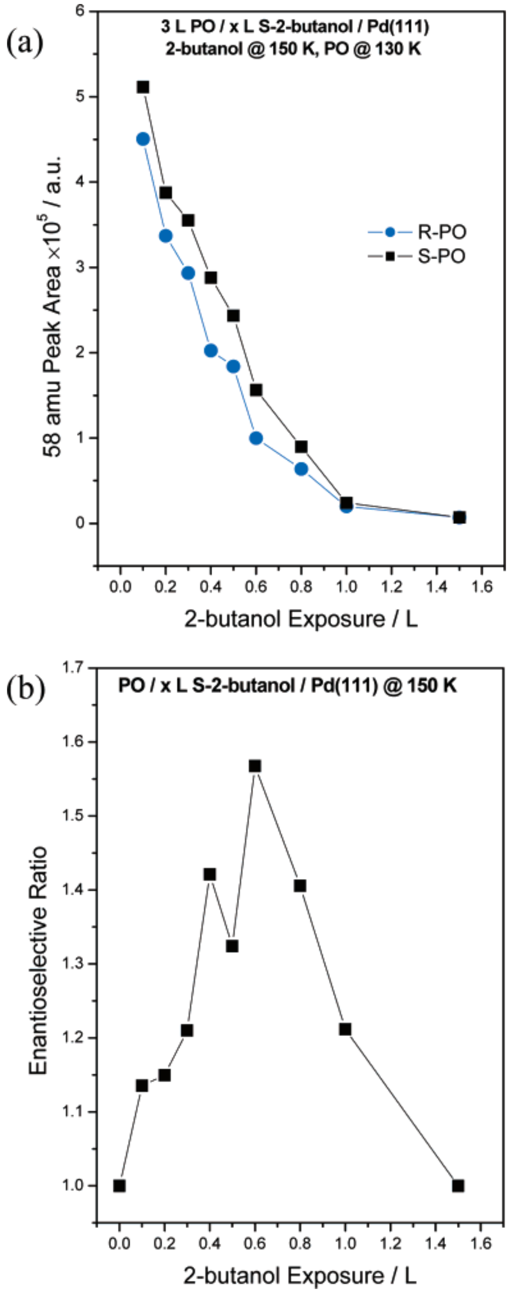

Figure 7. (a) Plot of the integrated propylene oxide desorption yield as a function of 2-butanol exposure at 150 K for *R*-propylene oxide (●) and *S*-propylene oxide (■). (b) Plot of the resulting enantioselective ratio (defined as $(\Theta_{S-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})/(\Theta_{R-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})$) versus *S*-2-butanol exposure.

Figure 10a plots the *S*-PO (58 amu) desorption profiles versus *S*-2-butanol exposure where *S*-2-butanol and *S*-PO are adsorbed at 200 and 130 K, respectively, and Figure 10b displays the corresponding desorption profiles for *R*-PO. It is immediately evident, similarly to the ^{13}CO results, that an *S*-2-butanol overlayer adsorbed at 200 K does not completely suppress PO adsorption. Figure 11a plots the integrated PO desorption peak

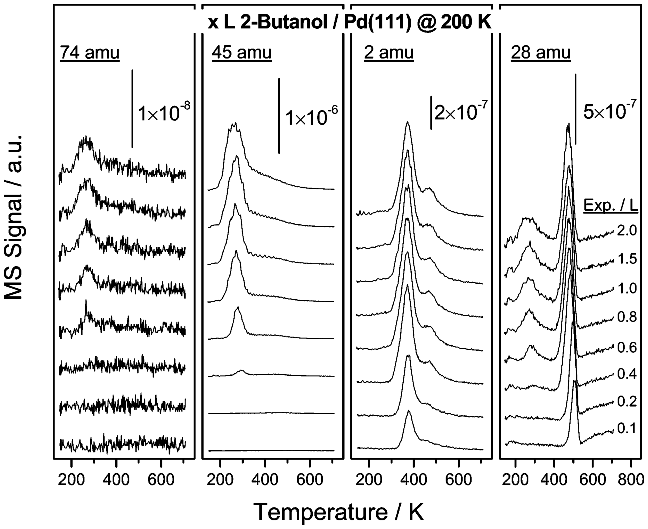

Figure 8. Temperature-programmed desorption profiles collected at 74, 45, 2, and 28 amu using a heating rate of 6.5 K/s following exposure of 2-butanol to clean Pd(111) at a sample temperature of 200 K where the 2-butanol exposures are indicated adjacent to the corresponding spectrum.

areas as a function of *S*-2-butanol exposure, and Figure 11b plots the corresponding enantioselectivity ratios. In this case, the largest enantioselective ratio of only ~1.15 is found at an *S*-2-butanol exposure of 1.0 L. In accord with this observation, no significant shifts in propylene oxide desorption peak temperatures are noted (Figure 10)

3.4. 2-Butanol Adsorption on Pd(111)−(2 × 2)-O Surfaces. The results described above strongly imply that adsorbed 2-butanol rather than 2-butoxide species enantioselectively modify Pd(111). In the experiments described above, 2-butoxide species are generated by adsorbing 2-butanol at 150 and 200 K. However, it is rather difficult to gauge the extent of 2-butoxide formation since it is both coverage and temperature dependent. RAIRS is useful for qualitatively judging the presence of 2-butoxides but is not sufficiently precise to directly measure the relative coverages of 2-butanol and 2-butoxide species. In order to generate a surface that is completely covered by 2-butoxide species, these are formed on a Pd(111)−(2 × 2)-O surface prepared by exposing a Pd(111) single crystal to oxygen at 300 K (100 L) to form a (2 × 2) overlayer.[10]

Figure 12a displays desorption profiles at 72 and 74 amu following exposure of clean Pd(111) to 0.9, 1.2, and 1.5 L of 2-butanol, and Figure 12b displays the corresponding results for Pd(111)−(2 × 2)-O surfaces. 72 amu signals contain contributions from both 2-butanone and 2-butanol. The desorption profile due to 2-butanone alone is readily obtained by performing a simple subtraction using the 72 and 74 amu (exclusively due to 2-butanol) signal intensity ratio of 2-butanol measured using our mass spectrometer (dashed lines). The dotted lines show the resulting 2-butanone desorption profiles. In the case of adsorption on the oxygen-covered surface (Figure 12b), the 72 amu signals are substantially more intense than the 74 amu signals, indicating almost exclusively 2-butanone desorption. The large difference in 2-butanone yield for these two cases suggests that the majority of chemisorbed 2-butanol coverts to 2-butoxide on oxygen-covered Pd(111) that rapidly dehydrogenates to form 2-butanone.

Figure 13 displays the PO desorption profiles on 2-butoxide covered surfaces, where *S*-2-butanol is first adsorbed on Pd(111)−(2 × 2)-O at 150 K to generate surface 2-butoxide species, following which the sample was cooled to 130 K and exposed to 3 L of PO. Figures 13a and b plot the desorption profiles of *S*-PO and *R*-PO, respectively, while Figure 14 plots the PO desorption peak areas versus *S*-2-butanol exposure. Within experimental error, it is clear that the adsorption of both *S*-PO and *R*-PO are identically blocked by *S*-2-butanol. Experiments were also performed by adsorbing 2-butanol on oxygen-covered Pd(111) at 130 and 200 K. In the former case, only very weak enantioselectivity is found, and in the latter case, no enantioselectivity occurs at all (data not shown).

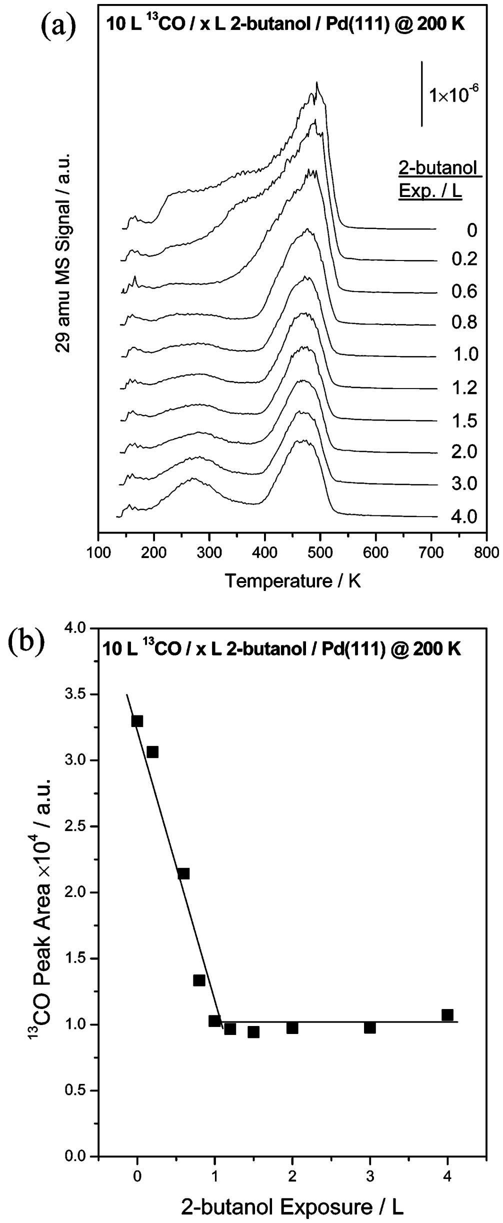

Figure 9. (a) Temperature-programmed desorption profiles collected at 29 amu after exposing 10 L of ^{13}CO to a Pd(111) surface exposed to 2-butanol at 200 K, where the 2-butanol exposures are displayed adjacent to the corresponding spectra. (b) Resulting plot of the integrated ^{13}CO desorption yield versus 2-butanol exposure.

4. Discussion

Adsorbing 2-butanol at 110 (Figure 4), 130 (Figure 6), and 150 K (Figure 7) on clean Pd(111) and then adsorbing PO at 110/130 K yields rather large enantioselectivity ratios with a

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[10] Conrad, H.; Ertl, G.; Küppers, J.; Latta, E. E. *Surf. Sci.* **1977**, *65*, 245.

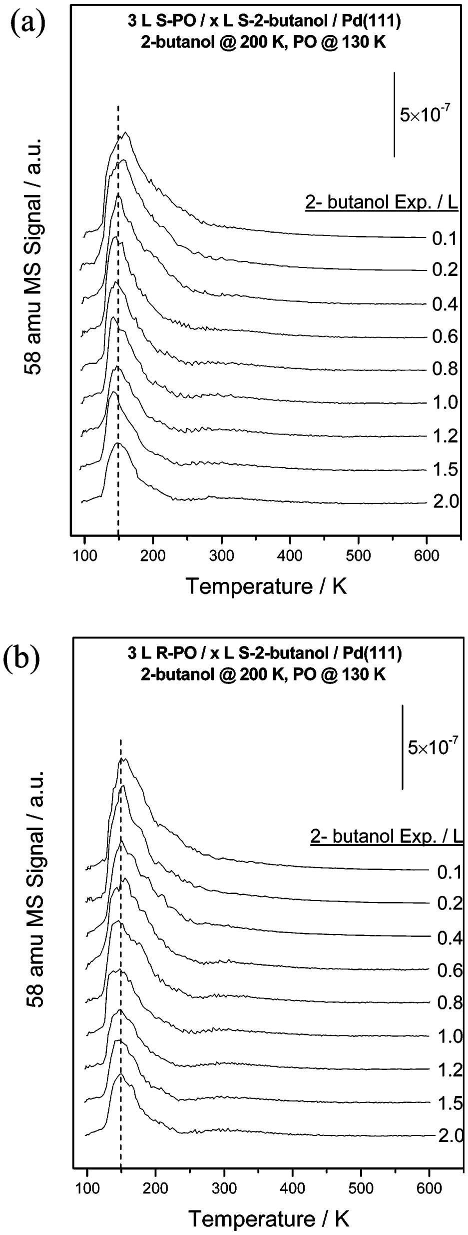

Figure 10. Temperature-programmed desorption profiles collected at 58 amu (propylene oxide) using a heating rate of 6.5 K/s following exposure of a Pd(111) surface covered by *S*-2-butanol at a sample temperature of 200 K and then exposure to (a) 3 L of *S*-propylene oxide and (b) 3 L of *R*-propylene oxide. The 2-butanol exposures are indicated adjacent to the corresponding spectrum.

slight decrease in maximum enantioselectivity ratio with increasing adsorption temperature. These results suggest that 2-butanol rather than 2-butoxide species are responsible for enantioselectively modifying the Pd(111) surface toward propylene oxide. This conclusion is confirmed by carrying out experiments on a Pd(111)−(2 × 2)-O surface, which contains predominately 2-butoxide species, where the data shown in Figure 14 demonstrate that no enantioselectivity occurs on this surface. It should be born in mind that the coadsorbed oxygen or OH species could affect the adsorption of propylene oxide and thereby the enantioselectivity. However, propylene oxide desorbs at the same temperature as that for desorption from the clean surface. This conclusion is confirmed by the very low enantioselectivity found following 2-butanol adsorption at 200 K (Figure 11).

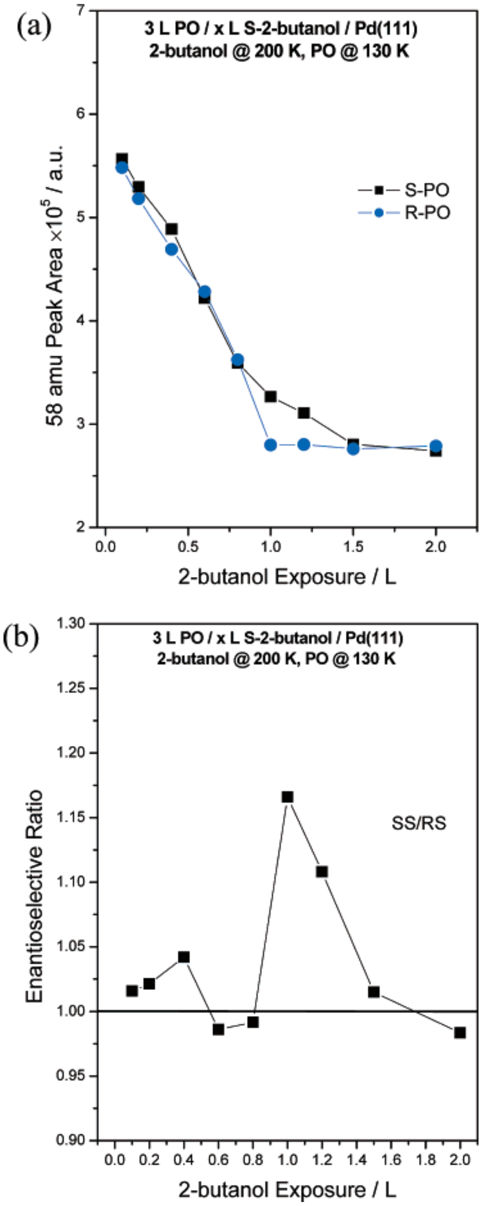

Figure 11. (a) Plot of the integrated propylene oxide desorption yield measured above 150 K to avoid inclusion of the desorption from multilayers as a function of 2-butanol exposure at 200 K for *R*-propylene oxide (■) and *S*-propylene oxide (●). (b) Plot of the resulting enantioselective ratio (defined as $(\Theta_{S-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})/(\Theta_{R-\mathrm{PO}}/\Theta_{S-2-\mathrm{butanol}})$) versus *S*-2-butanol exposure.

Clearly the central difference between 2-butoxide and 2-butanol on the surface is the presence of the −O−H group. Methanol adsorbs on Pd(111) with the C−O bond slightly tilted (at ∼15° to the normal) so that the O−H bond is close to parallel to the surface and is slightly elongated compared to isolated methanol.[11] In contrast, the C−O bond in an alkoxide is oriented perpendicular to the surface.[12] Thus, while the chiral centers in both 2-butanol and 2-butoxide species are identical, they are slightly differently oriented with respect to the surface in each case. In the case of 2-butanol, the tilt may be even less than that for methanol because of potential steric hindrance between the 2-butyl group and the surface. Hydrogen-bonding interac-

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(11) Zheng, T.; Tysoe, W. T.; Poon, H. C.; Saldin, D. K. *Surf. Sci.* **2003**, *543*, 19.

(12) Stacchiola, D.; Burkholder, L.; Zheng, T.; Weinert, M.; Tysoe, W. T. *J. Phys. Chem. B* **2005**, *109*, 851.

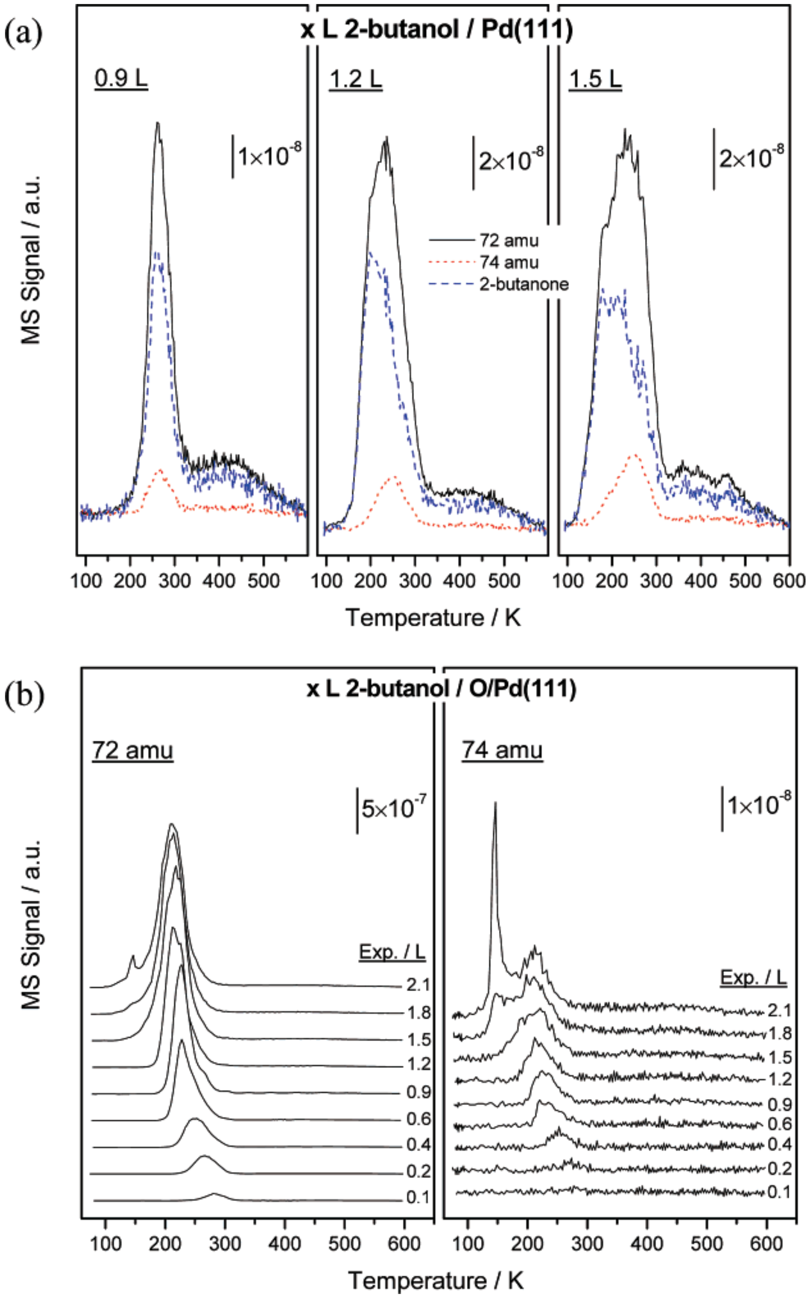

Figure 12. (a) Temperature-programmed desorption profiles collected at 72 (solid line) and 74 (dotted line) following various exposures of Pd(111) to 2-butanol. Shown as a dashed line is the desorption profile due to only 2-butanone calculated by subtracting the contribution due to 2-butanol (see text). (b) Temperature-programmed desorption profiles collected at 72 and 74 amu using a heating rate of 6.5 K/s following exposure of 2-butanol to a Pd(111)−(2 × 2)-O surface, where the 2-butanol exposures are indicated adjacent to the corresponding spectrum

tions are therefore the most likely origin for the difference between 2-butoxide and 2-butanol as chiral modifiers.

It has been found that chiral 2-methyl butanoate species adsorbed on Pd(111), where the chiral 2-butyl group is identical to that in 2-butanol and 2-butoxide species, do not act as chiral templates, while replacing a methyl group with an amine to form 2-amino butanoate species restores enantioselectivity.[12] This effect was previously ascribed to a possible freer rotation of the 2-butyl group that was suggested to average out the chiral asymmetry. The observation that 2-butoxide species do not provide chiral templates offers an alternative rationale for this observation, namely that 2-methyl butanoate also has no hydrogen-bonding sites, while the amino acid, which now imparts enantiospecificity to the surface, does have a site available for hydrogen bonding to the epoxide through the nitrogen-containing group, which is present as a zwitterion on the surface.[13,14] In this case, the hydrogen-bonding interaction would occur between the epoxide oxygen and hydrogen on the amide. The azimuthal rotational barrier for 2-butoxide species on Pd(111) is currently being calculated using density functional theory to explore this effect.[15]

Hydrogen bonding interactions[16] could occur either between adjacent adsorbed 2-butanol species, possibly to order them into

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[13] Gao, F.; Li, Z.; Wang, Y.; Burkholder, L.; Tysoe, W. T. *J. Phys. Chem. C* **2007**, *111*, 9981.

[14] Gao, F.; Li, Z.; Wang, Y.; Burkholder, L.; Tysoe, W. T. *Surf. Sci*. **2007**, *601*, 3276.

[15] Gao, F.; Wang, Y.; Burkholder, L.; Hirschmugl, C.; Saldin, D.; Chuk Poon, H. C.; Sholl, D.; James, J.; Tysoe, W. T. In preparation.

[16] Jeffrey, G. A. *An Introduction to Hydrogen Bonding (Topics in Physical Chemistry)*; Oxford University Press: U.S.A., 1997.

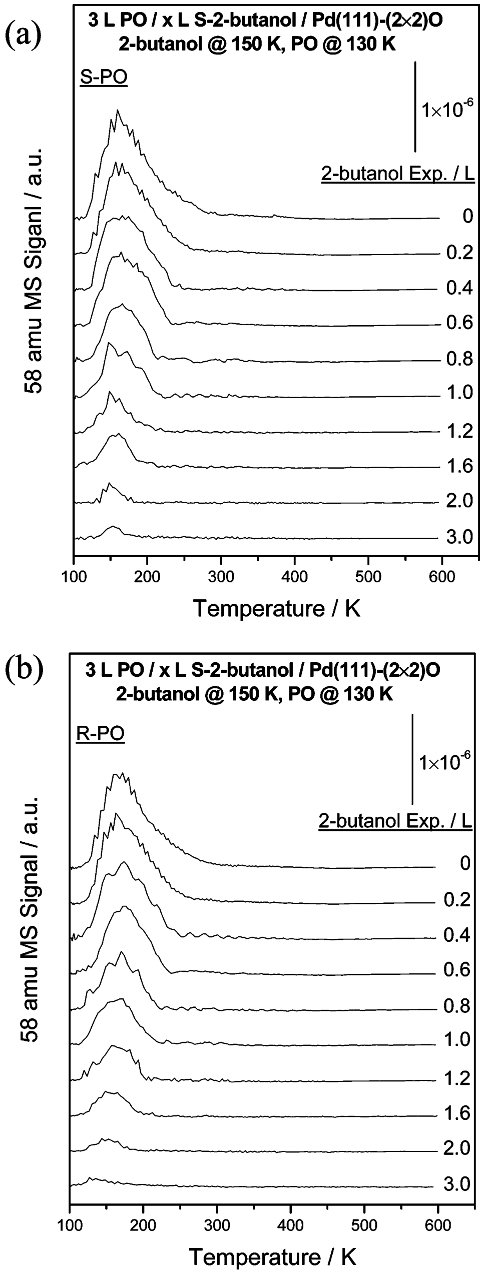

Figure 13. Temperature-programmed desorption profiles collected at 58 amu (propylene oxide) using a heating rate of 6.5 K/s following exposure of a Pd(111)−(2 × 2)-O surface covered by *S*-2-butanol at a sample temperature of 150 K and then exposure to (a) 3 L of *S*-propylene oxide and (b) 3 L of *R*-propylene oxide. The 2-butanol exposures are indicated adjacent to the corresponding spectrum.

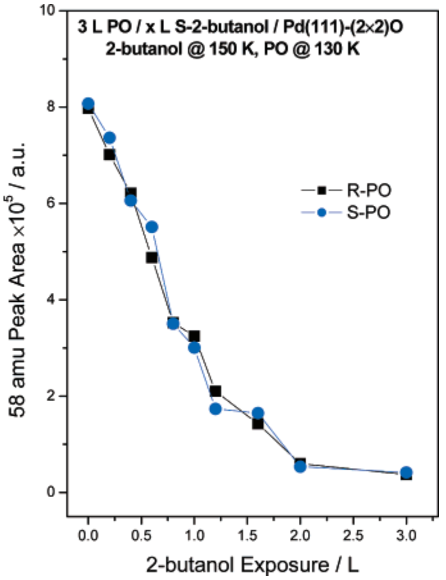

Figure 14. Plot of the integrated propylene oxide desorption yield as a function of 2-butanol exposure to a Pd(111)−(2 × 2)-O surface at 150 K for *R*-propylene oxide (■) and *S*-propylene oxide (●).

enantioselective ensembles, or between propylene oxide and 2-butanol to generate enantiospecific interactions. It is likely that short-range hydrogen-bonding interactions between adsorbed 2-butanol species would not generate an ensemble that would accommodate propylene oxide. In addition, no ordered low-energy electron diffraction pattens have been oberved for 2-butanol or methanol on Pd(111).[11,15] This suggests that enantiospecific hydrogen bonding interactions between 2-butanol and propylene oxide are responsible for the chemisorptive enantioselectivity. The data shown in Figures 4a and 6a, especially the latter, provide direct evidence for the existence of hydrogen bonding between 2-butanol and PO, manifest by the fact that, at low *S*-2-butanol exposures (≤0.3 L), the amount of *S*-PO that adsorbs on the surface is not blocked by adsorbed 2-butanol, and may even increase slightly. For *R*-PO, this behavior does not exist. Presumably, because of enantiospecific steric effects, a hydrogen bond is less easily formed between *S*-2-butanol and *R*-PO. In addition, the stronger interaction between *S*-2-butanol and *S*-PO is reflected by the higher desorption temperature of *S*-PO compared to *R*-PO (Figure 3) where desorption temperature differences of ∼5 K are noted. A Redhead analysis using the experimental heating rate of 6.5 K/s and assuming a standard pre-exponential factor of 1 × 10^{13} s^{-1} yields a desorption activation energy difference of ∼1.3 kJ/mol. Assuming that propylene oxide adsorption is not activated suggests that $\Delta\Delta H_{ads}$(Propylene Oxide) ≈ 1.3 kJ/mol also.

The evolution of various ensembles of modifying molecules with coverage and the resulting effect on enantioselectivity have been explored using Monte Carlo simulations.[17,18] These demonstrate that the enantioselectivity varies as a function of chiral modifier coverage as found experimentally (Figures 4, 6, and 7). The coverage at which the maximum enantioselectivity occurs depends critically on the number of modifiers with which a particular probe interacts, so that, for interaction with a single modifier, the coverage at which the enantioselectivity is a maximum is ∼0.25, interaction with two modifiers on neighboring sites maximizes the enantioseletivity at Θ(Modifier) = 0.5, and interaction with three modifiers predicts a maximum enantioselectivity at Θ(Modifier) = 0.75. The behavior displayed in Figures 4, 6, and 7 can be interpreted in terms of this model by assuming that two different environments provide enantioselective sites when 2-butanol is adsorbed at either 110 or 130 K, leading to the two maxima in the plots of enantioselective ratio versus coverage (Figures 4 and 6), while one type of interaction appears to predominate for 2-butanol adsorbed at 150 K (Figure 7). Note that data obtained at this 2-butanol adsorption temperature are in good agreement with previous

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(17) Roma, F.; Zgrablich, G.; Stacchiola, D.; Tysoe, W. T. *J. Chem. Phys.* **2003**, *118*, 6030.

(18) Roma, F.; Stacchiola, D.; Tysoe, W. T.; Zgrablich, G. *Physica A* **2004**, *338*, 493.

results where a single maximum was also observed.[1,2] This interpretation implies that the enantioselectivity maximum at low coverages (for a 2-butanol exposure of ∼0.2 L, Figures 4 and 6) is due to an enantiospecific interaction between propylene oxide and a single 2-butanol molecule (and is thus formally a one-to-one interaction), while the peak at higher 2-butanol exposures (∼0.6 L, Figures 4 and 6) arises from an interaction between propylene oxide and two 2-butanol templates. Hydrogen bonding between 2-butanol and propylene oxide will occur between the O−H group and the epoxide oxygen, which can clearly accommodate a maximum of two hydrogen-bonding interactions. In this case, enantioselectivity is imparted because of weak van der Waals' interactions between the chiral 2-butyl group and the C_3 portion of the propylene oxide. Presumably tailoring the probes and modifiers to induce stronger hydrogen-bonding interactions between them should result in an increase in enantioselectivity.

When adsorbing 2-butanol at higher temperatures, increasing the 2-butanol exposure will result in an increase in the coverage of both 2-butanol and 2-butoxide species so that the relative coverage of (enantioselective) 2-butanol will be lower at a particular exposure when adsorbed at higher temperatures. This may account for the slight increase in exposure at which the enantioselectivity ratio maximizes following 2-butanol adsorption at 130 K (Figure 6) compared to adsorption at 110 K (Figure 4). A possible explanation, therefore, for the appearance of only a single maximum following adsorption at ∼150 K (Figure 7), where a larger proportion of the surface includes 2-butoxide species, is that the probability of the presence of two adjacent 2-butanol species becomes very low and that this behavior is due to the interaction between propylene oxide and a single 2-butanol. This conjecture is in accord with the data of Figure 11b, where the surface is coveraged predominantly by 2-butoxide species where the maximum enantioselectivity is not observed until the surface has been exposed to ∼1 L of 2-butanol.

The conclusion regarding the importance of directed (hydrogen-bonding) interactions in controlling enantioselective adsorption for a simple model situation of 2-butanol modified surfaces is in complete accord with models used to understand the interaction of substrates with the active sites in enzymes. Furthermore, a model has recently been proposed for the one-to-one interaction between a naphthyethylamine (NEA) modifier and prochiral reactants[19] and was able to correlate stereospecific hydrogen-bonding interactions between a range of reactants and NEA that correleted well with measured ee values in heterogeneous catalysis.

5. Conclusions

The enantiospecific adsorption of either *R*- or *S*-propylene oxide is studied on surfaces modified by *S*-2-butanol, which is adsorbed either on clean Pd(111) at various temperatures to form surfaces with varying amounts of 2-butanol and 2-butoxide species or on oxygen-covered Pd(111) to form exclusively 2-butoxide-covered surfaces. It is found that the measured chemisorptive enantioselectivity decreases as more 2-butoxide species are present on the surface so that, for example, on an oxygen-covered surface, where exclusively 2-butoxide species form, no enantioselectivity is found. This suggests that the enantioselectivity originates from a hydrogen-bonding interaction between propylene oxide and 2-butanol. This also explains why 2-methyl butanoate species on the surface do not exhibit enantiospecificity toward propylene oxide, since there are no direct hydrogen-bonding interactions between the modifier and probe. The plots of enantioselective ratio versus 2-butanol exposure when 2-butanol is adsorbed on Pd(111) at low temperatures exhibit two maxima. This observation is interpreted in terms of a statistical model suggesting that the peak at low exposures is due to an interaction between propylene oxide and a single 2-butanol, while the maximum at higher 2-butanol exposure is due to an interaction between propylene oxide and two 2-butanol species.

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