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Metastable De-excitation Spectroscopy and Density Functional Theory Study of the Selective Oxidation of Crotyl Alcohol over Pd(111)

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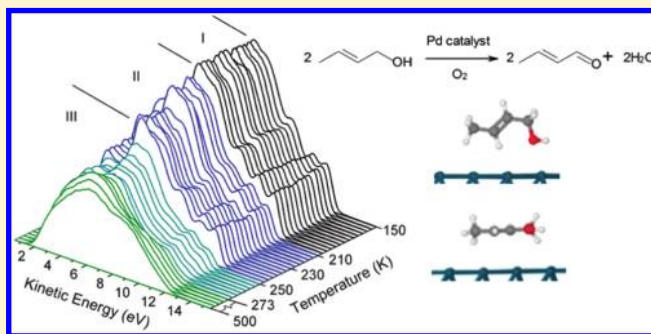
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ABSTRACT: The extremely surface sensitive technique of metastable de-excitation spectroscopy (MDS) has been utilized to probe the bonding and reactivity of crotyl alcohol over Pd(111) and provide insight into the selective oxidation pathway to crotonaldehyde. Auger de-excitation (AD) of metastable He (2^3S) atoms reveals distinct features associated with the molecular orbitals of the adsorbed alcohol, corresponding to emission from the hydrocarbon skeleton, the O n nonbonding, and C=C π states. The O n and C=C π states of the alcohol are reversed when compared to those of the aldehyde. Density functional theory (DFT) calculations of the alcohol show that an adsorption mode with both C=C and O bonds aligned somewhat parallel to the surface is energetically favored at a substrate temperature below 200 K. Density of states calculations for such configurations are in excellent agreement with experimental MDS measurements. MDS revealed oxidative dehydrogenation of crotyl alcohol to crotonaldehyde between 200 and 250 K, resulting in small peak shifts to higher binding energy. Intramolecular changes lead to the opposite assignment of the first two MOs in the alcohol versus the aldehyde, in accordance with DFT and UPS studies of the free molecules. Subsequent crotonaldehyde decarbonylation and associated propylidyne formation above 260 K could also be identified by MDS and complementary theoretical calculations as the origin of deactivation and selectivity loss. Combining MDS and DFT in this way represents a novel approach to elucidating surface catalyzed reaction pathways associated with a “real-world” practical chemical transformation, namely the selective oxidation of alcohols to aldehydes.



INTRODUCTION

The selective aerobic oxidation (selox) of allylic alcohols by heterogeneous catalysts presents a green and economically attractive route to their corresponding aldehydes. These compounds are important fine chemicals used as food preservatives, fragrances, and flavorings.^{1,2} Despite the obvious process, safety, and environmental advantages afforded by heterogeneously catalyzed selox, a lack of detailed knowledge regarding the adsorption mode, optimal reaction conditions, activation protocols and deactivation pathways hinders commercial allylic aldehyde production without recourse to stoichiometric oxidants or expensive homogeneous complexes.

To improve insight into the surface reaction pathway, deactivation mechanism and nature of the active site in selox, ultra-high vacuum (UHV) techniques have been employed to probe the chemistry of allylic alcohols on transition metal surfaces, e.g., allyl alcohol on Ag(110),^{3,4} Cu(110),⁵ Rh(111),⁶ Pd(111),⁷ and Pd(110).⁸ The most promising heterogeneous catalysts are derived from the platinum group and noble metal clusters, although these are prone to rapid on-stream deactivation.⁹ Crotonaldehyde (but-2-enal) is an important precursor to sorbic acid

and vitamin E and is prepared via the selox of crotyl alcohol (but-2-en-1-ol), as shown in Scheme 1. Supported Pd nanoparticles are particularly promising alternative clean technologies to traditional oxidizing reagents.^{1,9–11}

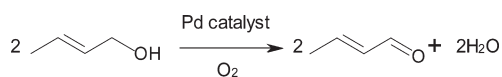
Our understanding of the deactivation mechanism in crotyl alcohol selox over palladium has been greatly enhanced through operando X-ray absorption studies (XAS) of nanoparticles,¹² and temperature programmed X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) measurements of Pd(111) model catalysts.¹³ XPS revealed that aldehyde decomposition and associated self-poisoning prevails over Pd(111), and XAS identified electron deficient Pd²⁺ centers as active for allylic alcohol selox.¹⁴ At low temperature, NEXAFS indicated the C=C bond in crotyl alcohol lay parallel to Pd(111), similar to allyl alcohol (2-propen-1-ol) on Ag(110).³ Although powerful synchrotron methodologies can offer invaluable insight

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Scheme 1. Selective Aerobic Oxidation of Crotyl Alcohol to Crotonaldehyde



into surface reaction mechanisms,¹⁵ demand for such facilities is high and complementary laboratory techniques are needed.

Metastable de-excitation spectroscopy (MDS), which utilizes the energy associated with the metastable states of rare-gas atoms (usually the 2^3S level of He) to induce electron emission from a surface or molecule,¹⁶ is well suited to studying molecular adsorbates but has been little exploited in catalysis. For adsorbates, de-excitation of He 2^3S atoms generally involves a pseudo-one-electron transition in a process that is similar to photoemission, but with the advantage that (unlike ultraviolet photoemission spectroscopy (UPS)) there is no penetration of the probe beam into the bulk. This renders MDS extremely surface sensitive and enables the adsorbate local density of states (LDOS) at energies close to the Fermi level, E_F , to be studied in isolation. Occupied electronic states appear in this energy region as a result of chemisorption bond formation but are largely masked in UPS due to dominant emission from metallic d-band states. As such, MDS has been widely employed in a number of previous studies investigating the electronic properties of simple chemical adsorbates on a variety of metal surfaces.¹⁶ Here we utilize MDS, in conjunction with density functional theory (DFT) calculations, to examine the adsorption mode and surface chemistry of crotyl alcohol in hitherto unprecedented detail over a catalytically active Pd(111) model catalyst. This approach has provided new physical insight into the molecular orientation and bonding of crotyl alcohol, and of the relative stability and electronic properties of the desired selox product, crotonaldehyde.

EXPERIMENTAL METHODS

Experiments were performed in a stainless-steel UHV system with a base pressure of $\sim 1 \times 10^{-10}$ Torr. The system comprises a preparation chamber; equipped with low energy electron diffraction (LEED), an analysis chamber; equipped with Auger electron spectroscopy (AES), and a beamline for metastable He 2^3S generation. Full details of the experimental setup are described elsewhere¹⁷ but will be briefly outlined below. The Pd(111) single crystal sample could be heated using a pyrolytic boron nitride (PBN) heater to 1000 K and cooled to ~ 150 K using a gas baffle cooled by liquid nitrogen. Preparation of a clean substrate was carried out in the preparation chamber and utilized cycles of Ar^+ sputtering followed by annealing to 1000 K until LEED showed a clean well-ordered surface. Oxygen (Air Liquide, 99.998%) was then dosed as received into the chamber background to obtain a pressure of 1×10^{-7} Torr, while the sample was heated to 800 K to remove residual carbon. The sample was also cooled in oxygen so as to saturate the surface, before flashing to ~ 930 K to desorb oxygen and any remaining contaminants. This procedure was repeated several times, until AES revealed no surface impurities. AES is insensitive to the presence of surface carbon on a Pd substrate below ~ 0.25 monolayer; however, the effectiveness of this cleaning procedure has previously been confirmed using temperature-programmed desorption (TPD) studies where the lack of CO or CO_2 desorption in the acquired spectra can be taken as evidence for a carbon-free surface.¹⁸

Once prepared, the sample was immediately transferred into an analysis chamber to record MDS spectra. Crotyl alcohol (Aldrich, 96%) was purified by repeated freeze–pump–thaw cycles prior to background dosing (purity checked by mass spectrometry (MS)). Quoted exposures are given in langmuirs ($1 \text{ langmuir} = 1 \times 10^{-6} \text{ Torr s}^{-1}$) and are uncorrected for ion gauge sensitivity. Generally, a clean Pd(111) surface was exposed to 3 langmuirs of crotyl alcohol with the substrate at 150 K. This dose is known to be large enough to produce a 0.15 monolayer saturation coverage of chemisorbed molecules for this system.¹³ Additional physisorbed molecules may also be present on top of this saturation layer depending on the substrate temperature.

The metastable He 2^3S beam was generated using a liquid-nitrogen cooled, copper cathode, dc discharge source, the output of which was manipulated using techniques of laser cooling to provide an ultrapure and intense He 2^3S atom beam at the sample.¹⁷ Electrons ejected as a result of metastable atom de-excitation were collected in the normal direction using a hemispherical energy analyzer (Omicron EA125). A He I discharge source (Focus GmbH) was used in UPS experiments with normally emitted electrons detected by the same analyzer as for MDS. For both spectroscopies, the angle of incidence of the probe beam was 45° .

THEORETICAL CALCULATIONS

DFT calculations were also conducted to aid interpretation of the MDS results. All theoretical calculations in this work used the CASTEP¹⁹ ab initio DFT code. The Perdew–Burke–Ernzerhof²⁰ generalized gradient approximation was used to represent exchange and correlation effects. We have used ultra-soft pseudopotentials with a cutoff energy of 350 eV and a Monkhorst–Pack²¹ reciprocal space sampling grid with a density of 0.04 \AA^{-1} . Convergence testing showed that the calculated energies and spectra were not affected by any further increase in the cutoff energy or the sampling grid density.

The supercell comprised three layers of bulk Pd with a vacuum gap of 20 Å. Additional layers were shown to have no effect on the DOS for the bare Pd surface. Molecules were adsorbed on one face of the slabs and to minimize interactions between vertical periodic images we used a large vacuum gap which meant that adjacent surfaces were over 30 Å apart. Adsorbates were arranged in a 3×3 grid, resulting in a lateral spacing of around 11 Å. The 0.15 monolayer saturation coverage for crotyl alcohol on Pd(111) has a 7×7 periodicity, although computational resources prevent the use of such a large supercell. The consequent small lateral interactions in the simulated energies and spectra are another source of approximation error to be considered when comparing experiment and theory.

The molecules were initially positioned a few Å above the surface in various specific orientations (Figure 3) and then relaxed to determine the optimum bonding geometry for each case. The optimization convergence tolerance for the forces was $0.01 \text{ (eV \AA}^{-1})$ and adsorption energies were calculated using the formula

$$E_a = E_{\text{CrOH/Pd}} - E_{\text{CrOH}} - E_{\text{Pd}}$$

where $E_{\text{CrOH/Pd}}$ is the total energy after optimization of the adsorbed crotyl alcohol molecule, E_{CrOH} is the relaxed energy of the isolated molecule, and E_{Pd} is the energy of the relaxed clean surface. DOS spectra for the optimized molecules were calculated

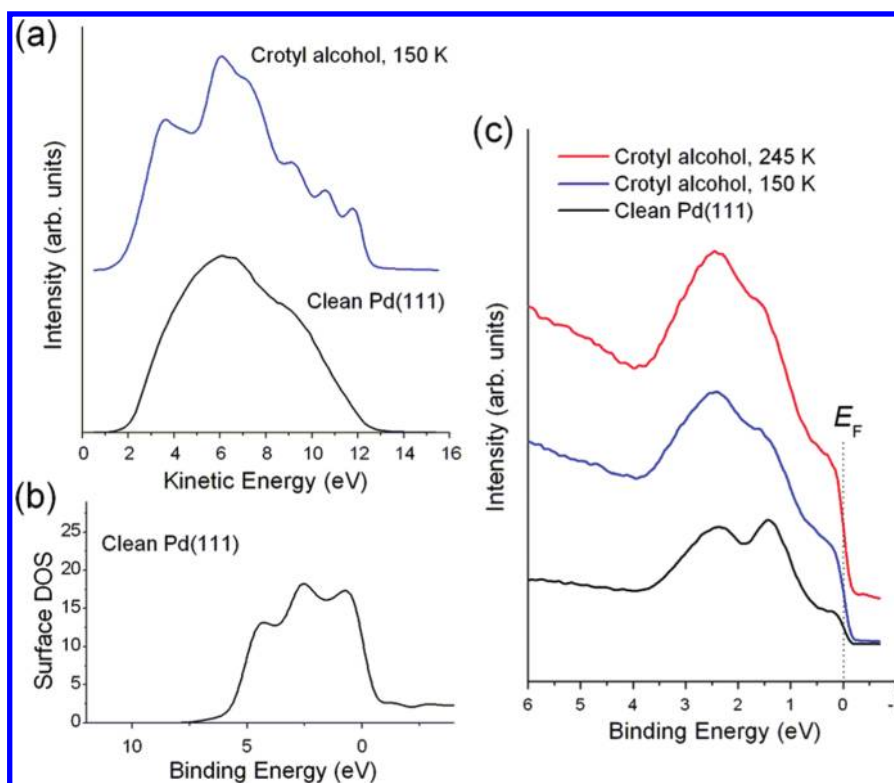


Figure 1. (a) MDS spectra from a clean Pd(111) surface where the dominant de-excitation mechanism is resonance ionization followed by Auger neutralization, and from a saturation coverage of crotyl alcohol where significant Auger de-excitation takes place. (b) DFT calculation for clean Pd(111) showing metallic d-band states close to E_F . (c) UPS spectra for clean Pd(111) and for a surface exposed to a 3 langmuir saturation coverage of crotyl alcohol at 150 and 245 K.

using Mulliken population analysis which determines the contribution from each energy band to a given atomic orbital.

RESULTS AND DISCUSSION

De-excitation of metastable He atoms at clean, transition metal surfaces is well-characterized and proceeds via the two-stage mechanism of resonance ionization (RI) followed by Auger neutralization (AN) (see ref 16 for a thorough review). When approaching a clean Pd(111) surface to within a distance of around 5 Å, overlap of the occupied 2s orbital of the He atom with an empty surface state above E_F allows a tunneling transition to take place (RI). The resulting He^+ ion continues to approach the surface until a further transition from the surface valence band to the empty ground-state He 1s level occurs to neutralize the atom. The energy liberated in this process results in the emission of a second electron from the valence band in an Auger-type process (AN). As the kinetic energy of this electron is determined by the binding energies of both initial valence band states involved in the de-excitation, the resulting energy spectrum for RI + AN is essentially a self-convoluted map of the surface DOS (SDOS) modified by the de-excitation transition probability (transition matrix elements),²² leading to broad and generally featureless spectra, as seen in the bottom spectrum of Figure 1a for the clean Pd(111) surface. Strong emission is observed in the region several eV below the kinetic energy maximum, $E_{k,\text{max}}$ which occurs when both electrons involved in the de-excitation process originate at E_F . Occupied Pd(111) surface states with a binding energy of 0–2 eV have been shown

to have a significant local density at the surface layer and at distances of up to 3 Å away from the surface where AN transition rates are highest,²³ and these account for the appearance of the spectrum at high kinetic energies. At lower energies, the spectrum is dominated by true secondary electrons.

In contrast to the dominant role the SDOS plays in the AN process, penetration of UV photons into the bulk-like second atomic layer and beyond leads to features in the corresponding UPS spectrum arising from the bulk DOS (BDOS), specifically d-band electronic states (Figure 1c). This assignment is confirmed by DFT calculations by ourselves (Figure 1b) and others,²⁴ which show strong d band peaks at energies of several eV below E_F , accounting for the peaks at ~ 1.4 and ~ 2.4 eV. Figure 1c also shows UPS spectra for a clean surface exposed to 3 langmuirs of crotyl alcohol with the substrate at 150 and 245 K. The metallic d states that feature so prominently in the clean spectrum are still dominant although are somewhat attenuated by the adsorbate layer. A previous UPS study utilizing gas-phase crotyl alcohol as part of a composite molecular determination of the spectral features of opiate narcotics revealed many distinct molecular orbitals (MOs),²⁵ as did a further UPS study of allyl alcohol.²⁶ However, for adsorption at both 150 and 245 K, direct emission from these orbitals is lacking. Considering the penetration of UV photons below the adsorbate layer, it is not surprising that metallic d states dominate the UPS spectra highlighting one of the benefits of using the more surface sensitive technique of MDS to study the surface electronic properties of adsorbed molecules.

At adsorbate-covered surfaces, the empty electronic states of the substrate are effectively shielded by the molecule, thereby

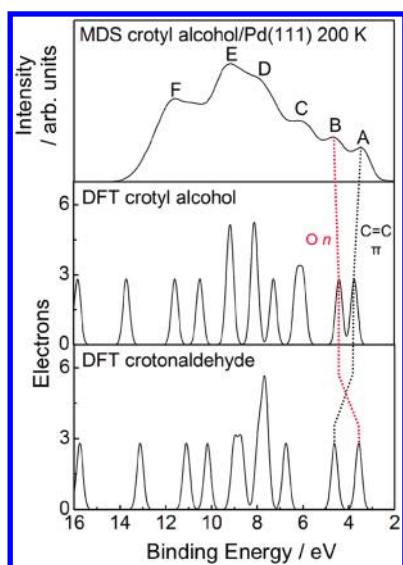


Figure 2. DFT calculated spectra for free crotyl alcohol and crotonaldehyde molecules, and the analogous MDS spectrum obtained after a Pd(111) surface at 150 K was exposed to 3 langmuirs of crotyl alcohol followed by subsequent heating to 200 K.

suppressing the RI process so that the He 2^3S atom continues to approach the surface. At a point where a molecular orbital (MO) of the adsorbate overlaps with the empty He 1s ground state, a tunneling transition occurs, stimulating the simultaneous release of the excited He 2s electron. As a quasi-one-electron process, this Auger de-excitation (AD) is reminiscent of photoemission and leads to emission spectra with features corresponding to distinct molecular electronic states. This is evident in Figure 1a, which also shows the MDS spectrum for a 3 langmuir saturation exposure of crotyl alcohol adsorbed onto Pd(111) at 150 K. Emission peaks are superimposed on a background arising from de-excitation via RI + AN. The exact balance between the two de-excitation channels is determined by their relative transition rates, Γ_{AD} and Γ_{RI} , with the former depending on the coverage, adsorption site, and geometry of the molecule. The AD spectrum reflects the DOS of the adsorbed species weighted by the overlap with the He 1s wave function meaning that electron emission from the outermost MOs of the adsorbed molecules is strongly favored. Therefore the features present in the spectrum represent the local DOS of the adsorbate in the energy range close to E_F , which may be strongly modified by interaction with the surface.¹⁶ For Γ_{AD} to be comparable to Γ_{RI} , the outermost electronic states of the adsorbed crotyl alcohol must extend beyond ~ 3 Å from the substrate surface to efficiently suppress RI. This is approximately equal to the van der Waals radius of sp^2 -hybridized carbon and so appreciable AD can be expected at a saturation coverage of crotyl alcohol even for a coplanar adsorption geometry.

DFT Results. DFT calculations were performed to gain further insight into the MDS spectra. Figure 2 shows the calculated DOS for the isolated molecules of crotyl alcohol and crotonaldehyde along with the MDS spectrum for the alcohol-adsorbed Pd(111) surface. The binding energy scale for the latter was calculated by taking the Fermi level position as the high-kinetic-energy cutoff for Auger de-excitation (Figure 6). Features D and E are most probably due to emission from both deeper lying MOs of the adsorbed alcohol and the clean Pd(111) surface. Low-energy secondary electrons account for feature F. Peaks attributed to

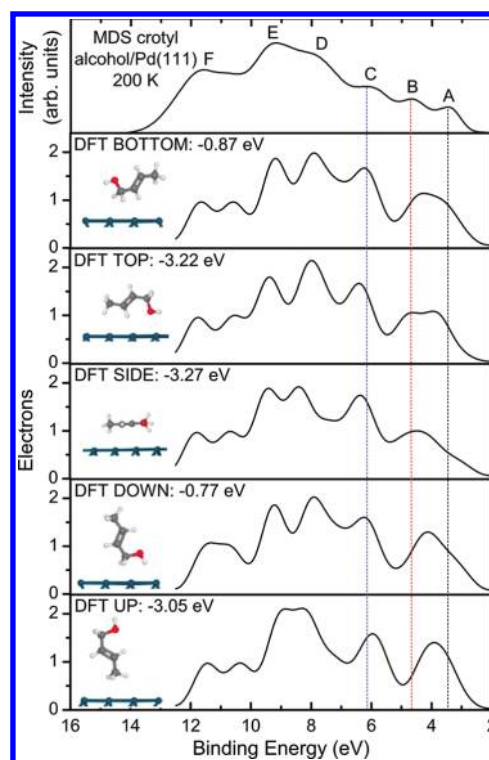


Figure 3. DOS spectra of crotyl alcohol calculated by DFT for the molecular adsorption states shown at the side of each panel. The MDS spectrum presented in Figure 2 (from a 3 langmuir exposure of crotyl alcohol) is also shown here for comparison along with the calculated adsorption energies for each molecular geometry.

emission from the hydrocarbon skeleton of the alcohol, the O n nonbonding, and $C=C$ π states are labeled as C, B, and A, respectively. Interestingly, a previous UPS comparison of allyl alcohol and acrolein²⁵ determined that the two lowest energy MOs of these molecules effectively switched positions, as indicated in Figure 2 and discussed further below.

DFT calculations were then performed to examine the energetics and calculate the spectra of five different molecular orientations of the adsorbed alcohol. Three calculations were performed with the molecule laid flat on the surface (labeled as TOP, BOTTOM, and SIDE) and two additional calculations with the molecule in an end-on configuration (referred to as UP and DOWN), the results of which are shown in Figure 3 along with the calculated adsorption energies for each molecular orientation. It should be noted that the lateral position above the surface does not appear to greatly affect the partial DOS, as the energy differences are below the level of noise and therefore not significant. From this data, we can observe that energetically, the most favorable orientation is that of the molecule adsorbed parallel to the surface, on its side (SIDE = -3.27 eV). The energy of the molecule adsorbed flat onto the surface, with the oxygen and carbon backbone in contact with the Pd, is comparable to that of the "TOP" configuration (TOP = -3.22 eV). Interestingly, our work also shows that it is also favorable for the molecule to adsorb in an end-on configuration with the oxygen pointing up, away from the surface (UP = -3.05 eV). It is unlikely that such a geometry would provide the bonding interactions necessary to account for the observed high binding energy suggesting that van der Waals interactions may be contributing. A future extension

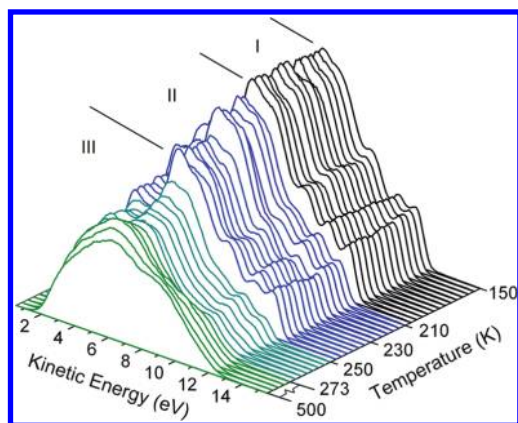


Figure 4. Temperature evolution of MDS spectra for a Pd(111) surface exposed to a 3 langmuir dose of crotyl alcohol at 150 K. Temperature regimes where noticeable changes in the spectra occur are highlighted with different colors and grouped together into three distinct adsorption regimes. Note the nonlinear temperature scale above room temperature.

of this work could see these explicitly incorporated in a DFT-D calculation.

The DOS for each orientation is also shown in Figure 3 along with a comparative MDS spectrum of the alcohol presaturated Pd(111) surface. As mentioned previously, peaks C, B, and A are due to emission exclusively from the adsorbed molecule, and as such the following analysis will focus on these states. It should be noted that DFT calculations reflect the plane-averaged DOS so that although the general trends and positions of electronic states may be compared to MDS spectral features, their relative intensities may differ due to the surface sensitivity of MDS. With that said, from both sets of data, judging by the shape and intensity of the peaks and also the calculated adsorption energies, it is clear that the “SIDE” and “TOP” molecular orientations yield the best agreement between theory and experiment although distinguishing between these is not possible on the basis of the present data. “BOTTOM” and “DOWN” can be excluded on the basis of their calculated energies whereas the “UP” configuration has the poorest agreement with the experimental spectrum. It may be possible that a tilted geometry or molecular distortion yields an adsorption geometry that is somewhere between “SIDE” and “TOP”. It is clear, however, that both the C=C and O bonds are somewhat coplanar to the substrate, allowing access to the metastable He probe and giving rise to the features observed. This assertion is supported by previous NEXAFS studies of crotyl alcohol on Pd(111)¹³ and allyl alcohol on Ag(110),³ which suggest these molecules adsorb with the allyl moiety coplanar to the Pd substrate, a geometry that permits strong bonding. Additionally, previous DFT calculations²⁷ have shown that, over Pd(111), allylic alcohols predominantly chemisorb via di- σ coordination of the C=C π bond complemented by a weaker interaction between an O lone pair on the $-H_2C-OH$ functionality and an atop Pd site.

Temperature Programmed MDS. With the assignment of states complete, we now address the temperature evolution of the spectra.

Figure 4 shows the evolution of MDS spectra taken after a clean Pd(111) surface was exposed to a 3 langmuir dose of crotyl alcohol at 150 K and then allowed to warm to room temperature before being heated further to 500 K. Detailed analysis of the spectra reveal different temperature regimes, highlighted in the figure, with sometimes only subtle variations in the spectral

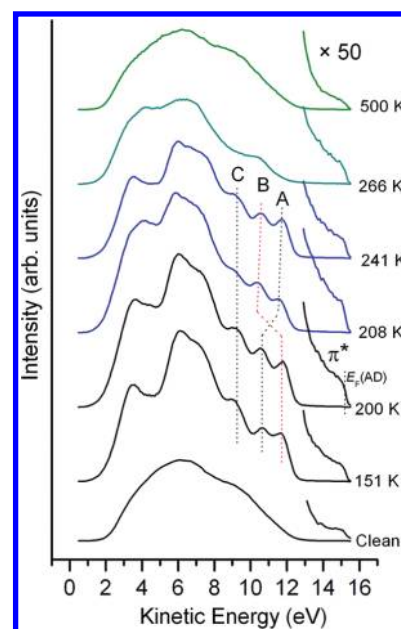


Figure 5. MDS spectra obtained at critical temperatures from a Pd(111) substrate exposed to 3 langmuirs of crotyl alcohol with the substrate at 150 K, and subsequent progressive heating to 500 K. Key features in the spectra are labeled A, B, and C, the assignment of which is detailed in section I.

features. To emphasize these differences and aid a discussion of the reaction mechanism, representative spectra from each temperature regime are presented in Figure 5. Temperature-programmed C 1s XPS has shown the reaction of crotyl alcohol over Pd(111) to proceed via three distinct steps with the intact adsorbed molecule first transforming to crotonaldehyde beginning at 200 K before decarbonylating at room temperature.¹³ At higher annealing temperatures, carbonyl and CO surface species are removed from the surface, leaving only graphitic carbon. The MDS spectra in Figures 4 and 5 broadly support this interpretation, as will now be discussed in more detail.

I. <200 K: Low-Temperature Crotyl Alcohol Adsorption. Low-temperature crotyl alcohol adsorption at 150 K leads to MDS spectra that display distinct features typical of AD at a molecular adsorbate. Particularly, well-resolved peaks at high kinetic energies are observed (labeled A, B, and C in Figure 5), which have been assigned to emission from the first few MOs of the adsorbed alcohol (see the above DFT Results section). However, it is probable that a significant proportion of He 2³S atoms interacting with the surface de-excite via RI, accounting for the steadily rising background of emission on which the AD peaks are superimposed. To focus on these latter features and gain further insight into evolution of the reacting adlayer, a peak-fit analysis for each temperature was performed. This involved approximating the RI emission in the energy region of peaks A–C by a straight line and subtracting this from the overall spectrum to yield a qualitative picture of the temperature-dependent AD process. Figure 6 shows representative data from the three identified temperature regimes. As we are now only considering the photoemission-like AD channel, the energy scales for these data may be converted to binding energy using knowledge of the Fermi level which occurs at the high kinetic energy cutoff (indicated in Figure 5).

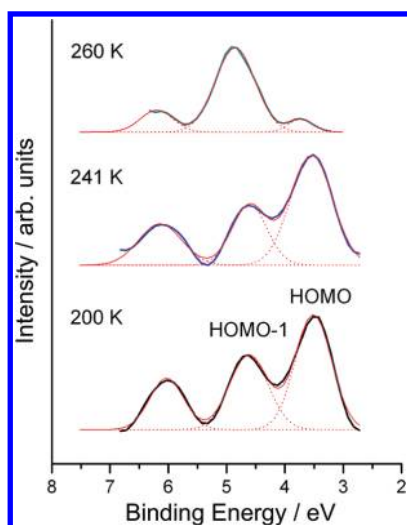


Figure 6. Molecular orbitals and peak analysis of the MDS data shown in Figure 5 at three distinct temperature regimes. The dotted red lines show the fitted individual components.

As previously mentioned, assignment of the MOs shown in Figure 6 has been accomplished using both DFT calculations and also relatively early valence-band photoemission studies and MO calculations of gas-phase allyl alcohols.^{25,26} Emission from both HOMO and HOMO−1 states in the MDS spectra is relatively strong, as would be expected for a parallel adsorption mode where incoming He 2³S atoms are able to access these molecular states. A comparison of UPS spectra from allyl alcohol, acrolein, and propene²⁶ also supports this overall assignment. Additionally, in a separate UPS study of crotyl alcohol,²⁵ the binding energy difference between the first three MOs agree to within 0.1 eV with those shown for the 200 K spectrum in Figure 6.

As the temperature of the substrate increases within regime I from 150 K toward 200 K, subtle changes in the appearance of the emission peaks occur (Figures 4 and 5). At lower temperatures, peaks A and B are closer together and therefore less well-defined with peak C also appearing to shift in energy with increasing temperature. To track these temperature-related changes in greater detail, the peak-fitting procedure used to produce Figure 6 was applied to the data shown in Figure 4 to obtain the peak positions of the first three MOs. The resulting graph, displayed in Figure 7, shows that, in heating from 150 K to around 190 K, all three peaks undergo a small (<0.2 eV) shift in binding energy, before stabilizing up to 200 K. To presaturate the Pd(111) surface with crotyl alcohol at low temperature, a previous study showed that a minimum dose of 1.5 langmuirs is required,¹³ with higher exposures leading to a broadening of XPS features due to the formation of molecular multilayers. For the 3 langmuir exposure used here, multilayers are also expected to form, yielding AD spectral features that are closer in form to those of gas-phase crotyl alcohol than the chemisorbed molecule. As the substrate warms, the physisorbed multilayer molecules desorb, revealing the chemisorbed saturation coverage and allowing He 2³S atoms to access π^* states induced around E_F as a result of the molecule–substrate interaction. The lack of any major MO energy difference between the multilayer and chemisorbed phases indicates that the molecule is relatively undistorted upon adsorption.

To emphasize the induced π^* states, the data in Figure 5 are also replotted with the intensity scale multiplied by a factor of 50.

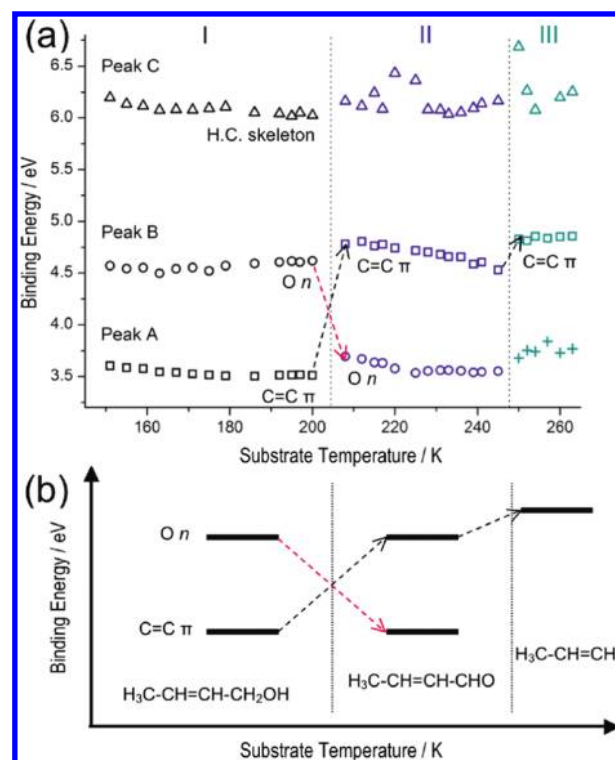


Figure 7. (a) Peak positions of the first three molecular orbitals (assigned in Figure 5) as a function of substrate temperature. (b) Resulting schematic of the energy level correlation of the O n and C=C π MOs.

As the substrate temperature increases and the multilayers desorb, emission at energies close to E_F intensifies, signifying increased metastable He de-excitation at the π^* states induced by chemisorption. Electron donation/back-donation exchange between metallic d states and molecular π and σ states results in rehybridization of the adsorbate–metal system and the filling of empty molecular antibonding π^* states, which redistribute above and below E_F in the LDOS. In the gas phase and when adsorbed in multilayers, crotyl alcohol molecules have a band gap around E_F and would not give rise to emission in this region. Similar effects have been observed in MDS studies of many other adsorbate systems, for example, benzene adsorption on Fe(110).²⁸ However, in the corresponding UPS spectra for crotyl alcohol adsorption (Figure 1c), these states are masked by emission from the Pd substrate.

Emission at high kinetic energies is also observed in the magnified MDS spectrum for the clean Pd(111) surface, which is unexpected as the de-excitation mechanism here is RI + AN. This feature is indicative of slight CO contamination as this molecule is known to strongly chemisorb to Pd(111), yielding bonding states that arise, according to the Blyholder model, due to mixing between CO $2\pi^*$ orbitals with substrate d orbitals. That these states are visible, despite the surface being clean to the standards of LEED, AES, and UPS, highlights the extreme sensitivity of MDS.

Changes in the relative intensity of the features assigned to emission from C=C and O n states provide further insight into the chemistry of crotyl alcohol on Pd(111). As the substrate temperature increases from 150 K, the peak related to the latter states becomes increasingly prominent (Figure 4), reflecting the

changing coverage of the substrate as molecules desorb upon warming. For the adsorption of crotonaldehyde on Pt(111) at low coverage, the C=C and C=O bonds are known to both align parallel to the surface,² although as the coverage increases, the C=O bond undergoes a significant reorientation by tilting strongly toward the surface. A similar effect may be occurring here with the C–O bond of the alcohol forced closer to the surface at high coverages and tilting further away from it as the coverage reduces to saturation. This would explain the increasing intensity of emission observed for O *n* states as the substrate temperature rises. Additionally, at low coverages, the C=C bond has a smaller separation from the substrate allowing a greater interaction and thus yielding more intense π^* emission. Although this picture of C–O bond behavior provides a qualitative description of the trends observed, it is not possible to state the degree of tilt, if any exists. However, a significant tilt would yield a more pronounced feature in the MDS spectrum when compared to emission from the C=C bond. The presented data can therefore be taken as evidence for an adsorption mode in which the C–O bond of the alcohol is aligned somewhat parallel to the substrate, in addition to the C=C bond.

II. 200–250 K: Selo of Crotyl Alcohol to Crotonaldehyde. Above a substrate temperature of 200 K, distinct changes in the MDS spectra occur, marking a transition to a second adsorption regime that ends at around 250 K. The evolution of spectral features across this temperature range is apparent in Figures 4–6, although it is perhaps clearest in Figure 7. Initially, peaks A and B shift to a higher binding energy by ~ 0.2 eV while emission from peak C is reduced, resulting in its position becoming less well-defined. After 225 K the system is more stable with peaks A and B tending toward slightly lower binding energies and peak C again becoming more prominent. The selective oxidation of crotyl alcohol to surface bound crotonaldehyde over Pd(111) is known to proceed via a reaction pathway that accounts for $\sim 90\%$ of the adsorbed molecule with the activation of this process commencing at 200 K. We therefore interpret the changes in the MDS spectra at this intermediate temperature range to originate from the onset and continuation of this reaction channel, generating emission from the resultant aldehyde product. A minor channel for crotyl alcohol reaction to 2-butene and water also exists over Pd(111)¹³ although a clear signature of this is not apparent in the MDS spectra possibly swamped by emission from the alternative process.

For low coverages of crotonaldehyde on Pt(111), the C=O and C=C bonds both align parallel to the substrate² with the π system of the carbonyl functionality not utilized in the adsorption.²⁷ DFT calculations have shown crotonaldehyde to adopt a similar η_4 quasi-planar adsorption mode over Pd(111).²⁶ For this in-plane adsorption geometry and a hydrocarbon backbone that is structurally unaltered, MDS features for the aldehyde may be expected to have the same origin as for the alcohol. Although this is qualitatively correct, a previous UPS comparison of allyl alcohol and acrolein²⁵ determined that the two lowest energy MOs of these molecules effectively switched positions with the HOMO of the aldehyde due to C=C π emission and HOMO–1 state due to O *n* nonbonding states, in direct anticorrelation to the alcohol. We suggest an equivalent redistribution occurs when adsorbed crotyl alcohol oxidizes to crotonaldehyde over Pd(111). This energy-level realignment is schematically illustrated in Figure 7b and is supported by the DFT results of the isolated molecules presented earlier in this study, which show MO shifts that are similar in magnitude to those

observed experimentally (Figures 2 and 7). Additionally, considering the known planar geometry of crotonaldehyde on Pd(111), the fact that the relative intensities of peaks A and B are not greatly different for the alcohol and aldehyde lends further evidence to the assertion that the C–O bond of the alcohol is somewhat aligned parallel to the substrate.

Low binding energy MOs are particularly susceptible to modifications to the conjugation and inductive interactions within a molecule. The additional electronegativity associated with the carbonyl group formed upon crotyl alcohol oxidation leads to further inductive delocalization of electron density toward the O atom, thus stabilizing the C=C π orbital and allowing the O *n* states to acquire more bonding character. Resonance effects may also contribute to the MO binding energy determination although, due to the large energy separation of the C=C π and O *n* states and the in-plane geometry of the aldehyde molecule, these are expected to be small in comparison to inductive interactions.²⁸ With these intramolecular changes in mind, for peaks A and B to occupy the same approximate energetic positions for both the alcohol and aldehyde would certainly seem unexpected and a reversal in the assignment of the first two MOs, albeit coincident in energy, is altogether more likely.

III. >250 K: Decarbonylation. At a substrate temperature of ~ 250 K, a further transition in the adsorbate system occurs accompanied by more distinct changes in the MDS spectra. Peaks A and C reduce dramatically in intensity and eventually disappear at around room temperature whereas peak B shifts to a higher binding energy where it remains approximately stable both in position and in intensity. C 1s XPS has shown that surface-bound crotonaldehyde decarbonylates to propene and CO at room temperature with the former either desorbing or dehydrogenating to graphitic carbon as the temperature increases above ~ 330 K.¹² With propylidyne being the dominant adsorbate species above 250 K, peak B in this temperature regime is assigned to the C=C π orbital (HOMO) of such molecular fragments. A previous MDS study of CO/Pd(111) by Ertl and co-workers²⁹ shows spectral features at 7.7 and 10.8 eV at 300 K. However, in this study this region is swamped by emission from both low-energy secondary electrons and deeper lying molecular orbitals (F, E, and D) making these specific features difficult to observe.

Earlier studies of olefin adsorption on Pd(111)^{27,30} have shown that significant hybridization of the C=C π bond with metallic d states results in substituent functionalities (the methyl group in the case of propene) tilting away from the surface. In the gas phase, the C=C π orbital of propene is destabilized with respect to acrolein²¹ due to a combination of hyperconjugation and inductive interaction with the methyl group. This leads to the orbital energetically locating between the two outer lying orbitals of acrolein, as illustrated in Figure 7b. However, when adopting a di- σ -coordination mode in the formation of a chemisorption bond, the C=C π orbital is stabilized and shifts to a higher binding energy explaining its relative position when compared to the MOs of crotonaldehyde (Figure 4a). A large shift in binding energy of the C=C π orbital upon chemisorption indicates a significant electron donation/backdonation interaction between propene and the Pd substrate, in similarity to ethylene adsorption on Pd(111).³¹ Emission from induced π^* states is also high providing further evidence for a strong chemisorption bond. Heating above room temperature results in the loss of clear, identifiable features in the MDS spectra suggesting that the RI de-excitation channel is now strongly dominant. Propene almost

completely desorbs by 500 K and only a small coverage of graphitic carbon remains bound to the surface so that the spectra become increasingly characteristic of clean Pd(111).

CONCLUSIONS

In this study, MDS has been combined with DFT calculations to provide a deeper understanding of the selective oxidation of crotyl alcohol to crotonaldehyde over a model Pd(111) catalyst, revealing new insight into the adsorption mode, molecular orientation, and surface chemistry associated with this important reaction. At a substrate temperature of 150 K, predominant Auger de-excitation for crotyl alcohol adsorbed on a clean Pd(111) surface gives rise to three distinct molecular features in the MDS spectra that are interpreted with the aid of early valence band photoemission studies, MO calculations of gas-phase allyl alcohols, and DFT calculations. States centered around 6 eV (peak C) are attributed to the hydrocarbon backbone of the molecule whereas further states appearing at around 4.5 eV (peak B, HOMO−1) and 3.5 eV (peak A, HOMO) have been assigned to the C=C π bond and O lone-pair 2p n bonds, respectively.

DFT calculations for various adsorption geometries reveal that the lowest energy state results when crotyl alcohol adopts an adsorption geometry that is parallel to the surface. This assignment is also supported experimentally, as any significant tilt in the position of the oxygen would lead to a more pronounced feature in the MDS spectrum when compared to emission from the C=C bond. We can therefore conclude from both experiment and theory that the C—O bond of the alcohol is aligned somewhat parallel to the substrate, in addition to the C=C bond. Judging by the shape and intensity of the peaks, DOS calculations for such configurations are in excellent agreement with experimentally acquired MDS spectra.

The chemical transformation of the alcohol to the corresponding aldehyde has been investigated by temperature programmed MDS. Heating the presaturated substrate causes dramatic changes to be observed in the spectra. To track such changes, a peak fitting analysis was performed. Between approximately 200 and 250 K, the reaction of crotyl alcohol to crotonaldehyde predominates, generating emission from the aldehyde product resulting in a small shift in peaks to higher binding energy. As a result of intramolecular changes, a reversal in the assignment of the first two MOs occurs, albeit almost coincident in energy. This switchover is supported by DFT calculations of the isolated alcohol and aldehyde, which show shifts in similar magnitude to that observed experimentally.

At higher temperatures, the peaks associated with emission from the hydrocarbon skeleton and O n states dramatically decrease due to decarbonylation of the aldehyde, meaning that propylidyne is the dominant adsorbate species above 250 K. Peak B (\sim 4.75 eV) therefore arises from C=C π orbital (HOMO) of adsorbed propylidyne. Spectral features indicative of CO (7.7 and 10.8 eV)²⁹ are not observed, due to dominant emission from secondary electrons and lower energy orbitals from 7 to 14 eV. Heating the sample further results in the loss of identifiable features in the spectra, indicative of dominant resonance ionization de-excitation, and consistent with propene desorption by 500 K and residual carbon present on spectra increasingly characteristic of clean Pd(111).

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