Determining Oxygen's Effects on

Multifunctional Alcohol Decomposition on Pd(111)

by

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

ABSTRACT

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Determining Oxygen's Effects on Multifunctional Alcohol Decomposition on Pd(111)
Thesis directed by Associate Professor J. Will Medlin

Oxidation of alcohols and aldehydes is one route to value-added chemicals from biomass. Because catalytic oxidation reactions on transition metals usually involve participation of oxygen, it is important to understand oxygen's surface-level effects on these complex reactions. Surface investigations of the thermal oxidation chemistry of a range of multifunctional alcohols on quarter-monolayer oxygenprecovered Pd(111) (O/Pd(111)) is presented here.

The surface chemistry of 1,2-propanediol (PDO) on O/Pd(111) showed a strong dependency on relative concentration of PDO and $O_{(a)}$ (adsorbed atomic oxygen). When the concentration of $O_{(a)}$ is large compared to the dialkoxide produced following PDO adsorption (-OCH(CH₃)CH₂O-), PDO completely decomposes. Conversely, when the concentration of $O_{(a)}$ is small, the co-adsorbed oxygen increases the overall coverage of PDO that can undergo decomposition, which in turn strongly influences decomposition activation barriers and product distributions.

To investigate how surface oxygen participates in the reaction of important aromatic oxygenates, the surface chemistry of benzyl alcohol (PhCH₂OH), benzaldehyde (PhCHO), furfuryl alcohol (C₄H₃OCH₂OH) and furfural (C₄H₃OCHO) has been studied on ¹⁸O/Pd(111). In the presence of surface O, some benzaldehyde and furfural desorbed from a weakly bound η^1 (O) aldehyde state. Benzaldehyde and furfural also react with surface oxygen to produce benzoate (PhCOO-) and furoate (C₄H₃OCOO-), respectively. The benzylic reactions revealed exchange occurring between surface O and the benzaldehyde and benzoate intermediates. This exchange has not been reported for other alcohols, suggesting that aromatic binding effects strongly influenced alcohol oxidation on Pd. At high coverages, deoxygenation of furfuryl alcohol to methylfuran (C₄H₃CH₃) and benzyl alcohol to toluene (C₆H₃CH₃) was observed simultaneously with the relevant aldehyde production, possibly through a disproportionation reaction of two alcohol molecules. Surface reactions of furan, furfural, and furfuryl alcohol on O/Pd(111) suggest the presence of surface oxygen resulted in a new, higher-temperature desorption channel for furan; this channel coincided with desorption of partial oxidation products, 2(5H)-furanone and maleic anhydride. Furfural may be decarbonylated to furan and subsequent ring opening of furan (C₄H₄O) through O-C^{α} scission was observed. Isotopic product distributions suggest that partial oxidation of furan occurs through a ring-opened carboxylate.

Dedicated to my parents and grandparents – Laurence and Janice Justin and Margaret Thomas and Mary

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It has taken a village to help me reach this point in life. I would like everyone to know how truly grateful I am for the mentorship, support, advice and listening ears along the way. Thank you for helping me to persevere.

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Much love and good cheer from your colleague/daughter/sister/film lover/friend,

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Your life is a movie, so direct it!

It's not that I'm so smart, it's that I stay with a problem longer. – Einstein To be successful you have to do things you don't think you want to do. – Dad

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CHAPTER 1

Introduction and Literature Background

At a green chemistry and engineering conference, a speaker shared some sage advice. They said, "Find a career field where big changes are taking place, because that's where opportunities will abound." This guidance led me to pursue my doctorate in chemical engineering. When deciding a thesis project to take on five years ago, I was attracted to catalysis since it is innately "green", superior to stoichiometric reagents, and one of the twelve principles of green chemistry.¹ Now I am able to appreciate my chosen field even more, putting it further into context by recognizing the impressive record of Nobel Prize winning catalysis-related research;² from Paul Sabatier in 1912 and Irving Langmuir in 1932, to Gerhard Ertl in 2007 and Richard Heck, Akira Suzuki and Ei-ichi Negishi in 2010. Catalysis is complex to fully understand, but worthwhile to study because of its far-reaching practicality and necessity.

1.1 Introductory Motivations

The demand for energy, fuels and chemicals is expected to rise steeply as the world population continues to increase. To meet these needs, multiple resources must be utilized including those in the biomass refining supply chain. Yet biomass derivatives bring forth the new issue of high-oxygen content (\sim 50 wt%)³ compared to petroleum-based feedstocks with less than 2 wt% oxygen.⁴ The oxygenate functionality of biomass makes it difficult to selectively react a single functional group (alcohol, aldehyde, ester, etc.) since each one is potentially reactive on the surface (Figure 1-1). This selectivity issue remains a major challenge in promoting specific reaction pathways in heterogeneous catalysis. Better catalytic processes are pertinent to energy and chemical production via biomass conversion in order to make it economically viable.⁵⁻⁷



Figure 1-1. A variety of biomass-derived molecules demonstrating the potential for multifunctionality.

Practically every consumer product in our world has some relation to a catalytic process and yet many people do not recognize what "catalysis" means. Materials for health, clothing, fuels, plastics, etc. rely heavily on chemical and biochemical catalysts,⁸ and thus catalysis has become an important research field. One quarter of the developed countries' GDP in the world is comprised of products that originate through catalytic processes, with the world market for catalysts currently on the order of 15 billion US dollars.⁹ Industrial catalysts are chosen for their high selectivity, high activity and high durability under reaction conditions.¹⁰ Heterogeneous catalytic reactions—those that occur over solid catalysts—have the advantage of easy catalyst recovery. Since catalysis is a complex science and technology, our understanding of heterogeneous catalyst design is largely dependent on experience or trial and error instead of rational design at a molecular or atomistic level.⁹ While adding to the catalysis toolbox, we hope to employ rational molecular design of catalysts for particular reactions; one such reaction is alcohol oxidation, which is the focus of this thesis.

1.2 Oxygen and Metal Catalysts

Oxidation of alcohols and aldehydes is one route to value-added chemicals from biomass. In 1984 it was estimated that 5% of crude oil consumption went toward fine chemical production¹¹ while more recently that number has grown to 13-18%.¹² As a major reaction pathway in organic syntheses, oxidation of biomass-derived building blocks to fine chemicals may provide economic viability towards the use of sustainable biorefineries.¹³ For example, glucose may be dehydrated to 5-hydroxymethylfurfural, which can be oxidized to 2,5-furan dicarboxylic acid (Figure 1-1). This has been highlighted by the Department of Energy as a target reaction and 2,5-furan dicarboxylic acid has been added to the top 30 list of valued chemicals that could be derived from biomass and one of 12 important building block molecules.¹⁴

Oxygen and Oxidation. Selective oxidation of alcohols is traditionally achieved using stoichiometric quantities of expensive and toxic oxygen donors. An alternative approach is to use molecular oxygen with a solid catalyst to produce (for example) the corresponding aldehyde, without generation of toxic byproducts that are both unsafe and expensive to dispose of. The traditional methods of oxidizing include the use of stoichiometric reagents such as sodium chlorite¹⁵⁻¹⁷ or sodium dichromate.¹⁸⁻¹⁹

Oxygen is important to catalysis because it is a participant in oxidation reactions as well as a component in metal oxide catalysts. The multiple charge states of oxygen allow oxidation reactions to be electrophilic (O_2 , O_2^- and O^-) or nucleophilic (O^{-2}).^{10, 20} Additionally, the O-O bond has a large bond energy (493.87 kJ/mol²¹), virtually precluding selective oxidation reactions with molecular oxygen in the absence of a catalyst. Thus, the catalyst used may be present simply to activate the molecular oxygen ($O_2(g)$), which can then start the oxidation process in its active, atomically adsorbed form ($O_{(a)}$).²⁰ Metals active for alcohol oxidations include Pt-group elements such as palladium.²²⁻²⁷

Oxygen can form various phases and states on a metal surface. The metal's level of d-orbital filling dictates how much electron-donating ability to the dioxygen the metal has. In the case of Pd, the d-band is relatively full and the energy of the d orbitals is low compared to the Fermi energy, meaning that Pd does not tend to form super/per/oxo complexes except at low temperatures.

Molecular oxygen has been successfully applied to oxidize a variety of alcohols over several supported metal catalysts. These oxidation reactions that have employed O₂ include benzyl alcohol over Pd/SiO₂-Al₂O₃,²⁸ ethanol over Au/TiO₂,²⁹ octanol over Pd/CeO₂,³⁰ cinnamyl alcohol over Pd/SiO₂,³¹ glycerol over Pt/TiO₂,³² and a variety of 18 primary and secondary alcohols over Ru/Al₂O₃.³³ Supported transition metal catalysts such as these are advantageous for oxidation reactions because they activate molecular oxygen dissociation and proceed at mild temperatures (295-350 K). Some remaining challenges for oxidation reactions with O₂ include over-oxidation of the metal surface or catalyst deactivation via strong byproduct adsorption on the surface.

Palladium Catalysts. Palladium is an important catalytic metal, a component in automobile catalytic converters and Pd allows for carbon cross-coupling, the 2010 Nobel Prize winning chemistry pioneered by Heck, Suzuki and Negishi.³⁴⁻³⁶ Palladium is used in a variety of applications (electronics, jewelry, photography, hydrogen storage), but predominantly in catalysis. Metals that do not bind oxygen too strongly or too weakly are preferable for oxidation reactions. The metal also needs to dissociate the oxygen while not forming an oxide with strong O-M bonds.³⁷ Palladium exhibits these properties and has therefore been used extensively for alcohol oxidations.^{22-23, 38-41} While Au and Ag are used for some oxidation reactions because of their relatively weak O-M bond energy, they are less useful for alcohol oxidation because of the conditions at which reactions are carried out, often resulting in reduced activity and selectivity.⁴²⁻⁴⁵ However, Pt and Pd have shown good performance at a wide range of temperatures, easily activating alcohols and molecular oxygen and producing high yields of selectively oxidized products such as aldehydes.²²

Atomic Oxygen on Pd(111). A primitive (2×2) $(p(2 \times 2))$ structure of atomic oxygen on a (111) facet corresponds to 0.25 ML,⁴⁶ where the oxygen adsorbs in the three-fold hollow sites of the fcc metal,⁴⁷⁻⁴⁸ shown in Figure 1-2. The coverage is controlled by the amount (e.g., in Langmuir) and temperature of oxygen exposure to the surface. The 0.25 ML coverage is achieved by an O₂ dose on the order of 1-10 Langmuir at ambient temperatures, which leads to surface dissociation and atomically adsorbed O.⁴⁹⁻⁵² Higher dosing temperatures and exposures of more than 40-Langmuir O₂ allow a

coverage of 0.37 ML to be reached.^{50, 53-54} At coverages greater than 0.25 ML, the oxygen will start to penetrate the surface and distinctly change the surface structure by releasing Pd atoms, forming islands and peninsulas.⁵⁰ A 0.50 ML coverage of oxygen leads to the surface oxide phase of O/Pd(111).⁴⁷ High coverages of oxygen can only be achieved by using oxidants such as O_3 ,⁵⁵ NO or NO₂.^{46, 56-57} For these reasons, the experiments presented in this thesis take place on 0.25 ML O-precovered Pd(111), consistently achieved by dosing $O_2(g)$ and allowing it to dissociate on the surface above room temperature. The 0.25 ML coverage is also advantageous for its stability over a wide temperature range (100-800 K).



Figure 1-2. Depiction of face-centered cubic (111) surface with the primitive, $p(2 \times 2)$, unit cell (black dashed line) for the atomic oxygen adsorbate (black circles) adsorbed in the three-fold hollow sites. Figure taken from reference.⁵⁸

Surface Oxygen Effects. Many studies have considered the surface chemistry of alcohols on a variety of oxygen-covered metal surfaces including Pd(111),⁵¹ Pt(111),⁵⁹⁻⁶⁰ Au(111),⁶¹⁻⁶² and other surfaces.⁶³⁻⁶⁷ The roles of oxygen adatoms generally include Brønsted or Lewis acid-base reactions with adsorbates, site blocking, and electronic modification of the metal surface. These roles in turn promote certain elementary reaction steps like selective O-H and C-H scission. Adsorbed oxygen is

electronegative, thus it withdraws electrons from neighboring metal atoms. The change in electron density may result in a different reactivity for that metal surface site.⁶⁸

Oxygen as a Brønsted base readily accepts a hydrogen transfer, such as in the breaking of the O-H bond of an alcohol. Oxygen also acts as a nucleophile, attacking electron deficient centers of a molecule and forming new intermediates. For example, O can attack an aldehyde, easily breaking the C-H bond and forming metastable carboxylates, COO-. Direct oxidation of the aldehyde to a carboxylate by nucleophilic attack on the carbon often yields CO_2 , H_2O and H_2 , where CO_2 is the non-selective oxidized product.^{37, 69} Other side reactions exist when surface oxygen is available, i.e., oxidation will compete with reactions that normally occur on the clean metal surface. Madix and coworkers have stated that heterogeneous oxidation reactions may be identified as one of two reaction types: 1) a scavenger mechanism that is generally non-selective, resulting from reaction of co-adsorbed oxygen and decomposing molecular fragments such as C_xH_x , which would form on the clean surface independent of oxygen's presence or 2) an oxygen-activated mechanism that leads to partial oxidation of a molecule by cleaving particular O-H and C-H bonds and would otherwise not occur on a clean surface in the absence of oxygen.³⁷

1.3 Methods and Materials

Ultrahigh vacuum (UHV) studies with metal single crystals are model catalytic reaction systems. The UHV surface science approach has the ability to determine mechanistic processes, products, activation energies and rate-determining steps. The necessity for UHV conditions comes from the need for uncontaminated clean surfaces as well as the disallowance of gas phase scattering interference when low-energy electron and ion-based techniques are used.⁷⁰ The background pressure of a UHV chamber is on the order of 10⁻¹⁰ Torr, which is dictated by the nature of the reactive surface and the time frame that it can adsorb significant quantities of contaminating background gases.⁷⁰ The single crystal Pd(111) facet is useful for the fundamental studies presented in this thesis for several reasons. The low-index plane is thermodynamically stable and, as a result, the (111) surface is abundant on most catalysts. Heterogeneous

catalyst studies are complicated by their many surface facets, defects, and interface sites. This makes it more difficult to determine where the reaction is occurring. It is advantageous to use a single crystal because it simplifies the system of interest, providing a clearer understanding of the active sites.

The surface techniques used throughout this thesis are predominantly temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Some surface characterization was accomplished via low-electron energy diffraction (LEED). Each of the UHV chambers utilized for data collection had a base pressure of approximately 1×10^{-10} Torr (~1.3 x 10^{-8} Pa).

Temperature-Programmed Desorption. Madix describes the "temperature-programmed method" in a 1986 *Science* paper.⁶⁹ First, the reactant is adsorbed on the surface at a low temperature, T_0 , which must be lower than the temperature of the reaction(s) of interest. Products evolve at various temperatures based on the reaction rates for different surface processes and their temperature dependence. The reliance on a specific temperature is related to acquiring enough thermal energy, i.e., activation energy, to desorb from the surface. As the temperature is linearly ramped, products are separated over time and temperature because of the kinetic variability of activation energies for the elementary surface reaction and desorption steps. Temperature-programmed data plots such as Figure 1-3 include temperature (as a function of time) on the x axis and signal intensity on the y axis.



Figure 1-3. Example TPD spectrum showing the correspondence of various peak temperatures and shapes to binding strength of adsorbate. Figure taken from reference.⁷¹

A quadrupole mass spectrometer (QMS) is responsible for tracking the masses (1-300 possible with the Smart IQ+ in our system) as they evolve from the surface under UHV. A QMS functions by filtering the masses based on a certain mass-to-charge ratio (m/z); a voltage is created between the four parallel rods. The range of masses is tracked by varying the voltage and thus changing the m/z filter continuously. A cracking fraction, or pattern, analysis must be carried out to identify the separate products (which "crack" into various m/z fragments) of a complex reaction.

Figure 1-3 is an example TPD spectrum showing the correspondence of peak temperatures and shapes to binding strength of adsorbates. The lower-temperature peak corresponds to a weakly-bound adsorbate, thus it needs lower activation energy to desorb. The sharpness of the peak is related to desorption of a molecularly-intact molecule, likely being produced from a single adsorption orientation. The higher-temperature peaks correspond to higher activation energies and more strongly-bound intermediates that may undergo additional processes. For example, the high-temperature peak in Figure 1-3 corresponds to the dissociatively-adsorbed and strongly-bound atomic state of oxygen, which

recombines and desorbs molecularly once enough thermal energy is acquired. The width and high temperature of the ~800 K peak corresponds to the second-order recombinative process of two oxygen atoms that depends on the $O_{(a)}$ adsorption energy as well as the atoms' collision probability, each of which are coverage dependent.⁷²⁻⁷³ As an example, the oxygen peak temperature is seen to decrease as coverage of atomic oxygen increases, making collisions more probable.⁵⁰ The lower peak temperature is also a result of neighboring oxygen atoms repelling each other, which lowers desorption activation energy. Activation/binding energies are calculable from desorption peak temperature.⁷⁴

A product's evolution temperature from a reaction must be compared to its temperature of evolution when the molecule itself is alone on the surface and desorbs or decomposes. This provides evidence of the specific product's formation being a reaction-limited or desorption-limited process.⁶⁹ For example, if a product like CO evolves at a temperature higher than that determined from a CO TPD, then its evolution is being dictated by the rate of surface reaction producing that CO. Quantitative information may also be gathered from TPD spectra by integration of peaks, such as the CO peak from an experiment compared to a CO peak at saturation coverage.

The goal of the temperature-programmed method is to establish reaction mechanisms in detail such as the transfer of single atoms. Isotopically-labeled molecules are useful for these studies. Various reaction channels, like O-D or C-H bond breaking, can be monitored. Temperature-programmed desorption also helps quantify the products in each reaction channel (e.g., dehydrogenation products, decarbonylation products, decomposition products), then vibrational spectroscopy can be used to determine surface intermediate species' structure and modes of bonding to the surface.

Vibrational Spectroscopy. One of our UHV chambers is equipped with an ELS 5000 spectrometer (LK Technologies). High-resolution electron energy loss spectroscopy is a vibrational spectroscopy technique that uses a generated beam of electrons that is reflected off a sample covered with adsorbates. The impinging electrons excite vibrational modes of the adsorbed molecules; the various modes have different energies, with a corresponding loss in electron energy that is measured by an analyzer.⁷⁵ Various bonds have distinct vibrational frequencies (energies) that can be picked out in

HREEL spectra; an n²-aldehvde C=O stretch is near 1400 cm⁻¹ while methyl C-H stretching occurs around 2950 cm⁻¹ (Figure 1-4). The mechanism for electron scattering and detection is based on the dynamic dipole moments (μ), i.e., changes in the dipole moments during the physical vibration of the bond. The so-called surface selection rule for real and image dipoles of parallel and perpendicular dipole moments is depicted in Figure 1-5. For example, an asymmetric OCO vibrational mode has relatively low intensity because EELS intensity is dictated by the change in dipole moment with a non-zero component perpendicular to the surface.⁷⁶ The asymmetric OCO stretch of a carboxylate may be parallel to the surface, therefore the hardest for the EELS to detect. For a system that uses a specular angle of detection (i.e., incidence angle equals exit angle), the scattering of electrons occurs primarily by a long-range mechanism based on the dipole moments normal to the surface, whereby the resulting loss features of a spectrum are relatively intense.⁷⁷ However, some impact scattering, where the incidence angle does not equal the exit angle, is possible if the detectorate geometry is off-specular. This would result in weak vibrations because the mechanism of impact scattering is short-range.⁷⁷ One approach to assist in determining reaction intermediates is doing control experiments with the product or intermediate proposed. Figure 1-4 shows an example; ethanol on Pd(111) is annealed to 200 K and compared to a spectrum of the predicted intermediate, acetaldehyde, on Pd(111).⁷⁸ The spectra are virtually identical, and thus acetaldehyde formation was identified as a step in ethanol's decomposition mechanism on Pd(111).



Figure 1-4. Example of comparing HREELS data to see ethanol and acetaldehyde spectra similarities, thus able to identify the aldehyde forms on the surface by 200 K from reaction of ethanol on Pd(111). Figure taken from reference.⁷⁸



Figure 1-5. Depiction of the HREEL surface-selection rule, where the image dipoles are easily observed when vibrations normal to the surface are excitable, or may go unseen if parallel to the surface.⁷⁹

Surface Diffraction. Low-electron energy diffraction (LEED) is used to observe the surface adsorption structure of atomic oxygen on Pd(111). These experiments are carried out in the same UHV chamber as the TPD experiments with a RVL2000 LEED apparatus that includes an electron gun (LK Technologies). Low-energy electrons (50-500 eV) are scattered on the surface with only the elastically scattered electrons being detected. A pattern of these scattered electrons becomes apparent on a phosphorescent screen. We compared the pattern of our p(2x2)O/Pd(111) surface with that of the literature⁵⁰ and confirmed a 0.25 ML O-covered surface in Figure 1-6.



Figure 1-6. Low-electron energy diffraction pattern of p(2x2)O/Pd(111) surface captured prior to TPD experiments.

Ultrahigh vacuum studies are conducted with the understanding that a pressure gap of ~13 orders of magnitude exists between UHV and the reaction conditions used by industry.⁸⁰ A material gap also exists between a near-perfect single crystal surface such as (111) and complex catalysts of varying size particles with steps, edges, terraces, kinks, and planes ((100), (211), etc.). Despite the pressure and material gaps, there are many examples to date of UHV studies providing relevant catalysis insights. Ultrahigh vacuum studies have successfully been extended to steady-state catalytic reactions. For example, studies have shown larger furfuryl alcohol exposures on the Pd surface in UHV lead to

adsorption orientation and coverage effects, which promote deoxygenation to methylfuran.⁸¹ When applied under reaction conditions, self-assembled monolayers of alkanethiols were used to block surface sites on Pd and induce a coverage effect to increase the selectivity of hydrodeoxygenation of furfuryl alcohol to methylfuran.⁸² Another example is the successful extrapolation of UHV results with Fe and ammonia synthesis⁸³ to the industrial conditions of the Haber-Bosch process.⁸⁴⁻⁸⁵

1.4 Background Literature Review

Davis and Barteau's contributions to the understanding of alcohol and aldehyde surface chemistry on Pd(111)^{51, 78, 86-88} set the stage for the research presented in this thesis. In the late 1980s and early 1990s they studied C₁-C₃ alcohols, aldehydes, and acids on clean Pd(111) and O/Pd(111) using a combined TPD and HREELS approach. It is useful to review their work in a comprehensive manner as it constitutes the majority of previous knowledge of surface chemistry reactions on O/Pd(111). A helpful visualization of relevant oxygenated intermediates (alcohol, alkoxide, η^1 and η^2 aldehydes, acyl, carboxylate) that will be mentioned in this thesis, as well as the background literature review, is shown in Figure 1-7.



Figure 1-7. Visualization of oxygenated intermediates relevant to this thesis. Figure taken from reference.⁸⁹

Mechanisms of what are termed "simple alcohols" (methanol, ethanol, 1-propanol, 2-propanol) were established on clean Pd(111)⁸⁸ before oxygen was included as a co-adsorbate. A schematic of the proposed decomposition mechanism is shown in Scheme 1-1. It should be noted this mechanism is based solely on TPD experiments. The hydroxyl hydrogen of a simple alcohol is dehydrogenated to form an adsorbed alkoxy intermediate. Further dehydrogenation at the α -carbon forms a dihapto (η^2) aldehyde, which undergoes C^{α}-C scission, resulting in decarbonylation. Adsorbed CO and a hydrocarbon, one carbon unit shorter than the parent molecule, are formed. The aldehydes of the primary alcohols do not desorb intact from the clean Pd(111) surface. The remaining hydrocarbon chain may desorb intact or decompose to adsorbed surface carbon and hydrogen. For example, methanol in this reaction scheme desorbs molecularly at 200 K or forms CO and H₂ via decomposition. Ethanol creates methane, CO and

 H_2 . 1-propanol can produce ethylene, CO and H_2 while the secondary propanol reacts quite differently from the primary alcohol; 2-propanol forms acetone via selective dehydrogenation and dihapto acetone desorbs intact. Alternatively, methane, CO and H_2 are formed via further decomposition of the intermediate.



Scheme 1-1. Proposed reaction mechanism for C_1 - C_3 alcohols (methanol, ethanol, 1-propanol) on clean Pd(111) as determined by TPD. Figure taken from reference.⁸⁸

In a follow up study to the proposed mechanism of Scheme 1-1, vibrational spectroscopy (HREELS) was utilized to identify the various adsorbed intermediates in alcohol decomposition on Pd(111).⁷⁸ The key difference between their revised mechanism in Scheme 1-2 and Scheme 1-1 is the acyl intermediate. Decomposition of the acyl was rate-determining for the C₂-C₃ alcohols because the higher acyls have stabilizing pendant groups to the carbonyl. For example, ethanol is observed intact at 170 K with apparent v(CH) (2925 cm⁻¹), v_a(CCO) (1040 cm⁻¹), v(CH₃)/v(CH₂) (1300-1465 cm⁻¹) stretching. An η^2 -acetaldehyde species was characterized by the presence of v(CO) at 1415 cm⁻¹. Partial dehydrogenation of the aldehyde forms η^1 (C)-acetyl, observed as v(CO) at 1585 cm⁻¹. Acetaldehyde is a stable surface intermediate but does not desorb in TPD experiments from a clean Pd(111) surface. Adsorbed CO at 1830 cm⁻¹ signals decarbonylation of the acyl species by 340 K.



Scheme 1-2. Simple alcohol's decarbonylation mechanism on Pd(111) determined via HREEL vibrational spectroscopy. Figure taken from reference.⁷⁸

Experimental studies of simple aldehyde (formaldehyde, acetaldehyde, propanal) adsorption and reaction on Pd(111) revealed various decomposition temperature dependencies.⁸⁷ Formaldehyde decomposes to $CO_{(a)}$ and $H_{(a)}$ or polymerizes to paraformaldehyde between 170-200 K. Acetaldehyde adsorbs in a η^2 configuration and may lose a hydrogen to form a stable acyl intermediate, acetyl, which decomposes above 300 K. Desorption and decarbonylation of the C₂-aldehyde were found to compete. Propanal reacted similarly, forming propanoyl. High-resolution EELS was useful in identifying the v(CO) frequency of acyl intermediates near 1565 cm⁻¹. No polymerization of the C₂- and C₃-aldehydes was observed. The use of isotopic molecules revealed that C-H scission of the acyl intermediate in aldehyde decomposition was rate-determining.

A clear way to understand the effects of co-adsorbed oxygen on simple alcohol reactivity is to dose 0.25 ML of atomic oxygen prior to adsorbing the alcohol reactant. This is the approach taken by Davis and Barteau, whereby O/Pd(111) experimental results^{51, 86} are compared with the reaction on clean Pd(111).^{78, 87-88} Through TPD experiments with methanol, ethanol, 1-propanol and 2-propanol on O/Pd(111), five roles of oxygen were determined. These roles are summarized in Scheme 1-3.⁵¹ The

hydroxyl bond is the first to break, forming an alkoxide and surface hydroxyl (with the oxygen and abstracted hydrogen). Further dehydrogenation creates the corresponding aldehyde, which shifts to interact with the surface in an upright manner ($\eta^1(O)$). They propose the most likely explanation of the shift in aldehyde-surface interaction is the result of a reduced electron density in the Pd due to the electronegative $O_{(a)}$, which cannot donate as well to the carbonyl π orbital of a side-on aldehyde adsorbate ($\eta^2(CO)$). Figure 1-8 shows an example TPD of acetaldehyde where the desorption temperature of an η^1 -adsorbed aldehyde is lower from O/Pd(111) as a result of the weaker bonding interaction of oxygen's lone-pair electrons compared to an η^2 adsorption structure. The dominate reaction pathway is nucleophilic oxidation of the aldehyde to a carboxylate, which completely decomposes to CO₂ and H₂O or may be hydrogenated to the corresponding acid. Oxygen scavenging of hydrogen precludes formation of many hydrogenated products.



Scheme 1-3. The five roles of oxygen in the reactions of simple alcohols on O/Pd(111). Mechanism adapted from reference.⁵¹



Figure 1-8. Desorption temperature of a η^1 (monohapto)-adsorbed aldehyde is lower from O/Pd(111) compared to a η^2 (dihapto) adsorption structure on clean Pd(111), exemplified by these TPD experiments with acetaldehyde. Figure taken from reference.⁵¹

Pre-adsorbed oxygen interacts with C_1 - C_3 aldehydes on $Pd(111)^{86}$ in similar ways as the primary alcohols mentioned above. The aldehydes prefer to adsorb more weakly through the oxygen of the carbonyl group in a η^1 state in the presence of oxygen and desorb at lower temperatures than η^2 (by ~50-100 K) as a result. Oxygen attacks aldehydes and acyl intermediates to form carboxylates. If sufficient hydrogen is available, the carboxylate may be hydrogenated to form a carboxylic acid. However, oxygen tends to scavenge hydrogen and leave the carboxylate to decompose to CO_2 and H_2O .

In a similar approach to Davis and Barteau,^{51, 78, 86-88} this thesis will include comparisons of the surface chemistry of multifunctional alcohols and aldehydes on O/Pd(111) to precursor studies on clean Pd(111) in our group.^{81, 90-91} Previous work has shown that 1,2-propanediol (PDO, HOCH(CH₃)CH₂OH), a probe molecule for glycerol with both primary and secondary hydroxyl groups, decomposes on clean Pd(111) via O-H activation to a dialkoxide intermediate (-OCH(CH₃)CH₂O-).⁹⁰ The proposed reaction mechanism is depicted in Scheme 1-4. With increases in thermal energy, 1,2-propanedioxy undergoes dehydrogenation, methyl elimination, and formation of an adsorbed dialdehyde, glyoxal (O=CHCH=O),

or dehydrogenation and formation of an adsorbed dialdehyde, methylglyoxal ($O=CHC(CH_3)=O$). On clean Pd(111) the C-C scission reaction pathway forming CO and H₂ predominates over the C-O scission pathway, which forms ethylene and water. The mechanism of previous work (Scheme 1-4) also includes the diol ethylene glycol reacting on Pd(111). It proceeds through the same intermediates, but showed a lower level of thermal stability due to the missing methyl group of PDO.



Scheme 1-4. Proposed reaction mechanism of the diols, ethylene glycol and 1,2-propanediol, on Pd(111) taken from reference.⁹⁰

Furanic and benzylic compounds are obtained during biomass depolymerization. Benzyl alcohol (PhCH₂OH) and furfuryl alcohol (C₄H₃OCH₂OH) have been studied on clean Pd(111).^{81, 91} Each of their reaction selectivities has been shown to be highly dependent on adsorption orientation, depicted in Schemes 1-5 and 1-6, respectively. Vibrational spectroscopy experiments confirmed the adsorption-orientation effect. At low coverages, the absence of phenyl C-H in-plane stretches suggested the phenyl ring was parallel to the surface, which make the stretches undetectable by dipole selection rules. Benzyl alcohol proceeds through a flat-lying benzaldehyde adsorbate, which is easily decarbonylated to CO and benzene at these low coverages.⁹² However, at higher coverages, the phenyl C-H stretches (2900-3020)
cm^{-1}) become apparent and the molecule appeared to adsorb in a more-upright orientation. Here, the hydrodeoxygenation to toluene and H₂O is a promoted reaction pathway, confirmed by TPD experiments of varying exposures and resultant coverage effects.



Scheme 1-5. Proposed reaction mechanism of benzyl alcohol and benzaldehyde over clean Pd(111) taken from reference.⁹¹

Similarly to the benzylic molecules, furfuryl alcohol proceeds through a flat-lying furfural intermediate on Pd(111), which favors decarbonylation to furan and CO at low coverages. However, at higher coverages in the upright geometry, hydrodeoxygenation to methylfuran and H₂O is promoted. The furfuryl alcohol and furfural mechanism is shown in Scheme 1-6. Deuterium-exchange experiments showed that furan could incorporate up to two deuterium atoms prior to desorption from a D/Pd(111) surface. Temperature-programmed desorption results indicated that ring opening of furan to produce propylene was also possible.



Scheme 1-6. Reaction mechanisms of furfuryl alcohol and furfural over clean Pd(111) taken from reference.⁸¹

1.5 Thesis Objective

We have summarized some related results for the surface-level interactions of oxygen with simple alcohols and aldehydes on Pd(111). However, if oxidation of biomass-derived alcohols and aldehydes is to become a route to value-added chemicals, it is important to understand oxygen's surface-level effects on the reactions of more complex molecules. Here, "complex" refers to multifunctionality such as two hydroxyl groups or an aromatic ring with a pendant alcohol group. As reviewed above, 1,2-propanediol, benzyl alcohol and furfuryl alcohol have been studied on clean Pd(111). The objective of this thesis is to use UHV experimental studies with these same reactants on oxygen-precovered Pd(111)

to obtain a molecular-level understanding of how the presence of oxygen changes the mechanisms, selectivities, and product distributions.

1.6 Thesis Scope

The purpose of this thesis is to determine the effects of surface oxygen on multifunctional alcohol decomposition. Surface investigations of the thermal oxidation chemistry of a range of these molecules on O/Pd(111) are presented here. The following chapters of this thesis are briefly described below.

Chapter 2. O-H versus C-H Bond Scission Sequence in Ethanol Decomposition on Pd(111)

The first phase of the work includes a study of the low-temperature reaction sequence of a simple alcohol (ethanol) on Pd(111). Before we can understand complex alcohols' surface chemistry, we must be conclusive about the mechanism for simple alcohols. Recent literature has shown conflicting reports about ethanol decomposition through an alkoxide⁷⁸ or hydroxyethyl⁹³ intermediate. The objective of these studies is to experimentally determine whether O-H or C^{α}-H bond scission occurs first; we conclude ethanol decomposition proceeds directly to ethoxide.

Chapter 3. The Influence of Oxygen on the Surface Chemistry of 1,2-Propanediol on Pd(111)

Investigations of oxygen's effects begin with the reaction of 1,2-propanediol on O/Pd(111) in the second phase of this thesis. The relative concentrations of the $O_{(a)}$ to the reactant played a large role in product selectivities. Co-adsorbed oxygen increases the overall coverage of 1,2-propanediol that can undergo decomposition, which in turn strongly influences decomposition activation barriers and product distributions.

Chapter 4. Benzyl Alcohol Oxidation on Pd(111): Aromatic Binding Effects on Alcohol Reactivity

In the final phases of this research, we investigate how surface oxygen participates in the reaction of important aromatic oxygenates. With respect to the surface chemistry of benzyl alcohol and benzaldehyde on O/Pd(111), HREEL spectra show that oxidation of benzyl alcohol proceeds through a benzyl alkoxide intermediate to adsorbed benzaldehyde, which also reacts with surface oxygen to produce benzoate. Experiments conducted on ¹⁸O/Pd(111) reveal exchange occurring between surface O and the

benzaldehyde and benzoate intermediates. This exchange has not been reported for other alcohols, suggesting that aromatic binding effects strongly influence alcohol oxidation on Pd.

Chapter 5. Ring Opening and Oxidation Pathways of Furanic Oxygenates on Oxygen-Covered

Pd(111)

In this portion of the research, we focused on how changing the nature of the aromatic substituent group affected alcohol oxidation chemistry. Furfuryl alcohol is dehydrogenated to furfural, which is decarbonylated to furan; ring opening of furan subsequently occurs through $O-C^{\alpha}$ scission. The presence of surface oxygen results in a new, higher-temperature desorption channel for furan; this channel coincides with desorption of partial oxidation products, 2(5H)-furanone and maleic anhydride. The isotopic product distributions from experiments on ¹⁸O/Pd(111) suggest that partial oxidation of furan occurs through a ring-opened carboxylate intermediate.

Chapter 6 contains a summary of conclusions. These findings have practical implications for catalyst design, where it is useful to understand the elementary steps of a reaction such as oxidation of complex alcohols. The appendices provide supporting information to the final data chapters. Appendix A includes TPD and HREELS figures related to the study of benzyl alcohol and benzaldehyde on O/Pd(111). Appendix B includes additional TPD and HREELS figures for the study for furfuryl alcohol, furfural and furan on O/Pd(111).

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CHAPTER 2

O-H versus C-H Bond Scission Sequence in Ethanol Decomposition on Pd(111)

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2.1 Abstract

The low temperature reaction sequence of ethanol adsorption and decomposition on Pd(111) has been studied using temperature-programmed desorption and high-resolution electron energy loss spectroscopy. The goal of these studies was to experimentally determine whether O-H or C^{α}-H bond scission occurs first. This was accomplished by examining the reaction of two partially deuterated ethanol molecules (only the fully deuterated version has been studied previously); a deuterium atom at the hydroxyl (CH₃CH₂OD) or two deuterium atoms at the α -carbon (CH₃CD₂OH). Based on the thermal evolution of vibrational spectra together with the sequence of desorption of D₂O and H₂O during TPD, we conclude that the decomposition of adsorbed ethanol proceeds directly to ethoxide (not hydroxyethyl) on Pd(111).

2.2 Introduction

Ethanol (EtOH) is widely used as a fuel, feedstock, and solvent, and has received much research attention. EtOH can be produced in vast quantities from biomass carbohydrate fermentation ¹ and is cost-competitive with fossil fuel EtOH production on the industrial scale.² Ethanol serves as a hydrogen source in steam reforming³ and as an important base chemical for higher value organic products like acetaldehyde, acetic acid, and ethyl esters/amines/halides.⁴ Developing an understanding of ethanol's complete reaction pathway on catalysts is useful toward development of surfaces for the applications above, and as a key probe molecule for oxygenate surface chemistry in general.

Studies of ethanol's surface chemistry range over many surfaces, including Ni(111),^{5,6} Pt(111),^{7,8} Rh(111),⁹ Cu(110),¹⁰Ag(110),¹¹ Pd(111)¹²⁻¹⁴ and Pd(110).^{15,16} The originally proposed reaction mechanism of ethanol decomposition on clean Pd(111) was based on temperature-programmed

desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) experiments; it begins with O-H scission and formation of ethoxide (CH₃CH₂O), followed by sequential dehydrogenation to η^2 -acetaldehyde and η^1 (C)-acetyl, until it is decarbonylated to form CO and methane.¹³ Ethanol decomposition has also been studied on O/Pd(111) through TPD experiments by Davis and Barteau. The mechanism proceeds on O/Pd(111) via O-H scission to ethoxide followed by dehydrogenation to η^1 acetaldehyde, then (in the presence of sufficient oxygen) oxidation to acetate; decarboxylation follows resulting in methane formation.¹² Their evidence for the ethoxide intermediate formation was a weak stretch near 330 cm⁻¹ assigned as a Pd-O stretch, rather than direct experimental observation of O-H bond scission.

In the first reported density functional theory (DFT) study of ethanol's adsorption and decomposition on Pd(111) by Li, et al. it was calculated that a C^{α}-H bond was the first to break in this process.¹⁷ Ethanol adsorbs at a top site and dehydrogenates to hydroxyethyl (CH₃CHOH) with a barrier of 89.1 kJ/mol, then O-H bond activation occurs with a barrier of 51.9 kJ/mol. Li's sequence is in direct disagreement with the experimentally proposed mechanisms of initial O-H scission upon ethanol adsorption on Ni(111), Pt(111) and Pd(111).^{6,8,13} The mechanism proposed in those experimental studies (and the current work) would be consistent with observations of methanol decomposition on Pd(111) proceeding through O-H scission first is clear; a saturation dose of CH₃OD adsorbed on O/Pd(111) results in isotopic water products D₂O at 190 K and DHO at 240 K prior to H₂O near 280 K.¹³

The goal of these studies was to provide direct experimental evidence for initial O-H or C-H bond scission. While the reaction of ethanol on Pd(111) has been studied previously, only the non-deuterated (CH₃CH₂OH) and fully deuterated (CD₃CD₂OD) versions of the molecule were utilized.¹⁴ Here, two selectively deuterated ethanol molecules have been used; a deuterium atom at the hydroxyl (CH₃CH₂OD) or two deuterium atoms at the α -carbon (CH₃CD₂OH). High-resolution electron energy loss and TPD spectra presented here provide experimental evidence for the O-H bond being the first to break when ethanol adsorbs on Pd(111). Comparisons are made to DFT-calculated vibrational spectra for the

respective intermediates,³¹ which support the experimentally proposed mechanism of adsorbed ethanol proceeding directly to ethoxide on Pd(111).

2.3 Materials and Methods

All HREELS experiments were conducted in an UHV chamber described previously (base pressure ~1.3 x 10^{-8} Pa or 1 x 10^{-10} torr).³² The chamber is equipped with a LK5000 high-resolution electron energy loss spectrometer (LK Technologies) and a model 981-2046 sputter gun for cleaning (Varian). A specular angle of 60° with respect to the surface normal and beam energy of 6.32 eV were used in all HREELS experiments. The peak positions of HREEL spectra are reported to the nearest 5 cm⁻¹ with a resolution at or below 8 meV. All spectra are normalized to the same elastic peak value by dividing their intensities by the height of the elastic peak.

All TPD experiments were conducted in a stainless steel ultrahigh vacuum (UHV) chamber described previously (base pressure $\sim 1.3 \times 10^{-8}$ Pa or 1 x 10^{-10} torr).³³ The UHV chamber was equipped with a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) for TPD, a RVL2000 LEED optics unit with an electron gun (LK Technologies) and a NGI3000-SE sputter gun (LK Technologies) for cleaning the sample. The Pd(111) single crystal (Princeton Scientific) was cleaned by backfilling the chamber with oxygen while heating and cooling or by mild sputtering with argon. Sample cleanliness was verified by oxygen TPD. The crystal is mounted to a tantalum disk and held on a copper stage with clips. The temperature is measured by a thermocouple spot welded adjacent to the crystal mount. Cooling is accomplished by a liquid nitrogen reservoir.

To prepare an O-covered surface, approximately 15-Langmuir oxygen was dosed while cooling the sample between 973 K and 373 K. This treatment results in the formation of a p(2x2)O/Pd(111)surface as confirmed previously using LEED.³⁴ The same O₂ dosing procedure was used in the TPD and HREELS chambers. The deuterated ethanol compounds were dosed onto the crystal through a direct dosing line, where doses were characterized by the partial pressure in the line. Ethanol decarbonylation yields were tracked by comparing the CO TPD peak area to the coverage resulting from a saturating dose of CO, 0.67 ML.³⁵ Ethanol-*d* (CH₃CH₂OD) was obtained at reported 99.5+ atom % D from Aldrich and ethyl-1-1-*d*2 alcohol (CH₃CD₂OH) was obtained from CDN Isotopes at reported 99.1 atom % D. Ultrahigh purity O_2 , CO, and Ar were obtained from Matheson Trigas.

2.4 Results and Discussion

2.4.1 Vibrational Spectroscopy

High-resolution electron energy loss spectroscopy experiments were conducted to track bondbreaking processes in selectively deuterated ethanol as a function of temperature. Figure 2-1 compares low temperature spectra after exposure of clean Pd(111) to CH₃CH₂OD (EtOD). Vibrational mode assignments in Table 2-1 are based on visualization of the forces on each atom at a given frequency from DFT calculations and comparison with literature. Figure 2-2 depicts the structures of ethanol and ethoxy calculated using DFT.



Figure 2-1. High-resolution electron energy loss spectra following a 1.5 Langmuir CH₃CH₂OD dose on clean Pd(111) at 130 K followed by brief annealing to 170 K and 180 K. In both cases, the elastic peak was normalized to the same height and magnified as noted.

Mode	IR	DFT	CH ₃ CH ₂ OD	DFT	CH ₃ CH ₂ O	DFT	CH ₃ CH ₂
	CH ₃ C	CH ₃ CH ₂ O	130 K	CH ₃ CH ₂ OD	(ad) 180 K	CH ₃ CH ₂ O	$O(ad)^{14}$
	H ₂ OD	D gas ³¹		$(ad)^{31}$		$(ad)^{31}$	
	gas ³⁶						
v(OD)		2700	2290	2624			
v(CH ₃)	2941-	2939-3035	n.r.	2942-3034	2900	2947-3032	2925
	2996						
ν(CH ₂)	2953	2908-2997	2830	2907-2981	2830	2745-2777	2925
χ(CH ₂)	1490	1460	1330	1453	1400	1398	1465
χ(CH ₃)	1463	1439	1330	1432	1400	1442	1465
$\tau(CH_3)$	1401	1435	1330	1429	1400	1420	1400
$\rho(CH_2)$	801	761	780	764	780	787	745
$v_a(CCO)$	1064	1018	1050	999	995	964	1040
v _s (CCO)	897	847	950	835	880	861	855
χ(CCO)	408	397	410	406	410	557	450

Table 2-1. Vibrational mode assignments (cm⁻¹) of ethanol-OD adsorbed on clean Pd(111).

v=stretch χ =scissor τ =twist ρ =rock Υ =wag a=asymmetric s=symmetric n.r. = not resolved



Figure 2-2. Ethanol (left) and ethoxy (right) adsorbed on Pd(111) at 1/4 monolayer coverage. Red denotes O atoms, gray denotes C atoms, white denotes H atoms, light yellow denotes D atoms, blue denotes Pd atoms. The same structures were used to calculated vibrations for deuterated adsorbates, with the appropriate H atoms switched to D atoms; deuterium atoms in the structures are simply for visualization of selectively deuterated adsorbates.³¹

In general, good agreement exists between the experimental peak positions and DFT modes for adsorbed EtOD in Table 2-1; the only major difference is with the location of the v(OD) peak. Experimentally, it is observed at 2290 cm⁻¹ whereas it is calculated by theory to appear at 2624 cm⁻¹. A possible explanation for this discrepancy is that the 1/4 monolayer studied with DFT does not capture hydrogen bonding interactions between neighboring adsorbed ethanol molecules that are present in the experimental spectrum. Others have indicated that inclusion of additional adsorbed structures, particularly ones that can participate in hydrogen bonding, is important for ethanol adsorption and reaction on surfaces, and likely inclusion of these structures would further increase agreement between experiment and theory.³⁷ For an ethanol dimer on Rh(111), Yang, et al.³⁸ report a 562 cm⁻¹ red shift in the v(OH) mode when ethanol molecules are hydrogen bonded to each other, corresponding to a shift of 397 cm⁻¹ for v(OD) under the harmonic oscillator approximation. This shift puts the calculated v(OD) stretch in the same region as the experimentally observed v(OD). The other dominant modes correspond to CH₂ and CH₃ stretching around 2830-2900 cm⁻¹, CH₂ and CH₃ scissoring modes from 1330-1400 cm⁻¹.

Between 130 K and 170 K, vibrational spectra do not appreciably change with unperturbed $\chi(CCO)$, $\rho(CH_2) v_s(CCO)$, $\chi(CH_3)/\chi(CH_2)$, v(OD) and $v(CH_2)$ vibrations. However, when annealed at 10 K higher, 180 K, the O-D bond of EtOD clearly breaks on clean Pd(111), evidenced by the disappearance of the loss peak at 2290 cm⁻¹, forming ethoxide; meanwhile the CH₂ stretch at 2830 cm⁻¹ and CH₂ scissoring mode near 1330-1400 cm⁻¹ remain unchanged. However, these stretches are convoluted with the CH₃ stretch and scissoring modes. Below, we discuss experiments conducted to discern the convolved CH₂ and CH₃ peaks seen here. At 180 K both v(CCO) loss modes at 880 cm⁻¹ and 995 cm⁻¹ becomes apparent. In addition, the loss at 780 cm⁻¹ corresponding to $\rho(CH_2)$ becomes stronger. Theoretical vibrational modes for adsorbed ethoxy agree with experiment, the most obvious feature being the lack of a peak in the 2600 cm⁻¹ range, confirming that the OD bond has broken. As further confirmation of the ethoxy intermediate, the $\rho(CH_2)$ mode is calculated at 787 cm⁻¹ in good agreement with experiment. In contrast, the corresponding $\rho(CH)$ mode for hydroxyethyl (CH₃CHOD) is calculated at 826 cm⁻¹.

The surface chemistry of EtOD was also investigated on the O-precovered Pd(111) surface with HREELS. Figure 2-3 shows HREEL spectra for the same size EtOD exposure as Figure 2-1, but on O/Pd(111). The v(O-Pd) stretch appears at the lowest temperatures around 400-500 cm⁻¹. The spectra are essentially the same between 145 K and 170 K, but by 180 K v_a(CCO) (1020 cm⁻¹) weakens into the shoulder of the new strong peak, v_s(CCO) (860 cm⁻¹). The O-D bond activation energy appears to increase in the presence of surface O, breaking after 190 K instead of by 180 K, evidenced by the weakening 2350 cm⁻¹ stretch. Studies of ethanol on O/Pd(111) work is limited to TPD¹² and shows water desorbing at 200 K for a saturation dose, in line with the O-D bond still being intact at 180-190 K. The presence of χ (CH₂) (1395 cm⁻¹), v(CH₂)/v(CH₃) (2900 cm⁻¹), ρ (CH₂) (780 cm⁻¹) and v_a(CCO) (1020 cm⁻¹) and χ (CH₂) (1395 cm⁻¹) are still evident, so dehydrogenation at the α -C is not complete; a small peak at 660 cm⁻¹ for Y(CH₂) also becomes resolved. By 300 K, decarbonylation has occurred and adsorbed CO (evidenced at 1760 cm⁻¹) is present on the surface. The shoulder at low wavenumber is likely due to the presence of surface carbonaceous species.



Figure 2-3. High-resolution electron energy loss spectra following 1.5-Langmuir ethanol-OD (CH_3CH_2OD) adsorption on O/Pd(111) at 145 K followed by brief annealing to the temperatures indicated. In all cases, the elastic peak was normalized to the same height and magnified as noted.

Experiments using ethanol isotopically labeled at the α -C position help to confirm preferential low-temperature O-H scission and formation of the ethoxy intermediate. Figure 2-4 is a low temperature HREELS series for a saturating dose of ethanol-*d*2 (EtOH-*d*2) on clean Pd(111). Table 2-2 lists the vibrational mode assignments for all EtOH-*d*2 HREELS experiments on clean Pd(111). At 150 K v(OH) becomes clearer, so the alcohol is intact, the key modes of which are ρ (CD₂), v_a(CCO), χ (CD₂) and χ (CH₃). By 180 K it appears the O-H bond has been broken while ρ (CD₂) at 620 cm⁻¹ and χ (CD₂) at 1050 cm⁻¹ are still evident, along with v(CD₂). In Figure 2-1 the χ (CH₂) mode at 1400 cm⁻¹ is convolved with χ (CH₃) at 180 K; now in Figure 2-4 it is possible to see the coexistence of the χ (CH₃) and χ (CD₂) modes at 1340 cm⁻¹ and 1050 cm⁻¹, respectively. By 190 K the loss at 2000-2100 cm⁻¹ has disappeared, indicating the methylene C-D bonds have broken. Similarly, the χ (CD₂) mode at 1050 cm⁻¹, which is in the same position between 165 K and 180 K at the point where the O-H stretch has disappeared, is now gone at 190 K.



Figure 2-4. High-resolution electron energy loss spectra following a1.5 Langmuir dose of ethanol- d^2 (CH₃CD₂OH) adsorbed on clean Pd(111) at 130 K followed by brief annealing to the temperatures indicated. In all cases, the elastic peak was normalized to the same height and magnified as noted.

Mode	IR	DFT	CH ₃ CD ₂ OH	DFT	CH ₃ CD ₂ O	DFT	CD_3CD_2
	CH ₃ CH ₂ OH	CH ₃ CD ₂ OH	130-165 K	CH ₃ C	(ad) 180 K	CH ₃ CD ₂ O	$O(ad)^{14}$
	gas ³⁶	gas ³¹		D ₂ OH		$(ad)^{31}$	
				$(ad)^{31}$			
v(OH)	3676	3712	3140	3605			
$\nu(CH_3)$	2989	2939-3033	2880	2942-	2880	2947-3032	
				3031			
$v(CD_2)$		2120-2223	2070	2118-	2000-2100	1994-2053	2100-
				2212			2230
$\chi(CD_2)$		1098	1110	1099	1050	979	1070
χ(CH ₃)	1394	1445	1395	1441	1340	1440	
τ(CH ₃)	n.r.	1435	1340	1428	1340	1419	
$\rho(CD_2)$		647	685	651	650	660	560
$v_a(CCO)$	1089	934	920	913	870	908	960
$v_{s}(CCO)$	885	815	760	813	n.r.	815	740
χ(CCO)	419	398	370	401	n.r.	553	440

Table 2-2. Vibrational mode assignments (cm⁻¹) for ethanol-*d*2 adsorbed on clean Pd(111).

v=stretch χ =scissor τ =twist ρ =rock Υ =wag a=asymmetric s=symmetric n.r. = not resolved

Agreement with calculated vibrational spectra is generally good with the exception of the v(OH) peak, for reasons stated above. The major difference between the CH₃CH₂O spectrum (Figure 2-1) and CH₃CD₂O spectrum (Figure 2-4) is the shift of the v(CH₂)/v(CD₂) peaks to lower wavenumber, as expected, in concordance with experiment. In particular the ρ (CD₂) mode at 650 cm⁻¹ corresponds well with the calculated ρ (CD₂) mode at 660 cm⁻¹. The corresponding hydroxyethyl ρ (CD) stretch is calculated to appear at 694cm⁻¹, confirming production of ethoxy rather than hydroxyethyl.

One possible explanation for the discrepancy between the experimental evidence of ethoxy formation and Li, et al.'s³⁸ computational results of hydroxyethyl formation lies in the well-known overbinding by GGA functionals,³⁹ such as PW91 that Li, et al. used. This could lead to overstabilization of multidentate species, such as that formed at the transition state of C^{α}-H scission in ethanol, leading to an apparently lower reaction barrier. Sautet and coworkers³⁷ note that hydrogen bonding within an ethanol dimer plays an important role in dehydrogenation on Rh(111), leading to a lower barrier for O-H scission, in agreement with experiment. The same study also notes that the C^{α}-H dehydrogenation barrier from the ethanol monomer is lower than the O-H, but that inter-molecular or even intra-molecular hydrogen

bonding will lower the O-H barrier such that it is the favorable pathway, as is the case in the experiments presented here. The HREELS results presented here clearly indicate that ethanol decomposition proceeds through an ethoxy intermediate, rather than hydroxyethyl.

2.4.2 Temperature-Programmed Desorption

Temperature-programmed desorption experiments were used to complement the vibrational spectroscopy investigations. Experiments on clean Pd(111) are not particularly useful for determining the sequence of bond-breaking steps, since product desorption occurs at much higher temperatures than the key O-H and C-H scission steps occur. However, use of surface O as an H atom scavenger produces water, which desorbs at the temperature where the reaction is occurring. Due to the similarity of HREELS results clean and O/Pd(111) in Figure 2-3 we expect the bond scission sequence of O-H and C-H to behave here as it would on Pd(111). Figure 2-5 shows the water products D_2O , DHO, and H_2O during TPD from an EtOD-exposed O/Pd(111) surface. Peak deconvolutions were carried out to reduce contributions of the deuterated product fragments from the non-deuterated water products; D₂O's OD and DHO's OD fragment (m/z = 18) were subtracted from H₂O (m/z = 18), so the m/z = 18 signals reported are entirely due to H₂O desorption. D₂O desorbs first at 230 K, indicating the O-D bond is the first to break. DHO follows at 240 K and then H₂O at 280 K. Similarly, Figure 2-6 shows the water products of EtOH-d2 dosed on O/Pd(111). Water (H₂O) desorbs at 240 K, before DHO at 265 K and D₂O at 280 K, thus the O-H bond breaks before the methylene C^{α} -D. The water peak temperatures in both cases agree with Davis and Barteau's non-deuterated EtOH O/Pd(111) study for a sub-saturation EtOH dose.¹² The TPD temperatures of water are higher than indicated by the HREELS hydroxyl bond breaking presented above. There are three possible explanations for this behavior: (1) a difference in coverage during these experiments (saturated for HREELS, sub-saturated for TPD),¹² (2) water readsorption to surfaces near the mass spectrometer during TPD and (3) the more rapid temperature ramp used in TPD compared to the slow annealing treatment in HREELS. Despite the possible difference in coverage and absolute temperatures, both sets of data point to the same sequence of bond breaking, first O-H then C^{α} -H.



Figure 2-5. Temperature-programmed desorption spectra of water desorption following a dose of ethanol-OD dosed on O/Pd(111), corresponding to 0.08 CO ML.



Figure 2-6. Temperature-programmed desorption spectra of various water products when ethanol-*d*2 is dosed on O/Pd(111), corresponding 0.04 CO ML.

2.5 Conclusions

The goal of these studies was to experimentally determine whether O-H or C^a-H bond scission occurs first. Two partially deuterated ethanol molecules were used to accomplish this; a deuterium atom at the hydroxyl (CH₃CH₂OD) or two deuterium atoms at the α -carbon (CH₃CD₂OH). Agreement between HREELS and calculated vibrational spectra for the adsorbed alcohol and alkoxide is generally good, confirming vibrational mode assignments, particularly for ρ (CH₂)/ ρ (CD₂), which can be used to monitor the formation of ethoxy over hydroxyethyl. Temperature-programmed desorption trends for deuterated water desorption from selectively deuterated molecules confirm the bond breaking sequence proposed. Experimental (TPD and HREELS) evidence has been presented and compared to theoretical calculations for the O-H bond being the first to break when ethanol decomposes on Pd(111). This finding has practical implications for catalyst design, where it is useful to understand the elementary steps of a reaction such as alcohol oxidation.⁴⁰⁻⁴³ In this case, the rate limiting step to the corresponding aldehyde is C-H scission.

2.6 References

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CHAPTER 3

The Influence of Oxygen on the Surface Chemistry of 1,2-Propanediol on Pd(111)

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3.1 Abstract

The surface chemistry of 1,2-propanediol (PDO) has been studied on oxygen-precovered Pd(111) using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Adsorbed 1,2-propanedioxy (-OCH(CH₃)CH₂O-) forms from the activation of the O-H bonds. When the concentration of $O_{(a)}$ is large compared to 1,2-propanedioxy, no H₂ is produced and the dialkoxide reacts to form H₂O, CO through decarbonylation, and CO₂ through decarboxylation. Unreacted oxygen also desorbs as O₂ at high temperature. Conversely, when the concentration of O_(a) is small relative to 1,2-propanedioxy, the dialkoxide reacts to form decomposition products (H₂, CO), oxidation products (H₂O, glyoxal, methylglyoxal, formaldehyde) and hydrodeoxygenation products (ethylene, propylene). Co-adsorbed oxygen increases the overall coverage of PDO that can undergo decomposition, which in turn strongly influences decomposition activation barriers and products.

3.2 Introduction

The demand for fuels and chemicals is expected to rise steeply as the world population continues to increase. To meet these needs, multiple resources must be utilized including those in the biomass refining supply chain. Polyols such as glycerol, ethylene glycol, 1,2-propanediol, xylitol, and sorbitol are biomass derivatives that contain a high degree of oxygenate functionality. The oxygenate functionality makes it difficult to selectively react a single functional group since each function is potentially reactive on the surface. For example, glycerol is a polyol of interest because it is an abundant byproduct in the production of biodiesel.¹ Several value-added chemicals result from the oxidation of glycerol, e.g., dihydroxyacetone, glyceraldeyde, glyceric acid, and hydroxypyruvic acid. A catalyst capable of selectively oxidizing glycerol's secondary hydroxyl would produce dihydroxyacetone, a product worth

seventy-five dollars per pound (compared to glycerol's estimated worth of thirty two cents per pound).² Metals active for alcohol oxidations include Pt-group elements such as Pd.³⁻⁵

Previous work has shown that ethylene glycol (EG) and 1,2-propanediol (PDO) decompose on clean Pd(111) via O-H activation to a dialkoxide intermediate (ethylenedioxy and 1,2-propanedioxy, respectively). For 1,2-propanedioxy, increases in thermal energy lead to dehydrogenation, methyl elimination, and formation of adsorbed dialdehyde glyoxal, or dehydrogenation and formation of adsorbed dialdehyde methylglyoxal.⁶ On clean Pd(111) the C-C scission reaction pathway forming carbon monoxide and hydrogen predominates over the C-O scission pathway, which forms ethylene and water. Ethylenedioxy decomposes by a similar mechanism. While PDO studies are limited to clean Pd(111) and clean and oxygen precovered Ag(110) (O/Ag(110)), EG decomposition has been studied more extensively on Pt(111),⁷ Rh(100), ⁸ Rh(111),⁹ Ni(100),¹⁰ Ni(111),¹¹ Cu(110),¹² Ag(110),¹³ and Mo(110).¹⁴ Carbon-carbon and C-H bond scission are the favored reaction pathways on each of these single crystal surfaces, except for Ag(110), where EG adsorbs reversibly, and Mo(110), which favors C-O bond scission. One study of glycerol on a PtNi bimetallic surface showed complete decomposition to H₂ and CO, in agreement with the study of EG on Ni-terminated Pt(111).¹⁵ This is an important demonstration that reactions of smaller probe molecules like EG can be useful models for larger oxygenates.

Though polyol oxidation has received significant attention in the catalysis literature, surface studies of the interaction of oxygen with polyols have been rare. More common have been investigations of simple alcohol adsorption on O-covered surfaces. These oxygen-covered surfaces include Pd(111)¹⁶, Rh(111),¹⁷ Pt(111),¹⁸ Cu(100),¹⁹ Cu(110),²⁰ Au(111),²¹ and Mo(110).²² In these alcohol reactions, the roles of oxygen adatoms generally include Brønsted or Lewis acid-base reactions with adsorbates, site blocking, and electronic modification of the metal surface. Davis and Barteau reported that the reaction of simple alcohols (methanol, ethanol, 1- and 2-propanol) on O/Pd(111)¹⁶ were influenced in several ways by the co-adsorbed O. Oxygen serves as a nucleophile, hydrogen scavenger, and Brønsted base; it may also stabilize intermediates or alter reaction intermediates' interactions with the surface.¹⁶

The only study of polyol adsorption and reaction on O-covered surfaces has been for Ag(110).^{13,23} On clean Ag(110), PDO adsorbs reversibly at 175 K, undergoing no further decomposition.²⁴ Conversely, on O/Ag(110), PDO reacts with the adsorbed oxygen to form 1,2-propanedioxy and H₂O. 1,2-propanedioxy proceeds via C-H scission to the partial oxidation products acetol and lactaldehyde or further decomposes via C-C scission to the dialdehyde glyoxal, formaldehyde, CO₂ and H₂O. The key role of atomic oxygen on Ag(110) is activation of the O-H bonds, facilitating adsorption and further reaction of 1,2-propanedioxy. The relative concentrations of 1,2-propanedioxy and O_(a) affect the reaction by stabilizing the dialkoxide intermediate when there is an excess of surface O and promoting nucleophilic attack to produce surface carboxylates.

The chemistry of polyols on O-covered Pt-group surfaces that are more widely used for catalytic polyol oxidation has not been studied.³ While surface O is not necessary to induce O-H activation of a diol on Pd(111), its presence is likely to affect the reaction because surface O has been shown to play various roles in simple alcohol reactions with Pd(111), as summarized above.^{16,25,26} In the present study, the reactivity of PDO on oxygen precovered Pd(111) (O/Pd(111)) is studied in order to understand the reactivity of more complex alcohols, which may aid in catalyst design for selective oxidation. PDO is a probe molecule for glycerol and other polyols because it contains both primary and secondary hydroxyl groups. In the present study, temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) experimental results are reported. Our results indicate that co-adsorbed oxygen strongly influences decomposition activation barriers, desorption products, and the overall extent of alcohol decomposition. The relative coverages of the alcohol and oxygen also play a significant role on Pd(111).

3.3 Materials and Methods

All TPD experiments were conducted in a stainless steel ultrahigh vacuum (UHV) chamber described previously (base pressure $\sim 1.3 \times 10^{-8}$ Pa or 1×10^{-10} torr).²⁷ The UHV chamber was equipped with a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) for TPD, a RVL2000 LEED optics unit

with an electron gun (LK Technologies) and a NGI3000-SE sputter gun (LK Technologies) for cleaning the sample. The Pd(111) single crystal (Princeton Scientific) was routinely cleaned by heating and cooling in oxygen backfilled in the chamber or by mild sputtering with argon. Sample cleanliness was verified by oxygen TPD and the (111) surface orientation was verified by LEED. The crystal is mounted to a tantalum disk and held on a copper stage with clips. The temperature is measured by a thermocouple spot welded adjacent to the crystal mount. Cooling is accomplished by a liquid nitrogen reservoir. Similarly, all HREELS experiments were conducted in a UHV chamber described previously (base pressure ~1.3 x 10⁻⁸ Pa or $1x10^{-10}$ torr).²⁸ The chamber is equipped with a LK5000 high-resolution electron energy loss spectrometer (LK Technologies) and a model 981-2046 sputter gun for cleaning (Varian). A specular angle of 60° with respect to the surface normal and beam energy of 6.32 eV were used in all HREELS experiments. HREELS peak positions are reported to the nearest 5 cm⁻¹. All HREEL spectra are normalized to the elastic peak height.

To prepare an O-covered surface, approximately 15-Langmuir oxygen was dosed while cooling the sample between 973 K and 373 K. This treatment results in the formation of a p(2x2)O/Pd(111)surface as confirmed using LEED. 1,2-Propanediol was dosed onto the crystal through a direct dosing line, where doses were characterized by the partial pressure in the line. Decarbonylation yields were tracked by comparing the CO TPD peak area to the coverage resulting from a saturating dose of CO, 0.67 ML.²⁹ A correction factor for CO₂ versus CO desorption (in ML) was calculated by separately backfilling the chamber with the same pressure of each molecule and determining their intensities via the mass spectrometer. This analysis yielded a sensitivity factor of approximately 1.0 for the CO₂ (m/z = 44) signal. Fragmentation patterns for ethylene, propylene, and 1,2-propanediol were collected by backfilling the chamber. 1,2-Propanediol and 1,2-propanediol-*d*2 were obtained at reported >99% purity from Sigma-Aldrich and 98% D from Isotec, respectively. Ultrahigh purity ¹⁶O₂, CO, H₂, propylene and Ar were obtained from Matheson Trigas and ¹⁸O₂ from Sigma Aldrich via CortecNet. Ethylene was obtained at reported 99.5+% purity from Aldrich.

3.4 Results

3.4.1 Temperature-programmed desorption

Temperature-programmed desorption was employed to investigate the thermal decomposition of PDO on a p(2x2)O/Pd(111) surface as a function of initial PDO coverage. Figure 3-1 shows a representative TPD spectrum resulting from a relatively small dose of PDO on O/Pd(111). With an O_2 peak (m/z = 32) arising from unreacted oxygen centered at 800 K and no H_2 (m/z = 2) desorption, this is defined as the low PDO coverage regime. Carbon dioxide (m/z = 44) and H_2O (m/z = 18) were the major oxidation products desorbing with CO (m/z = 28) the only pure decomposition product. The absence of H_2 as a product is due to the presence of sufficient surface O to oxidize all H atoms resulting from decomposition, forming H_2O that begins desorbing at 250 K. Carbon dioxide desorbs at 425 K and 475 K, the result of two separate processes (carboxylate decomposition and CO oxidation), as discussed below. Carbon monoxide desorption at 475 K reflects desorption-limited kinetics.



Figure 3-1. Temperature-programmed desorption traces from a small 1,2-propanediol dose at 173 K onto O/Pd(111), corresponding to the low initial PDO coverage regime. Reported spectra are from a direct dose that led to 0.01 ML of CO desorption and 0.02 ML of CO₂. The masses plotted are hydrogen (m/z = 2), oxygen (m/z = 32), carbon dioxide (m/z = 44), CO (m/z = 28) and water (m/z = 18).

Figure 3-2 shows the results of isotopic labeling studies where Pd(111) was precovered with p(2x2)¹⁸O in order to track how surface O is incorporated into the reaction products. In such experiments the ¹⁸O content indicates the degree of surface oxygen incorporation in the products, whereas ¹⁶O originates from PDO. Similar to Ayre and Madix's work on O/Ag(110),²³ pre-dosed ¹⁸O was incorporated into the water and carbon dioxide products only. Figure 3-2 shows TPD results from two sub-saturation exposures of PDO on ¹⁸O/Pd(111) that illustrate three different mechanisms for CO₂ production. At the lower PDO coverage (Figure 3-2a), high-temperature (> 500 K) $C^{18}O_2$ peaks are evident from oxidation of surface carbonaceous species by two surface ¹⁸O atoms.²⁶ At this low coverage, there is little evidence for oxidation of $C^{16}O$ by surface ¹⁸O, consistent with a low decarbonylation yield. The evolution of $H_2^{18}O$ and C¹⁸O¹⁶O simultaneously at 465 K has previously been associated with the decomposition of a surface carboxylate, which only forms when the relative concentration of oxygen to diol is high.^{16,23} Interestingly, the temperature for carboxylate decomposition shifts downward at higher PDO coverage (Figure 3-2b) to 400 K, as also observed for simple alcohols.¹⁶ The second $C^{18}O^{16}O$ (m/z = 46) peak at 460 K is consistent with CO oxidation whereby molecular CO on Pd(111) reacts with $O_{(a)}$ between 400 and 500 K.³⁰ The single m/z = 48 desorption peak at 480 K likely results from the recombination of separate surface-bound C and ¹⁸O_(a).²⁶ For simple alcohols on O/Pd(111), CO₂ desorbed in a single peak at 410 K from ethanol and 390 K from 1-propanol sub-saturation exposures while no appreciable CO₂ production occurred from 2-propanol on O/Pd(111); H₂O desorption accompanied CO₂ desorption at these temperatures.¹⁶ In the reactions of aldehydes on O/Pd(111), CO₂ desorbed in a single peak at 420 K for acetaldehyde, 375 K for propionaldehyde, and 270 K for formaldehyde; in each case the evolution of CO₂ was attributed to the decomposition of the corresponding carboxylate (acetate, propanoate, and formate, respectively).²⁵



Figure 3-2. Isotopic products, water and carbon dioxide, desorbing in reaction of 1,2-propanediol on ${}^{18}\text{O/Pd}(111)$. (a) The 1,2-propanediol dose corresponds to 0.004 ML CO, 0.02 ML C ${}^{18}\text{O}{}^{16}\text{O}$ (m/z = 46) and 0.008 ML C ${}^{18}\text{O}_2$ (m/z = 48). (b) The 1,2-propanediol dose corresponds to 0.02 ML CO, 0.14 ML C ${}^{18}\text{O}{}^{16}\text{O}$ and 0.02 ML C ${}^{18}\text{O}_2$.

Isotopically-labeled 1,2-propanediol-*d*2 ((DO)CH₂CH(OD)CH₃) was used to further probe the reaction on O/Pd(111). Figure 3-3 shows labeled water, D₂O (m/z = 20), desorbs at 255 K before H₂O (m/z = 18) at 265 K, indicative of the hydroxyl bonds being the first to break. This is in agreement with HREELS evidence of 1,2-propanedioxy's stability up to 240 K on clean Pd(111).⁶



Figure 3-3. 1,2-Propanediol-*d*2 dosed on O/Pd(111) corresponding to 0.10 CO ML desorption, showing D_2O (m/z = 20) desorption prior to DHO (m/z = 19) and H_2O (m/z = 18). Water fragmentation patterns were used to deconvolve the m/z = 18 contributions from the D_2O and DHO products.

While the low PDO coverage regime is characterized by the presence of excess surface oxygen and extensive decomposition, the behavior changes when the initial PDO coverage is high. Figure 3-4 shows the TPD spectrum resulting from a saturation exposure of PDO on O/Pd(111) (in blue). For the purposes of comparison, the TPD spectrum of the same exposure of PDO on clean Pd(111) is shown in the same plot (in black). The spectra illustrate what we define as the high-coverage regime with a H₂ (m/z = 2) desorption peak and the total consumption of oxygen, which no longer exhibits a high-temperature TPD peak. The trace intensities are larger for all reaction products on the O/Pd(111) surface. In contrast, molecular desorption of 1,2-propanediol (m/z = 45), which occurs at 300 K, is less prevalent from O/Pd(111). The lower yield of molecular PDO from O/Pd(111) and higher yield of reaction products indicate that the surface oxygen leads to a greater extent of decomposition. Water (m/z = 18) desorbed at 265 K and 300 K, when surface oxygen recombined with hydrogen atoms produced from PDO decomposition. There are no peaks in the water desorption spectra above 300 K, with the long trailing edge consistent with high levels of background water under these conditions. Experiments with 18 O/Pd(111) (see for example Figure 3-2b) agree with oxygen coverage being low above ~ 350 K at the highest PDO coverage.



Figure 3-4. Comparative TPD spectra of 1,2-propanediol reaction products on O/Pd(111) (in blue) and clean Pd(111) (in black) from saturating PDO exposures that correspond to 0.40 ML CO (O/Pd(111)) and 0.12 ML CO (clean Pd(111)).

Hydrogen desorbs at 340 K as a result of recombining H atoms bound to the surface following C-H scission. Desorption of H₂ is indicative that the surface oxygen has been consumed. Methane (m/z = 14) desorbed at 360 K following hydrogenation of the methyl ligand after C-C scission in 1,2propanedioxy.⁶ The dialdehyde products, glyoxal (O=CHCH=O) and methylglyoxal (O=CHC(CH₃)=O), desorbed in peaks centered around 460 K, with additional low temperature peaks of methylglyoxal near 265 K and 300 K. The observation of propylene and ethylene between 425 K and 520 K follows C-O scission of the dialdehyde intermediates, which must be hydrogenated. Some formaldehyde (m/z = 30) desorbed at 460 K, likely following C-C scission of the intermediate glyoxal. This production of formaldehyde was not detected in previous studies of PDO on clean Pd(111).⁶ Carbon monoxide (m/z = 28) is produced in a desorption-limited process at 460 K.^{31,32} The CO₂ yield was low (not pictured) compared to that seen in the excess surface O regime, with no clearly defined peaks. The dominant reaction pathway appears to be O-H, C-H and C-C scission, evidenced by the production of CO and dialdehydes. However, the production of alkenes was also observed, indicating that C-O scission is a viable reaction pathway on O/Pd(111). The greater extent of diol decomposition seen for the oxygen-covered surface is consistent with previous observations of methanol's increased uptake on O/Pd(111), which resulted in the desorption of more carbon-containing reaction products than clean Pd(111).¹⁶ The dominant reaction pathway appears to be complete decarbonylation to produce two molecules of CO per molecule of PDO; approximate yields of olefin and alkene products were found to be at least a factor of 8 and 3/4 lower than the CO yield (based on approximated mass spectrometer sensitivity factors), respectively.³³

Having outlined the behavior in the limit of high and low PDO pre-coverages on O/Pd(111), examining the TPD behavior over the complete range of initial PDO coverage is useful. Figure 3-5 illustrates the effect of increasing 1,2-propanediol exposure on the desorption of the reaction products CO, H₂, methane, ethylene, propylene, and CO₂. For the smallest initial PDO coverage there is little CO (m/z = 28) desorption, but it steadily increases with dose size and shifts to lower desorption temperatures.²⁹ As mentioned previously, H₂ (m/z = 2) does not desorb in the smallest doses where the relative concentration of oxygen is high. As the dose increases, a desorption-limited peak near 350 K becomes apparent, signaling consumption of the surface oxygen below this temperature. The high temperature reaction-limited H₂ production (\geq 450 K) in the largest doses is consistent with decomposition of hydrocarbon fragments that have been seen to evolve from olefins on Pd(111).^{34.37} Methane (m/z = 14) desorbs as low as 345 K at moderate coverage with its temperature increasing to 400 K at high coverages. The increase in temperature is consistent with surface crowding effects; an increase in number of surface adsorbates hypothetically makes it more difficult to find Pd to break the C-C bond.

Ethylene (m/z = 27) desorption also shifts from 400 K to around 520 K from moderate to high coverage. Propylene's predominant desorption peak shifts from 420 K to 520 K at high coverage, with a left shoulder still coinciding with its initial mode of production around 430 K. The new higher temperature mode of propylene and ethylene desorption indicates a coverage effect whereby their respective precursor's C-O activation barrier must be increased. An increase in temperature with coverage suggests the rate-limiting step is the decomposition and deoxygenation of the intermediate, which may be hindered on a crowded surface. Carbon dioxide (m/z = 44) desorption follows the trends discussed in detail previously with the isotopic studies. In the smallest dose there are two peaks at 390 K and 460 K, consistent with carboxylate decomposition and CO oxidation. As the dose increases, only the CO oxidation mode is apparent. At the highest initial PDO coverages no CO2 desorbs, suggesting the surface O has been consumed prior to the temperature at which a carboxylate may be formed, presumably in the reaction with hydroxyl hydrogens to form water. Formaldehyde (m/z = 30) desorption is not appreciable until medium coverages in a peak centered at 390 K. Methylglyoxal (m/z = 43) and glyoxal (m/z = 58) desorption becomes apparent at medium coverages near 410 K. However, as coverage is increased, additional small peaks at 260 K and 320 K seem consistent with desorption of the dialdehyde in a monodentate (η^1) configuration.



Figure 3-5. Temperature-programmed desorption spectra illustrating coverage effects as 1,2-propanediol exposure is increased on O/Pd(111). Starting with the bottom trace and increasing, the dose sizes correspond to 0.00, 0.01, 0.03, 0.18, 0.23, 0.39, and 0.47 CO ML desorption, respectively.

3.4.2 High-resolution electron energy loss spectroscopy

High-resolution electron energy loss spectroscopy was employed to aid in identifying the effect of oxygen on the surface intermediates produced during PDO decomposition. Table 3-1 lists the loss assignments of all the HREEL spectra. Figure 3-6 shows an HREEL spectrum following a sub-saturation dose of 1,2-propanediol on O/Pd(111). The bottom trace reflects the adsorption of atomic oxygen on Pd(111) with a peak at 480 cm⁻¹.³⁸ At 150 K the observed losses reflect intact PDO with a weak v(OH)

loss evident at 3400 cm⁻¹. By 170 K, CH₃ rocking and CH₃ in-plane deformation together indicate the methyl ligand is still intact, but the v(OH) stretch is weaker than at 150 K, thus some 1,2-propanedioxy has likely formed. By 250 K v(OH) has disappeared and the alcohol has been consumed, indicating dialkoxide formation has been completed and some further reaction has taken place. The disappearance of the 1390 cm⁻¹ loss strongly suggests the methyl has been abstracted by this temperature. The remaining 900 cm⁻¹ is assigned to hydrocarbon CH rocking (seen for ethylene degradation on Pd(111)^{36,39}), with some CH stretching near 3000 cm⁻¹ still apparent. After annealing to 325 K, a loss at 1830 cm⁻¹ becomes apparent, indicating that the diol has undergone some decarbonylation, while the CH stretching modes are weaker but still evident. In this temperature range, C-H scission to form an adsorbed dialdehyde is also expected; this dialdehyde is associated with a loss near 700 cm⁻¹, and the spectrum in Figure 3-6 is poorly resolved in that frequency range. In separate experiments (not shown), annealing of the surface to higher temperatures (425 K) resulted in CO desorption and observation of a broad peak centered near 750 cm⁻¹, indicative of adsorbed carbonaceous species.


Figure 3-6. High-resolution electron energy loss spectra of a 0.3 Langmuir dose of 1,2-propanediol on oxygen pre-covered Pd(111), annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.

To investigate the effect of oxygen under conditions of high PDO coverage, HREEL spectra were also collected following larger PDO exposures. Figure 3-7 shows the HREEL spectra following an exposure sufficient to produce PDO multilayers on O/Pd(111). The bottom trace reflects the adsorption of atomic oxygen on Pd(111). At a higher coverage the v(OH) stretch of the alcohol (3420 cm⁻¹) is clearly apparent at 150 K, below the multilayer desorption temperature. The CH₂ and CH₃ rocking and wagging modes coupled with the C-O and CCO in-plane deformation stretches show the diol is intact. At 170 K the spectrum is similar except v(OH) shifts up to 3520 cm⁻¹, likely evidence of water bound to the surface,²³ suggesting some 1,2-propanedioxy has formed. At 240 K the v(OH) of water persists and the C-

H stretching mode has weakened while the CH₃ wagging and rocking modes dominate. We cannot rule out the presence of an aldehyde in a η^1 configuration with the loss at 1620 cm⁻¹ becoming more resolved at 240 K (from the shoulder at 170 K). This falls near the location of η^1 (CO) seen at 1675 cm⁻¹ for formaldehyde²⁵ and 1670 cm⁻¹ for acetone on O/Pd(111)²⁶ and 1667cm⁻¹ for acetaldehyde on Pt(111).⁴⁰ By 255 K we would expect a strong loss for π (CO) of dialdehydes near 740 cm⁻¹, as seen on clean Pd(111),⁶ however the spectrum is too poorly resolved. By process of elimination, it is proposed dialdehydes are present on the surface since it is clear decarbonylation is not yet complete with adsorbed CO at a low frequency (1760 cm⁻¹) and yet the reaction has proceeded beyond a dialkoxide, with no clear v(CO) or v(OH) of water. By 345 K extensive decarbonylation has occurred as expected. The surface chemistry appears to be similar to that observed on clean Pd(111),⁶ but with greater intensities after multilayers desorption, consistent with more reaction taking place on O/Pd(111).



Figure 3-7. High-resolution electron energy loss spectra from a 2 Langmuir dose of 1,2-propanediol on O/Pd(111) at <150 K and annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.

Table 3-1. Vibrational mode assignments (cm⁻¹) of 1,2-propanediol adsorbed on O/Pd(111), O/Ag(110), clean Pd(111), clean Ag(110) and in the liquid phase.

Mode	Submonolayer	Multilayer	Pd(111) ⁶	Ag(110) ²⁴	$O/Ag(110)^{23}$	Liquid IR ⁴¹
	O/Pd(111)	O/Pd(111)				_
v(OH)	3400	3420-3520	3320	3200-3280	3400-3580	3365
v_a (CH ₃)	2950	2950	2960	2910	2940	2975
v_a (CH ₂)	2950	2950	2960	2910	2940	2935
v(CH)	2950	2950	2960	2930	2940	2935
$\Upsilon_{a}(CH_{3})$	1390	1420	1450	1430		1460
$\Upsilon(CH_2)$	1390	1420	1450	1430	1360	1455
$\delta_{s}(CH_{3})$	1390	1360	1370	1350	1360	1380
$\rho_r(CH_3)$	1060	1075	1080	1050	920	1079
v(CO)	1060	1075	1030	1060	1040	1046
$\rho_r(CH_3)$	n.r.	940	920	910	920	947
$\rho_r(CH_2)$	n.r.	850	840	830	825	839
δ(CCO)	n.r.	650	625	n.r.	560	660
Ύ(CCO)	n.r.	n.r.	500	460-510		527

 δ =in-plane deformation ρ_r =rocking v=stretch Y=wagging τ =twisting a=asymmetric s=symmetric n.r. = not resolved

3.5 Discussion

Figure 3-8 depicts the proposed mechanism for reaction of PDO on O/Pd(111). It is based on the mechanism for PDO decomposition previously proposed, but with new oxygen-assisted pathways included.⁶ At temperatures below approximately 170 K the hydroxyl O-H bonds are still intact. The first step is O-H scission and formation of adsorbed 1,2-propanedioxy (-OCH₂CH(CH₃)O-) between 170 K and 250 K (as indicated by the disappearance of the v(OH) peak in Figure 3-6 and the onset of water desorption during TPD). Water first desorbs when surface O combines with these hydroxyl hydrogens, seen in Figure 3-3. The dialkoxide undergoes dehydrogenation via C-H scission at the primary and secondary carbon atoms, forming carbonyl bonds with each oxygen atom. In one pathway, the methyl ligand remains intact while C-H scission occurs. The dialdehyde methylglyoxal (O=CH-C(CH₃)=O) forms from this reaction and desorbs at 460 K or may also decompose via competing C-C or C-O scission reactions. Carbon-carbon scission followed by dehydrogenation and decarbonylation forms CO by 345 K, shown in Figure 3-7. Deoxygenation followed by recombination with surface hydrogen forms reaction-limited propylene up to 520 K. In the second pathway, demethylation occurs, producing methane, which

desorbs between 345 K and 400 K, shown by the TPD experiments in Figure 3-5. The resulting surface structure is the dialdehyde, glyoxal (O=CHCH=O). Glyoxal either desorbs at 460 K or may undergo competing C-C or C-O scission. Carbon-carbon scission leads to formaldehyde (which desorbed near 460 K) or, when followed by dehydrogenation and decarbonylation, CO (which desorbed at 480 K). Carbon-oxygen scission in glyoxal and recombination with surface hydrogen forms ethylene, which desorbed between 400 K and 500 K. It is evident that the deoxygenation pathway to propylene and ethylene was improved as the initial PDO coverage was increased. Similar coverage effects and promotion of deoxygenation have been seen previously.⁴² This overall mechanism reflects the two PDO coverage regimes. When excess oxygen is present (at low initial PDO coverage), carboxylate formation and more complete decomposition occurs. When initial PDO coverage is high, surface O atoms are completely consumed at lower temperatures, resulting in similar chemistry to results obtained in the absence of oxygen. However, the oxygen allows greater coverages of decomposition intermediates to be formed, resulting in higher yields of decomposition products, and shifts in TPD temperatures that are consistent with a heavily crowded surface.



Figure 3-8. Proposed reaction mechanism of 1,2-propanediol on O/Pd(111) based on relative concentrations of reactant and surface oxygen. Temperatures with brackets relate to HREELS and those without brackets are TPD desorption ranges. Only desorption-limited hydrogen was detected and thus left out of this mechanism.

Under excess oxygen conditions it is proposed the C2 dialdehyde intermediate forms an oxygenated surface carboxylate. Figure 3-6 provides evidence of the methyl group being abstracted by 250 K when excess O is present on the surface, so the carboxylate is not likely a C₃. The carboxylate decomposes to H₂O and CO₂ in a single rate limiting step. For 1,2-propanediol on O/Ag(110), Ayre and Madix described O(a) attacking the dialkoxide, leading to C-C scission, creating acetate with the attacking oxygen and leaving formaldehyde. On O/Pd(111) we do not see any evidence of formaldehyde production or decomposition (which occurs below 300 K on $Pd(111)^{43}$). Similarly, pure acetate formation is improbable since no formaldehyde desorption is detected at this coverage. The relatively high temperature (> 280 K) of the carboxylate decomposition makes formate seem unlikely.⁴⁴ Acetate has been shown to decompose at 305 K and be stabilized by surface O to decompose at 420 K, while propanoate decomposes at 380 K on O/Pd(111).⁴³ Furthermore, the fact that the intermediate does not produce a hydrocarbon one unit shorter than itself suggests it is not a simple carboxylate, but rather an oxygenated carboxylate, as drawn in the mechanism. Note that a carboxylate intermediate was not directly detected in HREELS (Figure 3-6). One difficulty in detection of the proposed carboxylate is that its coverage is low, since it is only produced at low initial PDO coverages. The planar oxygenated carboxylate is furthermore expected to lie flat on the surface in a configuration similar to adsorbed dialdehydes, bonding through its delocalized pi-bond. Carboxylate intermediates are primarily considered to be in an upright orientation, not usually seen to lie flat or have multiple modes of adsorption. However, it is proposed that the modes of adsorption change with two multiple functional groups present here, each seeking interaction with the surface. A related idea has been proposed for the multifunctional 2(5H)-furanone on Pd(111), whereby the ring and carbonyl functions lie more parallel with the surface.⁴⁵ Also, for aromatic carboxylic acids on silver it has been seen that a planar molecule with no steric hindrance adsorbs flat on the surface involving the carboxylate's π -electron.⁴⁶ This would make its presence unclear in HREEL spectra due to selection rules, similarity of detectable vibrational modes to the adsorbed dialdehyde, and peaks at low wavenumber being hard to resolve. Carboxylate intermediates have been shown to form from PDO (after producing an intermediate aldehyde) during catalytic oxidation on supported Pd.47

Davis and Barteau have described several mechanisms by which oxygen affects the surface chemistry of simple alcohols on Pd(111). Many of these are apparent in the results from this study. For example, Davis and Barteau have shown that surface O acts as a Brønsted base to abstract protons from the alcohol group and form an adsorbed alkoxide. Likewise, we have found that the hydroxyl bonds are the first to break, producing H₂O in the TPD instead of the H₂ seen on clean Pd(111), and an adsorbed dialkoxide forms. It was also shown that surface O acts as a nucleophile, attacking adsorbed alcohols and aldehydes and oxidizing them to surface carboxylate species. We have clearly seen surface O nucleophilically attacking the aldehyde intermediate and forming carboxylates, as evidenced by the coevolution of H₂O and CO₂ in the TPDs in Figure 3-1 and Figure 3-2. This process occurs when O is still present on the surface in sufficient quantities following low-temperature water-forming reactions.

Extensive previous work with alcohols and aldehydes on Pd(111) has shown that coadsorbed oxygen commonly induces a shift in adsorbed aldehyde structure from $\eta^2(O,C)$ to $\eta^1(O)$.^{16,25} The $\eta^1(O)$ state is more weakly adsorbed, with TPD temperatures that are lower by ~100 K. From the TPD results presented in this study (Figures 3-4 and 3-5), it appears that the adsorption configuration of methylglyoxal may be altered upon initial oxidation of PDO; the dialdehyde desorbs in its first peaks between 250-300 K in the presence of excess surface O. The HREELS results provide possible indication of a η^1 species as well, with the peak at 1620 cm⁻¹ becoming more resolved at 240 K. The reaction limited desorption temperatures of glyoxal, methylglyoxal, and formaldehyde are the same or slightly higher on O/Pd(111) than on clean Pd(111). One interesting difference between the diol and simple alcohols and aldehydes is that the amount of η^1 aldehyde desorption from O/Pd(111) does not appear to be greater than that of η^2 .^{25,26}

Desorption of carboxylic acids was not detected in these studies but was for simple alcohols on O/Pd(111).⁵³ Davis and Barteau cited the availability of hydrogen as key in determining the reaction pathway of carboxylate removal from the surface (hydrogenation to a carboxylic acid near 280 K or decomposition above 350 K). When oxygen was in excess it scavenged H to form H₂O and prevented formation of acids; similarly we see some high temperature (> 300 K) H₂O formation rather than H₂ or

acid desorption. When H is plentiful on the surface (in the instance of higher PDO coverages), surface O preferentially recombines with it to form H₂O instead of nucleophilically attacking adsorbed aldehydes. While this could indicate there is a higher barrier to form the carboxylate from PDO, it may simply be a matter of the stoichiometry. It has previously been seen that the relative amounts of carboxylate decomposition products decreased with increasing alcohol exposure on O/Pd(111).¹⁶ With a diol like PDO, surface O is consumed even more rapidly in the sequential reaction of removing the hydroxyl H and oxidizing the intermediate aldehydes. It is also possible that the PDO-derived carboxylate intermediate is more strongly adsorbed than simple carboxylates due to its bifunctional nature.

The only previous study of 1,2-propanediol on an O-covered surface is that of Madix and Ayre on Ag(110) where 1,2-propanediol reacts with the adsorbed oxygen to form 1,2-propanedioxy and water. On O/Ag(110), 1,2-propanedioxy proceeds via C-H scission to the partial oxidation products acetol, lactaldehyde and methylglyoxal or it further decomposes via C-C scission to the dialdehyde glyoxal, formaldehyde, CO₂ and H₂O. A key aspect of their study is the report of a mixture of the mono-oxidized species acetol (CH₃C(=O)CH₂OH) and lactaldehyde (CH₃CH(OH)CH=O). Since oxygen was involved in both reactions, this points to the difference in metal surface causing the shift in reaction products. Pd has a much stronger decarbonylation activity than Ag (for which no CO production is observed), which may limit stability of monoaldehyde intermediates on Pd(111). Lastly, the relative concentrations of 1,2-propanedioxy and surface O play a major role on both Ag(110) and Pd(111), affecting the reaction by stabilizing the dialkoxide intermediate and promoting nucleophilic attack by the surface O to produce surface carboxylates.

3.6 Conclusions

The surface chemistry of 1,2-propanediol was investigated on O/Pd(111) to identify effects of surface oxygen on the reactivity of a diol. Initial O-H bond activation produces 1,2-propanedioxy at low temperature. Depending on the relative concentrations of surface oxygen to 1,2-propanediol, two regimes are possible: one of excess surface oxygen and one without excess oxygen. When the concentration of

 $O_{(a)}$ is large compared to 1,2-propanedioxy, no H₂ is produced and the dialkoxide reacts primarily to form H₂O, CO₂ through decarboxylation, and CO through decarbonylation. Conversely, when the concentration of $O_{(a)}$ is small compared to 1,2-propanedioxy, the dialkoxide reacts to form oxidation products (H₂O, glyoxal, methylglyoxal, formaldehyde), decomposition products (H₂, CO), and hydrodeoxygenation products (ethylene, propylene). At these higher initial PDO coverages, the primary role of oxygen is enhancing the coverage of PDO that undergoes decomposition; differences in reactivity relative to the clean surface are apparently a result of this difference in the coverage of decomposition intermediates.

3.7 References

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CHAPTER 4

Benzyl Alcohol Oxidation on Pd(111): Aromatic Binding Effects on Alcohol Reactivity

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4.1 Abstract

To investigate how surface oxygen participates in the reaction of important aromatic oxygenates, the surface chemistry of benzyl alcohol (PhCH₂OH) and benzaldehyde (PhCHO) has been studied on oxygen-precovered Pd(111) (O/Pd(111)) using temperature-programmed desorption (TPD) and highresolution electron energy loss spectroscopy (HREELS). On both Pd(111) and O/Pd(111), TPD using isotopically-labeled benzyl alcohol and low-temperature HREEL spectra show that oxidation of benzyl alcohol proceeds through a benzyl alkoxide (PhCH₂O-) intermediate to adsorbed benzaldehyde, so that the sequence of bond scission is O-H followed by C^{α} -H. In the presence of surface O, some benzaldehyde desorbs from the surface below 300 K, consistent with the presence of a weakly adsorbed η^1 aldehyde state that is bound to the surface through its oxygen lone pair. Benzaldehyde also reacts with surface oxygen to produce benzoate (PhCOO-). Shifts in the OCO stretching frequency suggest that the benzoate orientation changes as the surface becomes less crowded, consistent with a strong interaction between the phenyl group and the surface. Adsorbed benzaldehyde and benzoate undergo decomposition to CO and CO₂, respectively, as well as benzene. Deoxygenation of benzyl alcohol to toluene occurs at high coverages of benzyl alcohol when relative surface O coverage is low. Experiments conducted on ¹⁸O/Pd(111) reveal exchange occurring between surface O and the benzaldehyde and benzoate intermediates. This exchange has not been reported for other alcohols, suggesting that aromatic binding effects strongly influence alcohol oxidation on Pd.

4.2 Introduction

Selective oxidation of alcohols to aldehydes and carboxylic acids is a key reaction in the production of fine chemicals. Traditionally these reactions are conducted using stoichiometric quantities of expensive and toxic oxygen donors. An alternative approach is to use molecular oxygen with a solid catalyst to produce the aldehyde without generation of toxic byproducts that are expensive to dispose of. Palladium and palladium-gold alloy catalysts have been shown to be effective for selective oxidation of primary alcohols, including benzyl alcohol (PhCH₂OH).^{1,2} These systems can achieve high selectivity to benzaldehyde (PhCHO) and also have high activity.

While PhCH₂OH oxidation has received significant attention in the catalysis literature, few surface studies of the interaction of oxygen with benzyl alcohol have been reported. Instead, reactions of simple alcohols on oxygen-covered surfaces have been studied. These oxygen-covered surfaces include Pd(111)³, Rh(111),⁴ Pt(111),⁵ Cu(100),⁶ Cu(110),⁷ Au(111),⁸ and Mo(110).⁹ For example, on a Pd(111) surface covered with 0.25 ML oxygen (O/Pd(111)),³ surface O acts as a Brønsted base to abstract the hydroxyl H of the alcohol, alters the adsorption geometry of intermediate aldehydes, and scavenges hydrogen to form H₂O. Surface oxygen also acts as a nucleophile to oxidize aldehydes to carboxylates and stabilizes alkoxide intermediates to higher temperatures than on clean Pd(111). In general, on the other transition metal surfaces listed above, oxygen promotes reaction by initiating Brønsted or Lewis acid-base reactions with adsorbates, site blocking, and electronically modifying the metal surface.

1-2-Propanediol (PDO) and crotyl alcohol are the only complex alcohols known to have been studied on O/Pd(111).^{10,11} The reactivity of PDO was found to depend on the relative concentrations of surface O and PDO. The main role of surface oxygen in this reaction was increasing the amount of PDO that undergoes decomposition; the result is a greater coverage of decomposition intermediates. When the concentration of $O_{(a)}$ is large compared to PDO, formation and subsequent decomposition of a stable carboxylate intermediate was observed. Conversely, when the concentration of $O_{(a)}$ is small compared to PDO, a range of aldehyde (glyoxal, methylglyoxal, formaldehyde) and alkene (ethylene, propylene)

products were formed. Oxygen's effect on crotyl alcohol oxidation was improving desorption of crotonaldehyde before the decarbonylation pathway could occur.¹¹

Surface science studies of PhCH₂OH are limited to clean Pd(111), clean Au(111) and O/Au(111). On clean Pd(111),¹² the reaction of PhCH₂OH was shown to be highly dependent on its adsorption orientation. At low coverages, PhCH₂OH proceeds through a flat lying benzaldehyde adsorbate to produce CO and benzene, while at high coverages the molecule is more upright and additionally produces the deoxygenation products toluene and H₂O. On clean Au(111), the aromatic ring was proposed to interact strongly with the surface and lies nearly parallel to it.¹³ Approximately 30% of the initial adsorbed PhCH₂OH was found to undergo decomposition. On O/Au(111), surface O was shown to promote PhCH₂OH O-H scission to produce a benzyloxy intermediate; subsequent C-H scission produces PhCHO with a selectivity near 90% for low O coverages (≤ 0.05 ML). Benzyl benzoate, an ester, may also be produced at these relatively low oxygen coverages. Benzoic acid begins to evolve when more surface O is available (≥ 0.08 ML). Overall, it was determined that the kinetic barrier to aldehyde and ester formation is lower than the acid, thus the selectivity of the oxidation reactions was driven by the ratio of PhCH₂OH to surface O.

In the present study, the thermal chemistry of benzyl alcohol and benzaldehyde on O/Pd(111) is studied in order to understand the reactivity of more complex multifunctional alcohols and aldehydes on late transition metal surfaces. This may aid in catalyst design for selective oxidation because surface oxygen is generally present during catalytic alcohol oxidation, and is required for production of carboxylate products. The present study utilizes temperature-programmed desorption (TPD, also referred to in the case of reactive molecules as temperature programmed reaction spectroscopy) and high-resolution electron energy loss spectroscopy (HREELS) experimental results to determine the effects of surface O on these mechanisms.

4.3 Methods

High-resolution electron energy loss spectroscopy experiments were conducted in a stainless steel ultrahigh vacuum (UHV) chamber described previously (base pressure ~ 1.3×10^{-8} Pa or 1×10^{-10} torr).¹⁴ The chamber is equipped with an LK5000 high-resolution electron energy loss spectrometer (LK Technologies) and a model 981-2046 sputter gun for cleaning (Varian). A specular angle of 60° with respect to the surface normal and beam energy of 6.32 eV were used in all HREELS experiments. Peak positions in HREELS spectra are reported to the nearest 5 cm⁻¹ with a resolution at or below 8 meV. All HREEL spectra are normalized to the elastic peak height.

Temperature-programmed desorption experiments were conducted in an UHV chamber described previously (base pressure $\sim 1.3 \times 10^{-8}$ Pa or 1×10^{-10} torr).¹⁵ The UHV chamber included a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) for TPD and a NGI3000-SE sputter gun (LK Technologies) for cleaning the sample. The Pd(111) single crystal (Princeton Scientific) was routinely cleaned by backfilling the chamber with oxygen or mild sputtering with argon. The crystal is mounted to a tantalum disk held on a copper plate with clips. The temperature of the sample is measured by a thermocouple spot welded to the copper plate next to the crystal mount. Cooling for experiments is accomplished by a liquid nitrogen reservoir.

To prepare an O-covered surface, approximately 15-Langmuir oxygen was dosed while cooling the sample between 973 K and 373 K. This treatment results in the formation of a p(2x2)O/Pd(111)surface as confirmed using LEED.¹⁰ Benzyl alcohol and benzaldehyde were dosed onto the crystal through a direct dosing line where their respective dose size is characterized by the partial pressure in the line. Dose sizes of each of these molecules can be approximated by comparing the carbon monoxide peak area to that of a saturating dose of carbon monoxide, 0.67 ML.¹⁶ A correction factor for CO₂ versus CO desorption (in ML) was calculated by separately backfilling the chamber with the same pressure of each molecule and determining their intensities via the mass spectrometer. This analysis yielded a sensitivity factor of approximately 1.0 for the CO₂ (m/z = 44) signal. It should be noted that CO_x may evolve from decarbonylation or decarboxylation of reactant species, which would yield one CO_x molecule per decomposing reactant. However, CO_x can also be produced from oxidation of surface carbonaceous species as discussed below. Thus, the calculated CO_x yields only provide an upper bound for the coverage of reactant that undergoes decomposition. The cracking patterns for benzyl alcohol and benzaldehyde were acquired by direct dose at ~6.6 Pa (5 x 10⁻² torr) for 10 seconds. Benzyl alcohol was obtained from Sigma Aldrich at reported 99.8% purity. Benzaldehyde was obtained from Aldrich at reported >99.5% purity. Benzyl alcohol-OD and benzyl- α , α - d_2 alcohol were obtained from C/D/N Isotopes at reported 99.1% and 99.5% D atom, respectively. Ultrahigh purity ¹⁶O₂ was obtained from Matheson Trigas and ¹⁸O₂ was obtained at reported 97% atom ¹⁸O from Aldrich.

4.4 Results

Previous studies have shown that a major pathway for PhCH₂OH surface chemistry on Pd is formation of a PhCHO surface intermediate that undergoes decarbonylation.¹² In addition to this PhCHOmediated pathway, PhCH₂OH also undergoes hydrodeoxygenation to toluene. In each section, we therefore first investigate the reaction of PhCHO before considering the additional reaction pathways that are observed from PhCH₂OH.

4.4.1 Temperature-Programmed Desorption

Temperature-programmed desorption was used to study the volatile products formed during the thermal chemistry of benzaldehyde on ¹⁸O/Pd(111); results following two different-sized PhCHO exposures are shown in Figure 4-1. Figure 4-1a represents a sub-saturation exposure of benzaldehyde and Figure 4-1b corresponds to saturation coverage. In both cases, surface ¹⁸O is incorporated into the H₂O, CO_2 , CO and PhCHO products. All of the products from PhCHO decomposition on clean Pd(111)¹² are observed here, as expected. However, CO_2 is a new product that is not observed from the clean surface.

As shown in Figure 4-1b, molecular benzaldehyde (m/z = 106) desorbs in two peaks at 250 K and 370 K. The lower-temperature benzaldehyde feature is proposed to arise from a more weakly adsorbed η^1 geometry (where the aldehyde is bound through the O atom) as described below. The higher-temperature peaks are in the range generally assigned to a η^2 state in which both the C and O atoms of the carbonyl are

bound to the surface.¹⁷ Surprisingly, in addition to PhCH¹⁶O (m/z=106), some PhCH¹⁸O (m/z=108) is observed. This result indicates exchange between benzaldehyde's oxygen and the surface O, a result that has not been reported for aldehydes on O-covered Pd or Ag surfaces.

The decomposition products serve as proxies for various surface reaction steps. For example, water is generally expected to be produced when surface O combines with H that is formed during decomposition of surface organic species, where decomposition is rate limiting. Isotopic water (m/z = 20) desorbs below 300 K at both low and high initial PhCHO coverages. At low initial coverage, a second $H_2^{18}O$ peak at 395 K exists, whereas at high coverage this peak is absent. Hydrogen desorbs near 500 K and only occurs after all surface oxygen has been consumed. Interestingly, the low yield of H_2 and H_2O in the temperature range between 325 and 450 K on the high-coverage surface (Figure 4-1b) compared to the low-coverage surface (Figure 4-1a) is consistent with a decreased rate for C-H bond scission reactions at higher coverage. That is, at these temperatures, surface H generated from C-H scission is expected to rapidly combine with surface O or H atoms to produce H_2O and H_2 . The diminished yield of H-containing products at 325-450 K is perhaps consistent with limited availability of sites for C-H scission on the more crowded surface.

Carbon monoxide and carbon dioxide are also produced during the reaction, suggesting a combination of benzaldehyde decarbonylation and benzoate decarboxylation. It is worth considering the observed isotope distributions in some detail, starting with the low initial coverage of PhCHO (Figure 4-1a). The $C^{18}O^{16}O$ peak intensity is much greater than the other CO_2 isotopes at 405 K (and in a visible shoulder below 400 K), consistent with the dominant CO_2 production pathway resulting from reaction of surface oxygen with a carbonyl group from the reactant. This lower-temperature CO_2 feature is attributed to decomposition of a surface benzoate intermediate, with a desorption temperature below what is normally associated with CO or surface carbon oxidation¹⁸ but within the range associated with carboxylate decomposition.^{3,17,19} On the other hand, both $C^{16}O_2$ and $C^{18}O_2$ also evolve, with the intensity for the latter product being relatively more prominent at temperatures near 430 K. This higher-temperature peak is in the range expected for CO oxidation, and may also be associated with oxidation of

decomposing hydrocarbon fragments by surface oxygen.¹⁰ However, the presence of all three isotopes of CO₂ provides strong indication for exchange between O atoms that are adsorbed on the surface and those that are incorporated in PhCHO-derived intermediates. For the higher PhCHO pre-coverage, the CO₂ desorption temperature shifts slightly higher and the isotope distribution shifts toward more ¹⁶O-containing products, consistent with a reduced availability of ¹⁸O for oxidation of surface CO and carbonaceous species. Overall, the results suggest that CO₂ is produced from at least two pathways: a low temperature pathway consistent with carboxylate decomposition and higher temperature pathways associated with oxidation of carbonaceous species and CO.

Each of the possible isotopes of carbon monoxide (m/z = 28, 30) desorb at 460 K at both PhCHO precoverages, with the relative amount of $C^{18}O$ being lower in the case where the initial coverage of PhCHO is higher. This is expected because higher initial PhCHO coverages produce more water with the surface oxygen and thus less ¹⁸O is available to be incorporated into the molecule during the course of reaction. The higher PhCHO pre=coverage is seen to result in a much larger CO yield (approximately a factor of three higher) compared to the low pre-coverage. In contrast, the CO₂ yield does not appreciably increase, again pointing to the limited availability of the surface oxygen needed for oxidation reactions at high precoverages. The presence of surface ¹⁸O in desorbing carbon monoxide is also consistent with exchange between O on the surface and in intermediates that ultimately undergo decarbonylation. Oxygen exchange between an aldehyde and surface ¹⁸O to our knowledge has only been reported on Au(111) for the aldehyde 2-butanone, which desorbs from the reaction of 2-butanol.²⁰ However, C¹⁸O was not a product of the reaction because Au is not active for decarbonylation.



Figure 4-1. Thermal desorption spectra of benzaldehyde on ¹⁸O/Pd(111). (a) The benzaldehyde exposure at 130 K is sub-saturating and corresponds to desorption yields of 0.06 ML CO (m/z = 28), 0.05 ML C¹⁸O (m/z = 30), 0.04 ML C¹⁶O₂ (m/z = 44), 0.09 ML C¹⁸O¹⁶O (m/z = 46) and 0.04 ML C¹⁸O₂ (m/z = 48). (b) The benzaldehyde exposure at 130 K is saturating and corresponds to desorption yields of 0.30 ML CO, 0.07 ML C¹⁸O, 0.08 ML C¹⁶O₂, 0.08 ML C¹⁸O¹⁶O and 0.02 ML C¹⁸O₂ desorption.

It is also useful to investigate the effect of coadsorbed oxygen on the reactivity of benzyl alcohol, which has previously been found to decompose through a benzaldehyde intermediate (Appendix A Figure A-1). For simplicity, to provide an overview of the chemistry without isotopic oxygen labeling, Figure 4-2 shows a TPD spectrum following a saturating dose of benzyl alcohol on O/Pd(111). Molecular benzyl

alcohol (m/z = 108) begins to desorb at 265 K and extends through a broad peak centered at 350 K. A number of decomposition products are also observed; these are largely the same products observed in the absence of surface oxygen, with the important additional product of CO_2 .¹² Benzaldehyde (m/z = 106), which is produced from dehydrogenation of benzyl alcohol's pendant alcohol and methylene functional groups, desorbs at 290 K, a slightly higher temperature than in Figure 4-1, but still suggestive of the aldehyde proceeding from a η^1 configuration.^{3,12,21} As expected, products arising from benzaldehyde decomposition on O/Pd(111) are observed. H atoms resulting from PhCH₂OH dehydrogenation combine with surface O to form the first H₂O (m/z = 18) peak at 290 K.

In addition to the products from the PhCHO pathway, the hydrodeoxygenation product toluene (m/z = 92) (shown in Appendix A Figure A-1) is observed from O/Pd(111), desorbing over a broad temperature range from 400-520 K. Water (m/z = 18) is also expected to be produced in the HDO process, and desorbs over a similarly broad range 455-600 K. Previous studies of toluene's reaction on O/Pd(111)²² do not show molecular desorption at temperatures greater than 300 K, indicating that toluene production here is reaction-limited. The simultaneous desorption of hydrogen (m/z = 2) and H₂O at high temperature (> 500 K) is unexpected due to the much more rapid reaction of hydrogen oxidation compared to recombination. However, this suggests that surface O has been incorporated into an intermediate by 450 K and is not readily available to combine with hydrogen on the surface. The H available to form H₂ is consistent with evolution from decomposing benzene.¹² Benzaldehyde is also a reaction product at high temperatures, desorbing in a broad feature from 440-520 K that is shifted to higher temperature compared to PhCHO (Figure 4-1).



Figure 4-2. Thermal desorption spectra of a saturating dose of benzyl alcohol on O/Pd(111) at 120 K. The dose corresponds to 0.14 ML CO (m/z = 28) and 0.11 ML CO₂ (m/z = 44) desorption.

Isotopic labeling experiments with ¹⁸O/Pd(111) were performed to track incorporation of surface O in the products of PhCH₂OH surface chemistry. Two different coverages are shown in Figure 4-3. The lowest exposure in Figure 4-3a corresponds to a submonolayer coverage of PhCH₂OH and the presence of excess surface oxygen, which desorbs in a peak centered at 700 K (not shown). Figure 4-3b corresponds to a saturating dose of PhCH₂OH (m/z = 108). Significant isotope scrambling was observed only in CO, CO₂, and H₂O, so Figure 4-3 focuses only on those products. We did detect a weak signal from m/z =

110, which is attributed to benzyl alcohol that incorporates surface ¹⁸O (Appendix A Figure A-2); this signal is small enough that it may originate from defect sites.

The main reaction pathway for PhCH₂OH is dehydrogenation to PhCHO, and thus a similar distribution of isotopic products is observed. For example, as in the case of PhCHO (Figure 4-1), there is an overall trend that the mixed $C^{16}O^{18}O$ isotope product desorbs preferentially at temperatures up to 405 K, consistent with decomposition of a carboxylate intermediate,^{3,23} i.e., benzoate, containing one O atom that originated from the surface and one that originated from PhCH₂OH. At higher temperatures, the relatively greater abundance of $C^{18}O_2$ is suggestive of combustion of organic intermediates.²⁴ Finally, the significant yield of all possible isotopes again signals exchange between O on the surface and O present in adsorbed intermediates. The incorporation of surface O into carbon monoxide has not been seen for other multifunctional alcohol reactions on ¹⁸O-covered Ag or Pd surfaces.^{10,23}



Figure 4-3. Thermal desorption spectra of benzyl alcohol on ¹⁸O/Pd(111). (a) The benzyl alcohol exposure at 120 K has excess ¹⁸O₂ and corresponds to 0.01 ML CO (m/z = 28), 0.02 ML C¹⁸O (m/z = 30), 0.007 ML C¹⁶O₂ (m/z = 44), 0.022 ML C¹⁸O¹⁶O (m/z = 46) and 0.011 ML C¹⁸O₂ (m/z = 48) desorption. (b) The benzyl alcohol exposure at 120 K is saturating and corresponds to 0.05 ML CO, 0.017 ML C¹⁸O, 0.011 ML C¹⁶O₂, 0.017 ML C¹⁸O¹⁶O, and 0.005 ML C¹⁸O₂ desorption.

Finally, to identify the sequence of bond breaking for the oxidation of benzyl alcohol to benzaldehyde, isotopically-labeled benzyl alcohol-*d*2 (PhCD₂OH) was dosed on O/Pd(111). Temperatureprogrammed desorption spectra in Figure 4-4 show H₂O (m/z = 18) desorbing at 275 K before HDO (m/z = 19) at 285 K and D₂O (m/z = 20) at 295 K, indicating that O-H scission occurs first to produce benzyl alkoxide on the surface. This bond scission sequence is the same as that of other alcohols on O/Pd(111).^{3,10,25}



Figure 4-4. Thermal desorption spectra of benzyl alcohol-*d*2 on O/Pd(111) at 120 K corresponding to 0.031 ML CO and 0.035 ML CO₂ desorption, showing D₂O (m/z = 20) desorption after H₂O (m/z = 18) and DHO (m/z = 19). Water fragmentation patterns were used to deconvolute the m/z = 18 contributions from the D₂O and DHO products.

4.4.2 High-Resolution Electron Energy Loss Spectroscopy

High-resolution electron energy loss spectroscopy was employed to study benzaldehyde decomposition on O/Pd(111) in order to provide insight about potentially oxidized reaction intermediates. Figure 4-5a shows a comparison following the same 2-Langmuir PhCHO exposure on both clean and O/Pd(111) to highlight differences caused by the presence of oxygen. It should be noted that clean Pd(111) HREELS data was first presented by Pang, et al.,¹² but the spectra presented here were gathered independently and included for a more direct comparison to O/Pd(111). Table 1 lists the vibrational mode assignments for PhCHO on clean and O/Pd(111) at 130 K. The spectra at 130 K are essentially the same between clean and O/Pd(111), with clear indications of the phenyl C-H stretches (2940 cm⁻¹), phenyl C-H out-of-plane bends (665 cm⁻¹), phenyl C-C-H out-of-plane bends (925 cm⁻¹) and phenyl C-C stretches (1550 cm⁻¹). The aldehyde C-H stretch is weak but appears at 2770 cm⁻¹ and is assigned for the molecule in a multilayer state as seen previously.¹² The aldehyde C=O stretch is expected near 1700 cm⁻¹; this peak

appears to be in the shoulder of the clean Pd spectrum and is not clearly resolved on the oxygen-covered surface. Molecular CO is already present on the clean Pd(111) surface (~1630 cm⁻¹) by 200 K. The low frequency has been attributed to a change in the work function of Pd caused by coadsorption of aromatic molecules.^{12,26} However, PhCHO appears to still be intact on O/Pd(111) at 200 K, the spectrum not changing as dramatically from 130 K. The surface seems to be largely covered by an intact aldehyde, consistent with a η_1^1 geometry.

At 240 K a stark contrast between the scans of PhCHO on clean and O-covered Pd(111) exists. The clean Pd(111) spectrum has not changed from 200 K, yet a new peak at 1340 cm⁻¹ appears in the O/Pd(111) spectrum by 240 K. Based on the fact that CO₂ is a unique TPD product for O/Pd(111) compared to Pd(111), we propose that this new peak arises from an intermediate that ultimately produces CO_2 , namely a carboxylate. In the literature, simple carboxylate stretches are usually at higher frequency (1400-1450 cm^{-1 17,19}); however, the frequency of the OCO stretch is expected to be lower due to the presence of the aromatic functional group and delocalization of electrons away from the carboxylate functional group. In an effort to assign the unique peak at 1340 cm⁻¹, a control experiment was performed (Appendix A Figure A-3) with acrylic acid on O/Pd(111), similar to that of Davis and Barteau.²⁷ It is difficult to dose benzoic acid under UHV conditions because it is a solid with low vapor pressure, thus acrylic acid was chosen for its ability to provide an understanding of the vinyl substituent effect on a carboxylate stretch. While acrylic acid catamerizes on clean Pd(111), in the presence of surface O, acrylate forms at 170 K with a v_s(OCO) peak at 1390-1430 cm⁻¹. As such, the 1340 cm⁻¹ peak in Figure 4-5 is assigned to a $v_s(OCO)$ mode of a benzyl carboxylate intermediate, or benzoate, similar to the reported 1360cm⁻¹ v(OCO) in-plane mode of benzoate on O/Au(111)¹³ and other $v_s(OCO)$ stretch assignments in the literature (Table 4-2). Further, the peak near 730 cm⁻¹ in the shoulder is consistent with a δ (OCO) mode;¹⁹ its relative intensity compared to the v_s(OCO) mode is indicative of a "two-legged" carboxylate geometry bound through both its oxygen atoms but tilted with respect to the surface.²⁸

Figure 4-5b shows the spectra for PhCHO on O/Pd(111) annealed to temperatures of 300 K and higher. The 300 K spectrum shows that decarbonylation has begun on the O/Pd(111) surface with the

appearance of a 1645 cm⁻¹ peak. The peak at 875 cm⁻¹ is assigned to a C-H out-of-plane bending mode. Its frequency and intensity suggests the adsorption orientation of the intermediate has changed. The increase in the C-H out-of-plane bending intensity may be indicative of aromatic rings being oriented more parallel to the surface, as demonstrated on Pt(111), whereby the closer proximity of the C-H to the surface results in a greater image dipole.²⁹ The peak at 1225 cm⁻¹ is assigned to the $v_s(OCO)$ mode of the carboxylate, with the adsorption orientation change creating the redshift. This could again be explained by the delocalization of electrons and a shift in bond order of the carboxylate; as the interaction of benzoate with the surface increases, the two carboxylate C-O bonds may become more similarly hybridized to the C-phenyl bond. The 350 K spectrum shows peaks associated with a strong benzene ring deformation mode at 1170 cm⁻¹ and C-H in-plane bending mode (1375 cm⁻¹), indicative of further decomposition. At 400 K the O/Pd(111) spectrum appears similar to that from the benzaldehyde-covered Pd(111) surface heated to the same temperature (Appendix A Figure A-4), indicating the carboxylate has been consumed, consistent with the lower-temperature CO₂ channel observed in TPD. Finally, by 475 K, CO has desorbed and the visible peaks suggest benzene-derived intermediates are adsorbed on the surface with C-H out-of plane bending (665-750 cm⁻¹), C-H in-plane bending (1375 cm⁻¹) and C-H in-plane stretching (2940 cm⁻¹) ¹). though the ring deformation stretch at 1100-1200 cm⁻¹ is not resolved.



Figure 4-5. High-resolution electron energy loss spectra from a 2 Langmuir exposure of benzaldehyde on clean (in black) and O/Pd(111) (in blue) at 130 K, annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.

Table 4-1.	Vibrational	mode a	assignments	(cm^{-1})	of benzaldeh	yde ad	lsorbed on	O/Pd(111)), clean	Pd(111),
and in the l	iquid phase.									

Mode	Benzaldehyde	Benzaldehyde	Benzaldehyde	Benzaldehyde
	O/Pd(111)	clean Pd(111)	clean Pd(111)	IR Liquid ³⁰
	130 K	130 K	130 K ¹²	-
Phenyl v(CH)	2940	2940	3050	1165, 1205,
				3030, 3085
Aldehyde v(CH)	2770	2770	2760	2735, 2815
Aldehyde v(CO)	n.r.	1700	1700	1310, 1700
Phenyl v(CC)	1550	1550	1300, 1580	1455, 1583,
				1595
Phenyl C-H out-of-plane bend	n.r.	760	760	n.r.
Phenyl C-H in-plane bend	1200	n.r.	1190	1205
Phenyl C-H in-plane bend	1080	1080	1020	1070
Phenyl C-C-H out-of-plane	925	925	840	860
bend				
Phenyl C-H out-of-plane bend	665	665	690	620

n.r. = not resolved

Mode	Benzaldehyde O/Pd(111) 240 K, 300 K	Benzyl Alcohol-OD O/Pd(111) 240 K, 300 K	Benzyl Alcohol O/Au(111) 300 K ¹³	Benzoic Acid Cu(110) ³¹	trans-3- hydroxycinna mic acid SERS on Ag nanoparticles ³²	Styrene O/Ag(111) RAIRS ³³	Benz -oic Acid IR ³⁴
v _s (OCO)	1340, 1225	1375, 1175	1360	1426	1380-1394	1371	139 0
δ(OCO)	730	825	n/a	850	723	n/a	n/a

Table 4-2. Vibrational mode assignments (cm⁻¹) of benzoate v(OCO) and δ (OCO) compared to the literature.

n/a = not reported

High-resolution electron energy loss spectroscopy was also used to investigate the decomposition of PhCH₂OH on O/Pd(111). Figure 4-6 compares the same exposure of benzyl alcohol-OD (PhCH₂OD) on clean and O-covered Pd(111). Again, the clean Pd(111) HREEL spectra presented here were gathered independently but first presented by Pang, et al.¹² The dominant vibrational modes at low temperatures (130-200 K) are summarized in Table 3. In both cases, at 130 K, benzyl alcohol is intact with v(OD) apparent at 2440 cm⁻¹ as well as phenyl ring out-of-plane deformations (450 cm⁻¹) and C-O-D bending (660 cm⁻¹). A portion of the PhCH₂OD spectrum at 160 K is included to show that peaks of CH₂ deformations (1400 cm⁻¹) and phenyl C-C stretching (1575 cm⁻¹) in molecular PhCH₂OH become resolved on O/Pd(111). It is clear the O-D bond is broken by 170 K on both clean and O/Pd(111), though little else is well resolved. Each of the 200 K scans resembles those of adsorbed PhCHO on the respective surfaces at 130 K (seen in Figure 4-5a).

Decarbonylation, indicated by the presence of adsorbed CO at 1660 cm⁻¹, is significant by 240 K on Pd(111). However, the CO signal intensity is much lower on O/Pd(111) at 240 K, suggesting that surface O increases the barrier for decarbonylation and/or results in the production of other intermediates. Instead, the spectrum more closely resembles that of PhCHO on O/Pd(111) at 240 K (Figure 4-5a) with a v_s (OCO) loss near 1375 cm⁻¹. This, coupled with the phenyl C-C stretching and phenyl C-H out-of-plane

bending, suggests a benzoate intermediate has formed by 240 K on O/Pd(111). Adsorbed CO and phenyl C-H out-of-plane bending with some C-H in-plane bending are the dominant modes at 300 K on clean Pd(111). The 300 K O/Pd(111) spectrum is like that of PhCHO on O/Pd(111) at the same temperature (Figure 4-5), thus the surface intermediates are similar. The 350 K spectra (not shown) were quite similar to those of 300 K. At 400-475 K, the spectra collected from Pd(111) and O/Pd(111) once again become similar. This result is consistent with the decomposition of carboxylate intermediates from the O-covered surface near 400 K. Significant decarbonylation has occurred by 400 K while the other peaks are indicative of benzene's presence on the surface. By 475 K a majority of the CO has desorbed from the surface, leaving benzene to decompose.^{12,35} Through a comparison of the HREEL spectra of benzyl alcohol-OD and benzaldehyde on O/Pd(111) at intermediates to PhCHO on O/Pd(111).³⁶



Figure 4-6. High-resolution electron energy loss spectra from a 2 Langmuir exposure of benzyl alcohol-OD on clean (in black) and O/Pd(111) (in blue) at 130 K, annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height and scaled as indicated.

Mode	Benzyl Alcohol-OD O/Pd(111)	Benzyl Alcohol-OD clean Pd(111)	Multilayer Benzyl Alcohol clean $Pd(111)^{12}$	Benzyl Alcohol IR Solid ³⁷
Phenyl C-H in-plane stretch	2950	n.r.	3050	3010-3090
CH ₂ stretch	n.r.	n.r.	2900	2905-2989
v(OH)/v(OD)	2440	2440	n.r.	3170, 3305
CH ₂ deformations	1400	1400	1440	1435-1480
Phenyl C-C stretch	1575	1575	1300, 1560	1209-1379,
				1493-1608
Phenyl C-C-H in-plane	n.r.	n.r.	n.r.	1201-1206
bend				
CH ₂ bend	1175	1140	1160	1159
Ring deformation	1080-1200	1140	1120	
C-O stretch	1070	n.r.	n.r.	1023
Phenyl C-C stretch	n.r.	n.r	n.r.	1002-1009
Phenyl C-C-H out-of-	920	920	990	989-998
plane-bend				
Phenyl C-H out-of-	725-760	700-730	740	730-752
plane bend				
Phenyl ring out-of- plane deformation	450	450	n/a	408-485

Table 4-3. Vibrational mode assignments (cm⁻¹) of benzyl alcohol-OD adsorbed on O/Pd(111), clean Pd(111), and in the solid phase.

v = stretch n.r. = not resolved n/a = not reported

4.5 Discussion

A proposed decomposition mechanism for benzyl alcohol and benzaldehyde on O/Pd(111) is depicted in Scheme 4-1. Many of these reaction processes have been observed previously for clean Pd(111),¹² and thus this section will focus on changes induced by the presence of surface oxygen. Benzyl alcohol can be dehydrogenated through a benzaldehyde intermediate, which can further undergo decarbonylation to CO and benzene or oxidation to benzoate. Benzoate undergoes decarboxylation to benzene and CO₂. Finally, benzyl alcohol can proceed through a parallel pathway to produce toluene via hydrodeoxygenation.

Scheme 4-1 depicts the dehydrogenation of benzyl alcohol to benzaldehyde, followed by production of water and desorption of PhCHO, as well as the proposed oxidation mechanism of benzaldehyde to benzoate and the associated oxygen exchange. As discussed above, experiments with isotopically-labeled PhCH₂OH indicate a sequence of O-H followed by C^{α}-H scission, so that the reaction proceeds through a benzyl alkoxide intermediate. Desorption of PhCHO is only observed for the Ocovered surface. PhCHO that desorbs below 300 K on the O-covered surface is most likely weakly bound through the oxygen atom's lone pair of electrons.²¹ However, the expected η^1 (CO) loss of benzaldehyde on O/Pd(111) is not resolved in HREELS (Figures 4-5 or 4-6); it may be convoluted with the phenyl v(CC) and v(CO) of the aldehyde in the 1500-1700 cm⁻¹ range.¹⁷ The aldehyde ρ (CH) was similarly unresolved and possibly convolved in the peak between 665 cm⁻¹ and ~750 cm⁻¹.³⁸



Scheme 4-1. Product distribution for proposed decomposition mechanism of benzyl alcohol and benzaldehyde on O/Pd(111). First, the dehydrogenation of benzyl alcohol to benzaldehyde, which can adsorb through its carbonyl oxygen, followed by production of water and desorption of η^1 benzaldehyde. Then the oxidation of benzaldehyde to benzoate and the resulting products, which undergo oxygen exchange.

In the benzaldehyde oxidation pathway, surface oxygen nucleophilically attacks the aldehyde to form benzoate by 240 K (Figure 4-5). We propose that benzoate's adsorption orientation has shifted by 300 K, evidenced by the v(OCO) red-shifting, perhaps consistent with an interaction between the phenyl group and the surface. Tilted structures have previously been observed for benzene on Pd(111).³⁹ This change in orientation may be enabled by desorption of PhCHO and water around this temperature. Temperature-programmed desorption results show that benzoate decomposes to produce CO_2 at temperatures close to 400 K.

The significant degree of oxygen exchange between the surface and PhCH₂OH-derived intermediates, as evidenced by the observation of all possible isotopes of CO and CO₂ in TPD experiments on an ¹⁸O-covered surface, suggests that the formation of benzoate may be reversible. Thus, in Scheme 4-1, we propose oxygen exchange for interconversion of acyl and carboxylate intermediates. While other sources of oxygen exchange such as unselective decomposition and surface C oxidation cannot be ruled out, the desorption temperatures of the various CO and CO₂ isotopes support our proposal. Also shown in Scheme 4-1 are decarbonylation and decarboxylation reactions, which are expected for aldehydes and carboxylates, respectively.^{19,40} However, production and desorption of benzoic acid is not observed as a volatile product. This may be due to the strength of adsorption of the multifunctional benzoate or the availability of H. Similarly, no acid was produced in the reaction of a diol on O/Pd(111), though carboxylate intermediates were invoked.¹⁰ Surface O delays the onset of decarbonylation to higher temperatures since adsorbed CO has a weak signal on O/Pd(111) at 240 K compared to clean Pd(111) at 1630 cm⁻¹ in Figure 4-5a. The effect of oxygen here is consistent with an electronic effect that increases the activation energy for this reaction and/or with site blockage where O reduces the concentration of vacant sites needed for decarbonylation. Davis and Barteau observed that the presence of surface O induces an $\eta^{1}(O)$ adsorption geometry and affects the thermal stability of simple C₁-C₃ aldehydes.^{3,17} They concluded this was the result of an electronic effect whereby the metal's electron density is reduced by the oxygen. A site blocking effect by surface O (creating upright aldehydes) was deemed unlikely based on a comparison to oxygen's effect on ethylene di- σ and π -binding configurations, analogous to $\eta^2(O,C)$ and $\eta^1(O)$, respectively. Stuve and Madix found oxygen suppresses the di- σ state in favor of the π state, which allows π donation to surface.⁴¹ Since the two ethylene binding states are similar in size, any physical effect by oxygen on the binding was ruled out. However, consideration of the difference in surface area taken up by the $\eta^1(O)$ and $\eta^2(O,C)$ benzaldehyde ensembles may be necessary. In this case, site blockage by surface O may also play a role, reducing the interaction between the phenyl group and the surface until higher temperatures when the O is consumed and decarbonylation can occur.

Though not shown directly in Scheme 4-1, it is also useful to consider the water isotopes formed in the temperature range associated with decomposition of benzoate (e.g., Figure 4-1a). Note that the benzoate (PhCOO-) intermediate does not have an H to contribute to water production except from the aromatic ring. Thus the hydrogen is likely produced by C-H scission on the ring and subsequent reaction of H with surface O, producing $H_2^{18}O$ at 395 K. At somewhat higher temperatures (~405 K in Figure 4-1a), water containing both ¹⁶O and ¹⁸O desorbs, with this water likely originating from C-O scission in the carboxylate.

Finally, it is interesting that benzaldehyde desorbs at 520 K with toluene and water in Figure 4-2, suggesting they result from a common decomposition process. One possible process is proposed to be a bimolecular reaction mechanism leading to these products. The mechanism is like that proposed by Pang, et al. on clean Pd(111).¹² There, it was hypothesized that intermolecular interactions allowed for direct H abstraction from an adsorbate to produce toluene (m/z = 92), rather than hydrogenating with the deuterium available on the surface (to produce m/z = 93). The C-O bond of benzyl alcohol is relatively weak (342 kJ/mol¹²) due to the aromatic ligand and thus has a proclivity towards breaking, which does not occur for simple alcohols like propanol (394 kJ/mol⁴²). The results reported here are consistent with a bimolecular mechanism. High-temperature PhCHO is not observed from the reaction of PhCH₂OH or PhCHO on the clean Pd surface,¹² nor was PhCHO desorption detected at high temperatures in Figure 4-1 on O/Pd(111). However, high-temperature PhCHO (Figures 4-2 and 4-4b) is observed when benzyl alcohol decomposes on O/Pd(111), suggesting that this aldehyde product is not produced from the dehydrogenation pathway, but rather as a result of the hydrodeoxygenation pathway. Further, the amounts of toluene and PhCHO desorbing at high temperature are roughly the same. The detailed mechanism for the toluene formation reaction is not clear from these results; in particular, the identity of the species that precedes C-O scission is not apparent, and is difficult to probe directly here because toluene production is only observed at high coverage, and is not the major reaction pathway. Density functional theory calculations may be useful for identifying the detailed surface pathway. Here, the desorption of hightemperature PhCHO from the O-covered surface indicates that one of oxygen's effects is to allow greater

coverages of decomposing intermediates to form and react; a similar effect occurred when 1,2propanediol decomposed on O/Pd(111).¹⁰

The only previous study of benzyl alcohol on an O-covered surface is that of Rodríguez-Reyes and Friend on Au(111).¹³ They found that PhCH₂OH undergoes partial oxidation to PhCHO through a benzyloxy intermediate or PhCH₂OH may be further oxidized to produce benzoic acid and CO₂. Their study used varying coverages of surface O (0-0.15 ML). The most selective and partial oxidation to PhCHO occurred at oxygen concentrations < 0.08 ML, but at \geq 0.08 ML further oxidation to benzoic acid and CO₂ occurs. ¹⁸O/Au(111) experiments resulted in isotopic CO₂ and benzoic acid. Another key aspect of their study is the report of benzyloxy and benzaldehyde coupling to form benzyl benzoate at low oxygen precoverages. Ester formation was not seen on O/Pd(111), likely due to the difference in metal; Au is highly active for esterification and O/Au for cross-coupling.⁴³⁻⁴⁷ Only recently has catalytic esterification of alcohols on Pd been reported,^{48,49} and not yet in any surface science studies on Pd. We have ruled out benzyl benzoate as a volatile product in this study because neither the parent mass m/z = 212 was detected, nor its key fragments m/z = 77, 91, 102.

Consistent with reactions on pure Pd catalysts,^{50,51} the present study shows high activity for O-H and C^{α}-H scission to form benzaldehyde. We see the C^{α}-H barrier is higher than O-H scission based on the evolution of D₂O at higher temperature than H₂O in Figure 4-4, as well as the presence of benzaldehyde on the surface in Figure 4-6 at 200 K, following benzyl oxide formation near 170 K. Further oxidation produces benzoate (precursor to benzoic acid) through the addition of oxygen to benzaldehyde; this step occurs by 240 K (Figure 4-5) on O/Pd. Thus, O addition has a slightly higher barrier than C^{α}-H, but the fact that these steps and O-H scission all occur by 250 K suggests a relatively low kinetic barrier for reaction on Pd. These results lead to an understanding of why Pd is active for the desired oxidation reactions, but also points to difficulty in achieving selective aldehyde production. Furthermore, it is apparent that Pd surface sites can bind the phenyl ring strongly, potentially causing surface poisoning. This analysis suggests that it is desirable to decrease the activation energy for benzaldehyde desorption relative to the activation energy for benzoate formation, and to decrease the binding affinity of the phenyl ring toward the surface. Thus, recent reports of the utility of AuPd catalysts for this reaction may be consistent with the Au promoter playing such a role.^{13,52} Gold surfaces have traditionally been found to favor adsorption of aldehydes in a more weakly adsorbed n¹ configuration that may help promote selectivity;^{53,55} Au surfaces are also much less reactive toward benzene,⁵⁶ potentially decreasing the tendency for formation of strongly adsorbed intermediates. However, the recent surface level study on O/Au(111) work indicates a high reactivity of this surface toward benzyl alcohol oxidation and a significant interaction with the phenyl ring.¹³ One possibility is that Au helps limit the surface oxygen under reaction conditions. Another effect of combining Au and Pd is altering the electronic structure of the metals. This type of hybrid behavior of AuPd for diol oxidation has been described by Griffin, et al.⁵⁷ as a decrease in the stability of strongly adsorbed intermediates. However, detailed surface-level studies of AuPd may be required to understand the detailed mechanism for their excellent performance in benzyl alcohol oxidation.

4.6 Conclusions

The surface chemistry of benzaldehyde and benzyl alcohol was investigated on O/Pd(111) using TPD and HREELS. The primary purpose was to identify effects of surface oxygen on the reactivity of multifunctional reactants and establish their surface pathways. Experiments conducted on ¹⁸O/Pd(111) reveal oxygen exchange between the surface and benzaldehyde occurs through the process of benzoate formation, which proceeds to isotopic benzaldehyde and CO₂ as well as isotopic CO. The observed isotopic scrambling has not been reported previously for reactions of aldehyde and alcohols on O-covered Pd surfaces, and suggests that the phenyl ring plays a strong role in moderating reactivity. Benzyl alcohol reacts to form oxidation products (PhCHO, H₂O, CO₂), decomposition products (H₂, CO, benzene) and the hydrodeoxygenation product toluene. These same products evolve from benzaldehyde's reaction on O/Pd(111), with the exception of toluene. Co-adsorbed oxygen increases the coverage of PhCH₂OH that

proceeds toward decomposition, and thus influences decomposition activation barriers and desorption products. Thus, coadsorbed oxygen was observed to have several effects: it oxidized the benzyl alcohol to benzaldehyde, induced a monohapto configuration of the aldehyde, nucleophilically attacked the carbonyl group to form benzoate, and scavenged hydrogen to form water.

4.7 References

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36. The HREEL spectra of benzaldehyde (Figure 4-5) and benzyl alcohol-OD on O/Pd(111) at intermediate temperatures are compared directly in Appendix A Figure A-5.

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CHAPTER 5

Ring Opening and Oxidation Pathways of Furanic Oxygenates on Oxygen-Precovered Pd(111)

5.1 Abstract

The surface reactivity of furan, furfural, and furfuryl alcohol on oxygen-precovered Pd(111) (O/Pd(111)) was studied via temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) to understand the oxidation processes of more complex alcohols and aldehydes. The primary reaction pathway explored was furfuryl alcohol dehydrogenation to furfural, followed by decarbonylation to furan and subsequent ring opening of furan (C_4H_4O) through O-C^{α} scission; however, furfuryl alcohol and furfural also underwent other parallel reactions. Furfuryl alcohol decomposed through sequential O-H and C^{α} -H scission to furfural. At high coverages, deoxygenation of furfuryl alcohol to methylfuran ($C_4H_3CH_3$) was observed simultaneously with furfural production near 320 K, possibly through a disproportionation reaction of two alcohol molecules. Observation of furfural as a reaction product at this temperature was related to an increased prevalence of a weakly bound $\eta^1(O)$ aldehyde state near 250 K on O/Pd(111) as compared to clean Pd(111). Furfural also reacted with surface O to produce furoate (C_4H_3OCOO -), which primarily underwent decarboxylation to furan and CO_2 . The presence of surface oxygen resulted in a new, higher-temperature desorption channel for furan at 340 K; this channel coincided with desorption of partial oxidation products 2(5H)-furanone and maleic anhydride. TPD experiments on ¹⁸O/Pd(111) showed incorporation of surface oxygen into furfural, H₂O, CO₂, CO, 2(5H)-furanone and maleic anhydride products, with the isotopic distributions suggesting that partial oxidation of furan occurred through a ring-opened carboxylate.

5.2 Introduction

Streamlined production of value-added chemicals and fuels from biomass is of great interest as we aim to decrease our dependence on crude oil. Integrated biorefineries rely on the conversion of biomass through complex carbohydrates and multifunctional oxygenates into platform chemicals.¹⁻² In 2004, the Department of Energy named furfural in the top 30 platform chemicals for a biorefinery.³ The list was revised to a top 10 in 2010, and still included furfural.⁴

Another multifaceted furanic molecule is 5-hydroxymethylfurfural (HMF), produced via acid catalyzed hydrolysis and dehydration from cellulosic biomass feedstocks. Oxidation of HMF has received attention in the catalysis literature,⁵⁻⁷ but no surface-level studies of the effects of oxygen on its smaller functional units (furan ring, alcohol-substituted furan, aldehyde-substituted furan) have been carried out. Since HMF can react with oxygen to form 2,5-furan dicarboxylic acid, another top 30 platform chemical,³ it would be useful to understand oxygen's roles in these reactions. Supported Pd/C catalysts are active for HMF oxidation⁵ while Pd/Al₂O₃,⁸⁻⁹ Pd/SiO₂¹⁰⁻¹¹ and Pd/C¹² have shown activity for furfural conversion to furfuryl alcohol and methylfuran. Thus, the present surface chemistry study utilizes Pd(111) to study the effects of oxygen on furanic molecules.

The effects of oxygen on reactions of simple alcohols such as methanol, ethanol and propanol on Pd(111) have been elucidated.¹³ With an initial coverage of 1/4 monolayer, atomic oxygen acts as a Brønsted base to promote extraction of the hydroxyl hydrogen, scavenges hydrogen to form water, alters the geometry of intermediate adsorbed aldehydes, nucleophilically oxidizes aldehydes to carboxylates and stabilizes alkoxy intermediates to higher temperatures. To date, only a handful of complex alcohols have been experimentally studied to determine the effect of oxygen on their Pd(111) reactivity: benzyl alcohol,¹⁴ 1,2-propanediol,¹⁵ and crotyl alcohol;¹⁶ the latter two have been summarized previously.¹⁴

The effect of oxygen on the reactivity of benzyl alcohol and benzaldehyde is particularly relevant for understanding reactions of furanic compounds; like furanic oxygenates, benzylic oxygenates are aromatic molecules with a phenyl ring in the place of furan. On clean Pd(111), benzyl alcohol has been found to undergo sequential O-H and C-H scission to produce benzaldehyde, which subsequently undergoes decarbonylation to produce benzene.¹⁷ In addition, at high benzyl alcohol coverage toluene is formed via hydrodeoxygenation. In the presence of surface O, more benzaldehyde desorbed from an $\eta^{1}(O)$ state and a carboxylate intermediate (benzoate) formed. Aromatic substituent effects were proposed to account for observed oxygen exchange between the surface and the benzoate.¹⁴

There have been several studies of the decomposition pathways of furan.¹⁸⁻²⁵ Temperatureprogrammed desorption (TPD) experiments show furan desorbs molecularly or decomposes to CO and H_2 , with the rate of decomposition being highly dependent on initial furan coverage.¹⁸ At low to medium coverages, furan lies flat on the surface as determined by scanning tunneling microscopy,²⁶⁻²⁷ near-edge xray absorption spectroscopy and scanned-energy mode photoelectron diffraction.²² However, at coverages near saturation, furan adsorbs with a tilted angle because the oxygen is slightly repelled from the surface.¹⁸ The suggested decomposition mechanism is C^a-H scission, followed by C-O scission to produce a molecule of CO, leaving behind a C₃ fragment.^{19, 28} Laser-induced thermal desorption experiments show evolution of benzene near 350 K from the C₃H_x fragments that undergo C-C coupling.¹⁹ One relevant study of furan on an oxygen-precovered Ag surface was carried out by Crew and Madix.²⁹ They found that furan reacted on O/Ag(110) to form CO₂ and H₂O as well as maleic anhydride, bifuran, and benzene.

While furan has been the focus of a variety of surface-level experimental studies, furfuryl alcohol and furfural have only been studied on clean Pd(111) using temperature-programmed desorption.³⁰ A summary of the proposed mechanism is provided in Scheme 5-1. Furfural decomposes to furan, propylene, CO and H₂. Furfuryl alcohol reacts similarly to furfural, proceeding through the aldehyde intermediate, but the alcohol may undergo a parallel pathway to the hydrodeoxygenated product methylfuran and its byproduct, H₂O. Experiments conducted with isotopically-labeled surface hydrogen suggested that adsorbate-adsorbate interactions between adsorbed furfuryl alcohol molecules assist the deoxygenation pathway to methylfuran and H₂O. Low-coverage reaction pathways for furfuryl alcohol on Pd(111) have been computed for the dehydrogenation, deoxygenation, and decarbonylation pathways using DFT.³⁰⁻³¹



Scheme 5-1. Furfuryl alcohol and furfural reaction pathways on clean Pd(111). Adapted from reference.³⁰

In the present work, the reactivity of furan, furfural, and furfuryl alcohol on oxygen-precovered Pd(111) was studied in order to understand the oxidation of more complex alcohols and aldehydes, which may aid in catalyst design for selective oxidation of biomass-derived molecules. The present study utilized TPD and high-resolution electron energy loss spectroscopy (HREELS) to determine the effects of surface O on these mechanisms.

5.3 Methods

All TPD experiments were conducted in an ultrahigh vacuum chamber described previously (base pressure ~1.2 x 10^{-8} Pa or 9 x 10^{-11} torr).³² The UHV chamber included a Smart-IQ+ quadrupole mass spectrometer (VG Scienta) for TPD and an NGI3000-SE sputter gun (LK Technologies) for cleaning the sample. The Pd(111) single crystal (Princeton Scientific) was routinely cleaned by backfilling the chamber with oxygen or mild sputtering with argon. The crystal was mounted to a tantalum disk, which was held on a copper plate with clips. The temperature of the sample was measured by a thermocouple spot-welded to the copper plate, right next to the crystal mount. Cooling for experiments is accomplished by a liquid nitrogen reservoir. High-resolution EELS experiments were conducted in an UHV chamber described previously (base pressure ~2 x 10^{-8} Pa or 1.5×10^{-10} torr).³³ The chamber is equipped with an LK5000 high-resolution electron energy loss spectrometer (LK Technologies) and a model 981-2046

sputter gun for cleaning (Varian). A specular angle of 60° with respect to the surface normal and beam energy of 6.32 eV were used in all HREELS experiments. Vibrational peak positions are reported to the nearest 5 cm⁻¹ and all HREEL spectra are normalized to the elastic peak height.

Furfuryl alcohol, furfural, furan and methylfuran were dosed onto the crystal through a direct dosing line where their respective dose sizes were characterized by the partial pressure in the line. Dose sizes of each of these molecules can be approximated by comparing the carbon monoxide peak area to that of a saturating dose of CO, 0.67 ML.³⁴ In order to report CO₂ desorption in these oxidation studies, a CO₂ versus CO desorption (in ML) correction factor was calculated by backfilling the chamber with the same pressure of each molecule (CO, CO₂) separately. The calculated CO_x yields provide an upper bound for the original reactant coverage that undergoes decomposition since CO_x evolves from both decarbonylation and decarboxylation of reactant species as well as oxidation of surface carbon. Cracking patterns for furfuryl alcohol, furfural, furan and methylfuran were obtained by direct dose at ~6.6 Pa (5 x 10^{-2} torr) for 10 seconds. Furfural was obtained from Sigma Aldrich at reported 99% purity. Furfuryl alcohol, furan and methylfuran Kere obtained from Sigma Aldrich at reported 99%, and 99+% purity, respectively. Ultrahigh purity ¹⁶O₂ was obtained from Matheson Trigas and ¹⁸O₂ from Aldrich at reported 97% atom ¹⁸O.

5.4 Results

To investigate the oxidation mechanism of furanic oxygenates, we studied the reaction of several compounds (furan, furfural, and furfuryl alcohol) on a Pd(111) surface precovered with 1/4 monolayer of ¹⁸O. Isotopic ¹⁸O is useful for observing incorporation of surface oxygen in various products, especially $H_2^{18}O$ because of issues with $H_2^{16}O$ desorption from the background. We first present results from the reaction of furan because it is a component of the more complex furanic reactants.

5.4.1 Furan

Figure 5-1 shows the TPD spectra following two different-sized furan exposures on ¹⁸O/Pd(111). Surface oxygen (which can be tracked based on isotopic ¹⁸O) is incorporated into the CO, CO₂ and H₂O products. Figure 5-1a corresponds to a sub-saturation furan exposure, where the presence of an ¹⁸O₂ (m/z = 36, not shown) peak at high temperature indicates excess surface oxygen, while Figure 5-1b represents a saturating dose without excess oxygen.

At the lower coverage of furan (m/z = 68) in Figure 5-1a, decomposition reactions to CO, CO₂, and H_2O are the dominant processes. On clean Pd(111), furan decomposes to hydrogen, CO, and surface carbon by 300 K.^{18, 25} However, on O/Pd(111), the hydrogen and CO reacted with surface O to form water (as early as 230 K) and carbon dioxide as well. No H_2 (m/z = 2) desorbed in the presence of excess surface O since any available H immediately combined with surface O to form water. Isotopic water, $H_2^{18}O$ (m/z = 20), desorbed in three peaks (230 K, 310 K and 350 K) indicating three surface C-H scission processes that liberate H for reaction. The H may evolve from a combination of ring C-H scission by 230-310 K and decomposition of C₃H₃ by 350 K, which has previously been found to form from furan ring-opening by 320 K.^{19, 24} The $H_2^{16}O$ (m/z = 18) peak at 230 K is attributed to desorption of water from the heating stage.³⁵ $C^{18}O^{16}O$ (m/z = 46) desorbed in a single peak centered at 430 K, consistent with CO oxidation³⁶ as observed in control experiments (not shown). $C^{18}O_2$ (m/z = 48) desorbed in multiple peaks over the range of 430-465 K, and is attributed to oxidation of surface C. Very little $C^{16}O_2$ (m/z = 44) desorbs at 430 K, thus there is no evidence for oxygen scrambling occurring between the surface and the furan ring. $C^{16}O$ (m/z = 28) and $C^{18}O$ (m/z = 30) desorbed in the range of 430-465 K, with additional C¹⁸O at 490 K, consistent with further oxidation of surface C. Carbon dioxide and CO peaks were assigned by recording separate TPDs of the relevant oxidation processes. First, 0.25 Langmuir CO was exposed on ¹⁸O/Pd(111); CO is oxidized by ¹⁸O to form $C^{18}O^{16}O$ (m/z = 46) at 425 K and higher, consistent with experiments on ¹⁸O/Pd(111) in Figure 5-1. Then an ¹⁸O₂ TPD was recorded showing C¹⁶O (adsorbed from the background) oxidation to $C^{18}O^{16}O$ occurs above 400 K and $C_{(a)}$ is oxidized to $C^{18}O_2$ (m/z = 48) or C¹⁸O (m/z = 30) near 475 K.

The peak shapes and temperatures changed considerably when the coverage of furan was higher (Figure 5-1b). Significant furan coverage effects were also observed during TPD studies on clean Pd(111).¹⁸ Furan (m/z = 68) desorbed molecularly in large peaks at 185 K, 255 K, and 340 K. The first two are consistent with multilayer and monolayer desorption whereas the 340 K peak was not observed during furan TPD on clean Pd(111) in the literature¹⁸ or in our own control experiments (Appendix B Figure B-1). The partially oxidized products, maleic anhydride (MA, C₄H₂¹⁶O¹⁸O₂) (m/z = 102) and 2(5H)-furanone (25HF, C₄H₃¹⁶O¹⁸O) (m/z = 55) were also detected, desorbing near 340 K. The evolution of 25HF (incorporating one surface ¹⁸O) is consistent with its serving as an intermediate between furan and MA, which incorporates two surface oxygen atoms.²⁹ In previous studies, 25HF has been shown to desorb at 335 K on clean Pd(111).³⁷ while MA was observed as a reaction product of furan in TPD by Crew and Madix on O/Ag(110).²⁹

Water (H₂¹⁸O) desorbs in two distinct peaks at 290 K and 325 K. The first peak likely results from a process similar to that observed in Figure 5-1a when the decomposing ring releases H to the surface and H recombines with surface O. However, the correspondence of the second H₂¹⁸O peak with a C¹⁸O¹⁶O peak of similar shape and relatively low desorption temperature is suggestive of the decomposition of a carboxylate intermediate.^{13, 15, 38-39} As discussed in detail below, this carboxylate intermediate is hypothesized to form from nucleophilic attack by surface ¹⁸O of a ring-opened form of adsorbed furan. Besides the decarboxylation route at 325 K, C¹⁸O¹⁶O peaks at 350 K, 370 K and 400 K appear consistent with CO oxidation at high coverages. C¹⁸O₂ (m/z = 48) has only one clear peak at 370 K and a shoulder near 425 K, consisent with surface carbon oxidation. C¹⁶O (m/z = 28) and C¹⁸O (m/z = 30) desorb at 455 K with a peak shape and temperature expected for high coverages of decomposition products.³⁰ At this higher furan coverage, with no excess surface O, some H₂ (m/z = 2) desorbs at 445 K, indicating that all surface O was consumed by this temperature in the formation of the H₂O, CO₂, and other oxidation products. Overall, the trends observed in the TPD of furan (Figure 5-1) show that a ring opening process on Pd(111) leads to producton of isotopic CO₂ as well as partially oxidized 2(5H)furanone and maleic anhydride.



Figure 5-1. Thermal desorption spectra of furan on ¹⁸O/Pd(111) dosed at 150 K. (a) The sub-saturating dose corresponds to 0.001 ML C¹⁶O (m/z = 28), 0.005 ML C¹⁸O (m/z = 30), 0.002 ML C¹⁶O₂ (m/z = 44), 0.05 ML C¹⁶O¹⁸O (m/z = 46), and 0.08 ML C¹⁸O₂ (m/z = 48) desorption. (b) The saturating dose corresponds to 0.15 ML C¹⁶O (m/z = 28), 0.15 ML C¹⁸O (m/z = 30), 0.0 ML C¹⁶O₂ (m/z = 44), 0.06 ML C¹⁶O¹⁸O (m/z = 46), and 0.02 ML C¹⁸O₂ (m/z = 48) desorption.

High-resolution electron energy loss spectroscopy was also utilized to study furan decomposition on O/Pd(111). Spectra collected after a 6 Langmuir furan exposure on O/Pd(111) are shown in Figure 5-2. It should be noted that furan on clean Pd(111) was originally studied using HREELS by Ormerod, et al.,¹⁸ but spectra were independently gathered here for direct comparison to the reaction on the oxygenprecovered surface at additional temperatures (Appendix B Figure B-2). Table 5-1 lists the vibrational mode assignments for furan on O/Pd(111) in this work. The intense C-H in-plane bending at 750 cm⁻¹, ring C-C stretching at 1400 cm⁻¹ and ring C-O stretching near 1700 cm⁻¹ visible at 175 K are consistent with a highly crowded surface containing tilted furan molecules. While not well-resolved at 175 K, further evidence of furan on the surface was seen at 140 K (Appendix B Figure B-2) with ring wagging near 550 cm⁻¹, ring stretching (950 cm⁻¹), and C-H stretching at (3100 cm⁻¹). Spectra at 270 K suggest the onset of ring opening and decarbonylation with a small peak at 1850 cm⁻¹ corresponding to adsorbed CO on the surface. However, some furan was still intact on the surface with the increased intensity of the ring C-O stretching mode at 1700 cm⁻¹ and C-H stretching at 3050-3100 cm⁻¹.

By 300 K, in-plane deformation of the ring at 820 cm⁻¹ and C-H stretching near 3100 cm⁻¹ are more intense, consistent with a stabilized furanic precursor to molecular desorption of mass 68 at 340 K in Figure 5-1b. Note that this contrasts to spectra for furan on clean Pd(111), where there is little evidence of intact furanic rings on the surface. Shifts in the spectra at 325 K indicate that further oxidation and decomposition have occurred on O/Pd(111). The peaks at 875 cm⁻¹ and 1390 cm⁻¹ are assigned to an OCO in-plane deformation and an OCO stretching mode, respectively, because they were not observed in the absence of oxygen (Appendix B Figure B-2). The relative intensity of the OCO deformation to its stretch suggests a one-legged carboxylate geometry.⁴⁰ Increased intensity of the adsorbed CO vibration in the 325 K spectrum is consistent with further decarbonylation. By 375 K, $\delta(OCO)$ and v(OCO) are no longer apparent, corresponding with desorption of the majority of products in the carboxylate pathway. A loss peak near 1330 cm⁻¹ was observed at 375 K that is possibly attributable to C-H deformation modes of decomposition intermediates, but adsorbed CO is most prevalent at this temperature. Extensive decomposition is apparent by 425 K with furan-derived decomposing carbonaceous species giving rise to stretching in the 650-1000 cm⁻¹ range and adsorbed carbon stretching, v(C-Pd), at 385 cm⁻¹. Molecular CO has desorbed from the surface, consistent with the onset of desorption near 390 K at high coverage (Figure 5-1b). Overall, the TPD and HREELS results indicate that surface oxygen altered the surface chemistry of furan by (i) stabilizing furan ring structures on the surface to higher temperature(ii) producing ring-opened carboxylate intermediates, and (iii) producing partial oxidation products 25HF and MA.



Figure 5-2. Vibrational spectra from a 6 Langmuir exposure of furan at < 175 K on O/Pd(111) and annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height and scaled as indicated.

Table 5-1. Vibrational mode assignments (cm⁻¹) of furan adsorbed on O/Pd(111) compared to clean Pd(111) and in the vapor phase.

Mode	Furan	Furan O/Ag(110)	Furan clean	Furan IR
	O/Pd(111)	29	$Pd(111)^{18}$	vapor ⁴¹
ring v(CH)	3050-3100	3120	3085	3140, 3167
ring v(C-O)	1700	n/a	1750	n/a
ring v(C-C)	1400	1470	1445	n/a
v(ring)	n.r	1390	1005	1384, 1491
δ(CH)	n.r.	1040	1005	995, 1066
δ(ring)	n.r.	860	n/a	871
Υ(CH)	750	770	750	n/a
Y(ring)	505	600	540	n/a

 δ =in-plane deformation v=stretch Y=wagging n.r. = not resolved n/a = not reported

5.4.2 Furfural

Previous surface studies of complex furanic molecules (furfural and furfuryl alcohol) on the clean Pd(111) surface suggest that the multifunctional substituent has a significant effect on reactivity and opens unique reaction pathways that the furan ring alone does not undergo, e.g., ring opening to produce propylene.³⁰ We begin with our study of furfural reactivity on ¹⁸O/Pd(111) and seek to observe the effect of the aldehyde substituent under these surface conditions.

TPD spectra of two different coverages of furfural on ¹⁸O/Pd(111) are presented in Figures 5-3a and 5-3b, representing sub-saturating and saturating exposures, respectively. All furfural decomposition products on clean Pd(111) were observed here except propylene; additionally, H₂O and CO₂ were produced on O-covered Pd(111). Surface oxygen was incorporated into the CO, CO₂ and H₂O products. Figure 5-2a corresponds to the presence of excess surface oxygen as indicated by a high-temperature ${}^{18}O_2$ peak (not shown). Furfural (m/z = 96) at low coverage fully decomposed on the O/Pd(111) surface, consistent with the effect of oxygen observed on other multifunctional aldehydes.¹⁴⁻¹⁵ H₂¹⁸O desorbed at 305 K, 375 K and near 450 K. The trends for isotopic CO_2 (m/z = 44, 46, 48) are distinct from those of the furan experiments in Figure 5-1a. Based on the same peak temperature at 375 K and shape of each of the CO₂ isotopes in Figure 5-3a, concurrent with $H_2^{18}O$ desorption, is suggestive of a decomposing furanic carboxylate, or furoate; this carboxylate would form from the oxidation of furfural's aldehyde substituent. Similar peak shapes of all three CO2 isotopes desorbing at 375 K suggest some oxygen scrambling occurs between the carboxylate and surface O prior to decarboxylation; a similar result has been seen for benzaldehyde oxidation to benzoate on ¹⁸O/Pd(111).¹⁴ C¹⁸O¹⁶O and C¹⁸O₂ desorbing around 435-445 K are again consistent with oxidation of CO and surface C, respectively. Similarly to Figure 5-1a, there was no H_2 desorption in the presence of excess oxygen.

With a saturating coverage on ¹⁸O/Pd(111) in Figure 5-3b, furfural (m/z = 96) desorbed molecularly at 245 K and in a broader peak centered at 375 K, similar to its desorption from clean Pd(111).³⁰ Exchange of surface oxygen with furfural through the course of reaction and desorption of heavy furfural (C₄H₄OCH¹⁸O) cannot be ruled out, as some m/z = 98 was detected. However, its

production at 400 K may only be attributable to surface defect sites because of the low signal. $H_2^{18}O$ was produced around 300 K, presumably when the aldehyde C-H bond broke and the resulting H combined with surface O. As in the decomposition of furan on O/Pd(111) (Figure 5-1b), desorption of furan, MA (m/z = 56), and 25HF (m/z = 55) near 340 K was seen here. The remaining two peaks in C¹⁸O¹⁶O desorption, along with C¹⁸O₂ (m/z = 48) and C¹⁶O₂ (m/z = 44), at 375 K and 390 K are similar to those observed for furan decomposition in Figure 5-1. The broad CO (m/z = 28, 30) desorption peak between 400-500 K is expected for the high coverage of furfural.³⁰ More water (m/z = 18, 20) desorbed at 415 K, consistent with the decomposition of the furan ring and release of H that combined with available oxygen (¹⁶O, ¹⁸O).³⁰ This was further corroborated in TPD experiments with furfural-*d3* (C₄D₃OCHO) on ¹⁶O/Pd(111) (Appendix B Figure B-3b), where D₂¹⁶O (m/z = 20) desorbed at 390-450 K.



Figure 5-3. Comparison of thermal desorption spectra of furfural dosed at 150 K on ¹⁸O/Pd(111) for two coverages. (a) The sub-saturating dose corresponds to 0.05 ML C¹⁶O (m/z = 28), 0.055 ML C¹⁸O (m/z = 30), 0.01 ML C¹⁶O₂ (m/z = 44), 0.04 ML C¹⁶O¹⁸O (m/z = 46), and 0.03 ML C¹⁸O₂ (m/z = 48) desorption. (b) The saturating dose corresponds to 0.44 ML C¹⁶O (m/z = 28), 0.10 ML C¹⁸O (m/z = 30), 0.005 ML C¹⁶O₂ (m/z = 44), 0.01 ML C¹⁶O¹⁸O (m/z = 46), and 0.05 ML C¹⁸O (m/z = 30), 0.005 ML C¹⁶O₂ (m/z = 44), 0.01 ML C¹⁶O¹⁸O (m/z = 46), and 0.05 ML C¹⁸O₂ (m/z = 48) desorption.

The goal of HREELS experiments was to evaluate the hypothesis that a carboxylate intermediate, furoate, was formed from O addition to furfural. Furoate was hypothesized as an oxidation intermediate based on the observation of simultaneous CO2 and H2O desorption in Figure 5-3, as well as by analogy with surface studies of other aldehydes (such as benzaldehyde) on O/Pd(111).¹⁴ Figure 5-4 shows HREEL spectra collected after a 1 Langmuir exposure of furfural on O/Pd(111) at low temperatures. This subsaturation exposure was selected because the fractional yield of CO₂ (the proposed end product of the furoate pathway) in TPD was highest at low furfural coverages. However, using very small furfural exposures resulted in low signal intensity due to the low surface coverage. Furfural was intact on the surface at 170 K as demonstrated by a clearly resolved aldehyde C-H stretching peak (2860 cm⁻¹); the

aldehyde C=O stretch is likely convolved in the shoulder between 1600-1660 cm⁻¹. By 200 K the aldehyde C=O stretch is more clearly resolved at 1660 cm⁻¹ while the aldehyde C-H stretch was no longer detected and the C-H out-of-plane bending mode shifted to higher frequency (700 to 750 cm⁻¹). A loss at 1375 cm⁻¹ became apparent by 200 K and persisted to 250 K; it is attributed to the OCO stretching mode of a furoate intermediate.⁴² A lack of ring v(CH) 2900-3100 cm⁻¹ at 215 K suggests the furan rings of adsorbed intermediates were parallel to the surface. The 1375 cm⁻¹ carboxylate peak was clearly resolved after heating the surface to 230 K. An observed shift in the CO stretching frequency from 1660 cm-1 to 1775 cm-1 shows that decarbonylation began as early as 230 K, highlighting the fact that multiple furfural reactions were proceeding in parallel on he O-precovered surface. At 250 K, the 1375 cm⁻¹ carboxvlate peak started to become convolved with other modes associated with decomposing furanic species (Appendix B Figure B-2). By 270 K the extent of decarbonylation increased, demonstrated by the greater vibrational intensity of adsorbed CO (1775 cm⁻¹). While vibrational intensity in the COO stretching frequency range persisted to this temperature, a peak was not clearly resolved due to overlap with other modes; based on the 325 K onset temperature for CO2 formation observed in TPD (Figure 5-3), it is expected that the carboxylate would persist to above this temperature. At higher coverages, differences between the clean and O-covered spectra were small (Appendix B Figure B-4, 140-475 K), consistent with the similar TPD trends for these surfaces. Here, the presence of excess furfural likely makes it difficult to characterize carboxylate intermediates, since CO2 formation via decarboxylation was a minor pathway (Figure 5-3b).



Figure 5-4. High-resolution electron energy loss spectra from a 1 Langmuir dose of furfural on O/Pd(111) at 140 K and annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.

Table 5-2. Vibration	al mode assignments (cm ⁻¹) of	furfural adsort	bed on clean Pd((111), O/Pd(111), and
compared to the liqui	d phase.			_
		1 T		1

Mode	1 L	Furfural IR
	Furfural	Liquid ⁴³
	O/Pd(111)	
	170 K	
ring v(CH)	2950-3090	3140
aldehyde v(CH)	2860	2817
ring v(C-O)	1660	n/a
aldehyde v(C=O)	1660	1675, 1690
v(C=C)	n.r.	1466, 1476
ring v(C-C)	1150, 1375	n.r.
v(ring)	900	n/a
δ(CH)	900	755, 770, 884
Υ (CH) out-of-plane bend	700	n.r.
Y(ring)	550	n.r.
δ(ring)	n.r.	505, 598, 630

 δ =in-plane deformation v=stretch Y=wagging a=asymmetric s=symmetric n.r. = not resolved n/a = not reported

5.4.3 Furfuryl alcohol

Next, we studied the reaction of furfuryl alcohol on ¹⁸O/Pd(111). Similar studies on clean Pd(111) revealed a unique deoxygenation process to methylfuran at high coverages and ring opening to produce propylene.³⁰ The same products from the clean Pd(111) reaction are observed on the O/Pd(111) surface, with the addition of CO₂. Figures 5-5a and 5-5b correspond to sub-saturating and saturating furfuryl alcohol exposures, respectively. Similar to the decomposition of furan and furfural on ¹⁸O/Pd(111), surface oxygen was incorporated into the CO, CO₂ and H₂O products.

At low coverage (Figure 5-5a), furfuryl alcohol (m/z = 98) completely decomposed on ¹⁸O/Pd(111); products such as furfural, furan, methylfuran, propylene and hydrogen are not detected. Water (m/z = 20) desorbed as low as 220 K, similar to the 220-230 K peaks in Figures 5-1 and 5-3. Observed H₂¹⁸O desorption at 310 K is consistent with the recombination of surface O with H following O-H scission and C^{α}-H scission.^{14, 35} Desorption of H₂¹⁸O and the CO₂ isotopes (m/z = 44, 46, 48) at 375 K precisely follows the trends of furfural's reaction in Figure 5-3a, consistent with the alcohol proceeding through a furfural intermediate, which was subsequently oxidized to furoate. Along these lines, the production of C¹⁸O¹⁶O and C¹⁸O₂ at 440 K as well as CO (m/z = 28, 30) at 470 K look similar to Figure 5-3a.

The reaction product distribution of furfuryl alcohol on O/Pd(111) becomes more interesting at higher coverage in Figure 5-5b. Furfuryl alcohol desorbed molecularly at 230 K and 250 K, slightly lower temperatures than the 245 K and 270 K from clean Pd(111). Water (m/z = 20) desorbed as low as 190 K. Whereas the furfural desorption signal was weak during furfuryl alcohol TPD on Pd(111), on O/Pd(111) furfural desorbed in two much more intense peaks.³⁰ The lower temperature furfural peak (250 K) suggests desorption from a weaker η^1 adsorption geometry, bound through its carbonyl oxygen; a similar peak is also seen in Figure 5-3b. It is interesting that the 315 K furfural peak corresponds with methylfuran (m/z = 82) desorption, suggesting that a common process resulted in evolution of both products. The higher peak temperature of the second methylfuran peak (365 K) indicates it was formed by a surface reaction with a higher activation energy. The furan, maleic anhydride (m/z = 56), 2(5H)-

furanone (m/z = 86), CO₂, H₂ and CO spectra have similar features to the furfural results in Figure 5-3b, further confirming that furfuryl alcohol's reaction proceeds through a furfural intermediate. Note that in additional experiments with ¹⁶O, we were able to observe a peak in m/z = 84 rather than m/z = 86 in this temperature range, corresponding to the expected decrease in mass to isotopically-labeled 25HF (m/z = 86) in Figure 5-5b. Non-isotopic maleic anhydride could not be distinguished from the large peak for furfuryl alcohol desorption near 330 K because they share the same parent mass of m/z = 98. It is also worth noting that some propylene (m/z = 42) formed by 340 K in the reaction of the alcohol on O/Pd(111), but was not produced from furfural in Figure 5-3 (or furfural-*d3* in Appendix B Figure B-6).



Figure 5-5. Thermal desorption spectra of furfuryl alcohol on ¹⁸O/Pd(111) dosed at 140 K. (a) The subsaturating dose corresponds to 0.07 ML C¹⁶O (m/z = 28), 0.04 ML C¹⁸O (m/z = 30), 0.01 ML C¹⁶O₂ (m/z = 44), 0.06 ML C¹⁶O¹⁸O (m/z = 46), and 0.04 ML C¹⁸O₂ (m/z = 48) desorption. (b) The saturating dose corresponds to 0.90 ML C¹⁶O (m/z = 28), 0.11 ML C¹⁸O (m/z = 30), 0.01 ML C¹⁶O₂ (m/z = 44), 0.04 ML C¹⁶O¹⁸O (m/z = 46), and 0.02 ML C¹⁸O (m/z = 48) desorption.

Finally, furfuryl alcohol HREELS experiments on clean Pd(111) were completed to identify reaction intermediates and complement previous TPD and DFT studies.³⁰ Table 5-3 lists the vibrational mode assignments for spectra in Figure 5-6. Furfuryl alcohol was intact at 140 K and likely in a multilayer state with a broad O-H stretch apparent near 3250 cm⁻¹. Further, C-C-O in-plane deformations (450 cm⁻¹), C-H out-of-plane bending (780 cm⁻¹), and furan ring stretching (1395 cm⁻¹) indicate the intact molecule. By 170 K, the O-H bond appears to have broken while symmetric methylene CH₂ stretching (2875 cm⁻¹) and ring C-H stretching (3075 cm⁻¹) were more intense. Furyl C-H wagging (650 cm⁻¹), C-C-H out-of-plane bending (900-925 cm⁻¹), ring C-C stretching (1150 cm⁻¹) and ring stretching (1395 cm⁻¹) become resolved at 170 K as well. In the 250 K spectrum, the ring C-O stretching mode at 1625 cm⁻¹ becomes noticeable. This feature is likely resolved following the multilayer desorption temperature of 245 K.³⁰ The similarity of the 270 K spectrum to furfural's 140 K clean Pd(111) scan (Appendix B Figure B-4) suggested furfural was present on the surface. The aldehyde CO mode is clear at ~ 1675 cm⁻¹ while an intense loss at 780 cm⁻¹ may correspond to some furfural being bound in an η^2 geometry.⁴⁴⁻⁴⁵ Decarbonylation of furfural is evident by 300 K and resulted in adsorbed CO on the surface; the lower frequency of the CO stretch (1700 cm⁻¹) is commonly observed with coadsorption of aromatic molecules⁴⁶ like furan. Further spectroscopic evidence of furfuryl alcohol proceeding through a furfural intermediate is apparent in the similarity of the 350 K scan in Figure 5-6 to that of clean Pd(111) at 350 K in Appendix B Figure B-4.

Similar experiments were not conducted for furfuryl alcohol on O/Pd(111) since the key differences in reactivity imparted by coadsorbed oxygen were probed more effectively using furfural on O/Pd(111). The oxygen-precovered surface created differences related to reactions of the aldehyde (enhanced desorption of furfural, formation and decomposition of furoate intermediates).



Figure 5-6. High-resolution electron energy loss spectra from a 2.5 Langmuir exposure of furfuryl alcohol at 140 K on clean Pd(111) and annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.

Table 5-3. Vibrational mode assignments (cm^{-1}) of a 2.5 Langmuir exposure of furfuryl alcohol on clean Pd(111) with comparisons to the liquid and vapor phases.

Mode	Furfuryl	Furfuryl Alcohol IR	Furfuryl Alcohol IR
	Alcohol clean	Liquid ⁴⁷	Vapor ⁴⁷
	Pd(111)		1
	140-170 K		
ν(OH)	3250	n.r.	3652, 3660
ring v(CH)	3075	3123, 3150	3121, 3159
$v_a(CH_2)$	n.r.	2928	2938
$v_{s}(CH_{2})$	2875	2870	2880
v(C=C)	n.r.	1503, 1599	1508, 1600
χ(CH ₂)	n.r.	1450	1462
v(ring)	1395	1361, 1379	1381
v(C-C), v(ring)	1150	1148	1155
$\tau(CH_2)$	n.r.	1077	n.r.
v(C=O) side group	n.r.	1055	n.r.
ring δ(CH)	900-925	1010	1019, 1024
v(C-C)	900-925	956	955
ring Υ(CH)	650, 825	740, 814, 885	732, 743, 810, 889
$\rho_r(CH_2)$	780	740	732
τ(C=C)	n.r.	597	599
δ(CCO)	450	420	421

 δ =in-plane deformation ρ_r =rocking v=stretch Υ =wagging τ =twisting a=asymmetric s=symmetric n.r. = not resolved

5.5 Discussion

A proposed decomposition mechanism for furan on O/Pd(111) is presented in Scheme 5-2. On the oxygen-precovered surface, furan may adsorb and remain intact, leading to desorption between 255-295 K. Alternatively, furan adsorption may occur by first breaking the C^{α}-H bonds and continuing toward ring opening. The hydrogen released to the surface combines with surface O to form H₂O that desorbs 220-310 K (Figure 5-1). Ring opening on Pd(111) has been suggested to occur via C^{α}-O scission due to its energetic favorability to C-C scission.⁴⁸ After ring opening, the reaction can proceed through two competing pathways. The first is similar to the mechanism on clean Pd(111) where decarbonylation leaves a C₃H₃ fragment. In an alternative route on O/Pd(111), a carboxylate is suggested to form via oxidation of the C^{α} that is attached to the original ring oxygen. The evolution of CO₂ and H₂O simultaneously at 325 K in TPD is consistent with decomposition of a carboxylate intermediate. Further, HREELS Figure 5-2 suggested a v(OCO) mode persists between 325-375 K. Decarboxylation produces CO_2 and leaves an unstable C_3H_x fragment. Oxygen exchange occurs through this carboxylate intermediate. In a minor pathway, the carboxylate appears to close and form 2(5H)-furanone or react with surface O, closing the ring to make maleic anhydride. Extensive decomposition above 400 K to CO and surface C allows for oxidation to CO_2 to occur while released hydrogen recombines to form H_2 or combines with released ring O and produces water.



Scheme 5-2. Proposed decomposition mechanism of furan on O/Pd(111). Noted temperatures relate to TPD spectra while temperatures in brackets correspond to HREEL spectra.

One of the most surprising results is the observation that the presence of coadsorbed oxygen results in desorption of furan at 340 K, whereas on the oxygen-free surface there is no furan desorption at such high temperatures. It is notable that the 340 K temperature is similar to that observed from the prior study of furfural decarbonylation on the clean Pd(111) surface.³⁰ Based on a combination of isotopic labeling studies and DFT calculations, furan desorption at this temperature was attributed to hydrogenation of cyclic C_4H_2O intermediates. DFT calculations showed that formation of C_4H_2O intermediates from furfural was thermodynamically favorable because of the effectiveness of the carbonyl function as a leaving group, but not favorable from furan because of the difficulty of the difficulty of the initial C^{α} -H scission. The observation of a new furan feature near 340 K during TPD of furan on O/Pd(111) implies that one role of oxygen may be to assist the required C-H scission. Both experimental and theoretical studies of oxygenate chemistry on Au surfaces have found that surface oxygen can assist

C-H activation.⁴⁹⁻⁵⁰ Theoretical studies of simple CH_x intermediates suggest that O-assisted C-H activation pathways may be less favorable or unfavorable on metals further to the left in the perdiodic table, but chemistry of oxygenates having complexity similar to furan have not been explored.⁵¹

Because the peak temperature and shape correspond well with the desorption of 2(5H)-furanone and maleic anhydride, formation of this intermediate may be important in partial oxidation processes on the Pd surface. Note that the formation of furan at 340 K from a carboxylate intermediate can be ruled out since no isotopically labeled furan ($C_4H_4^{18}O$) was observed in TPD. Further, decarboxylation is not a plausible mode of furan formation at 340 K since it would only leave a C_3 fragment, not the C_4 backbone of furan.

One relevent study of furan on $O/Ag(110)^{29}$ showed furan ring opening to products other than C₃H_x and CO. Similar to our study, CO₂, H₂O and maleic anhydride were produced. However, bifuran and benzene were also observed, while CO and 2(5H)-furanone were not. The lack of CO production in their work is attributable to Ag not being a decarbonylation-active catalyst. In their work, Crew, et al. analyzed the distribution of ¹⁸O in MA that desorbed from the ¹⁸O-precoved Ag(110) surface.²⁹ They showed that the ratio of m/z = 54 : m/z = 56 in their TPD signal was 1:3, and performed a detailed analysis to show this ratio indicated MA was formed by oxidative ring closure of a carboxylate intermediate. In our work, this analysis is somewhat more complex since 2(5H)-furanone was also a product of the reaction on O/Pd(111), with fragments that overlap with maleic anhydride including m/z = 54 and m/z = 56. We used a simple model to account for the contributions of 25HF to m/z = 54 and m/z =56 (Appendix B Figure B-5) and found that the ratio 54:56 attributable to MA is roughly equal to 1:2, neither 1:1 for a butenedial intermediate or 1:3 for the carboxylate intermediate proposed by Crew, et al. Thus, in the present study, we cannot rule out the butenedial intermediate based on isotopic distribution. Previous work with 25HF on clean Pt(111) and Pd(111) showed that its decomposition proceeded through an aldehyde rather than a carboxylate on Pd.³⁷ Given the presence of surface O in this work, the carboxylate may become more stabilized on Pd(111), providing some precedent for association of 25HF with a dial intermediate. However, overall, the evidence for the carboxylate intermediate in Scheme 5-2 is

strong since a carboxylate stretching mode was visible at 325 K in Figure 5-2 and isotopic CO_2 production in the same temperature range (340-350 K) suggests decomposition of a carboxylate, but a parallel pathway through a dial intermediate cannot be ruled out.

Scheme 5-3 depicts the proposed reaction mechanism for furfuryl alcohol and furfural on O/Pd(111). This section will focus on the unique processes observed on the oxygen covered surface since some portion of this mechanism is the same as reaction on clean Pd(111), reported previously.³⁰ Furfuryl alcohol is dehydrogenated to a furfural intermediate via sequential O-H and C^{α}-H scission. The furanic aldehyde may be decarbonylated to furan and CO or oxidized to furoate, which undergoes decarboxylation to furan and CO₂. The furan ring may decompose to C₃H₃ and CO or undergo ring opening (as shown in Scheme 5-2). In a parallel pathway, furfuryl alcohol may undergo deoxygenation to methylfuran.

Furfuryl alcohol loses its hydroxyl hydrogen first, forming an adsorbed alkoxy. Further dehydrogenation at the methylene α -carbon creates an adsorbed furfural intermediate. While an $\eta^{1}(CO)$ loss of furfural is not resolved in HREELS (Figures 5-4 and Appendix B, B-4), the low desorption temperature suggests it was bound in an upright orientation through its carbonyl oxygen. Water is produced when surface oxygen combines with the hydrogen that result from O-H and C^{*a*}-H scission. A second mode of furfural desorption occurs at higher temperatures from an η^{2} orientation. The $\pi(CO)$ mode of the adsorbed furfural in this orientation is observed at 780 cm⁻¹ in HREELS (Figure 5-6). Furfural that goes on to decompose may be decarbonylated to furan and CO by 250 K (Appendix B Figure B-4) or, if sufficient oxygen is available, the aldehyde may be oxidized to a furoate intermediate. There is TPD evidence of decarboxylation occurring by 325 K in Figure 5-3b. A peak at 1375 cm⁻¹ was apparent from 215-250 K in HREELS Figure 5-4 and assigned to a carboxylate v(OCO) mode. Desorption of small amounts of maleic anhydride and 2(5H)-furanone in TPD Figures 5-3b and 5-5b support that ring opening of furan occurs after it is released to the surface via decarboxylation or decarbonylation. We propose that MA and 25HF formation occurs in the same manner as Scheme 5-2.



Scheme 5-3. Proposed decomposition mechanism of furfuryl alcohol and furfural on O/Pd(111). Noted temperatures correspond to TPD spectra.

Low coverage of these reactants in excess oxygen experiments (Figures 5-3a and 5-5a) show desorption of all isotopes of carbon dioxide ($C^{18}O^{16}O$, $C^{18}O_2$, $C^{16}O_2$) at 375 K. This result supports that oxygen exchange occurs via the furoate intermediate, as seen for benzoate on ${}^{18}O/Pd(111)$.¹⁴ However, at the higher coverages in Figures 5-3b and 5-5b, this trend is not observed for the CO₂ products. Desorption of isotopic CO in these experiments implies some amount of exchange still occurs, but to a lesser degree since m/z = 30 desorption is no longer on the same scale as $C^{16}O$ (m/z = 28) in Figures 5-3b and 5-5b. We expected there to be some similarities between the reactions of furfural and furfuryl alcohol to previous studies of benzaldehyde and benzyl alcohol on O/Pd(111). Yet in the case of the benzylic reactants, exchange via the carboxylate intermediate to CO₂ products occurred at saturating coverages as well. The strength of the aromatic binding was proposed to be the cause of benzoate's stability on Pd(111). In comparison, the furan ring's binding interaction is weaker, evidenced by lower molecular desorption temperatures and oxygen exchange to a lesser extent. Thus we do not see evidence of oxygen exchange to the same extent for furanic oxygenates.

Furfural-*d3* experiments on clean and O/Pd(111) in Appendix B Figure B-6 reveal differing interactions with the respective surfaces. On clean Pd(111), furan incorporates an additional deuterium to form m/z = 72 or loses one deuterium to form m/z = 70. This result corroborates what Pang, et al. observed for deuterium exchange with the furan on Pd(111) when furfural was reacted on a deuterium-saturated surface. There, up to two H could exchange for surface D and masses 69 and 70 were observed (furan-*d1* or *d2*). Here, the deuterated furan ring begins with three D after the furfural C-C is cleaved. The

ring may gain one D to m/z = 72 (furan-*d4*) or it may lose one and become m/z = 70 (furan-*d2*). Overall, two ring C-H positions may change when interacting on the clean Pd surface. Alternatively, on the O/Pd(111), we observe no furan-*d2* (m/z = 70) and only furan-*d3* or *d4* (m/z = 71, 72). This may be caused by oxygen scavenging of any surface H which would exchange and may also suggest the ring has a weaker surface interaction on O/Pd(111). Also, it should be noted that propylene-*d3* (m/z = 45) desorbs from clean Pd(111) but not from O/Pd(111), in agreement with Scheme 5-3 and Figure 5-3b's lack of direct furfural-derived propylene.

We consider a disproportionation or bimolecular mechanism of two furfuryl alcohol molecules to be candidates for the simultaneous evolution of methylfuran, furfural and water at 315 K in Figure 5-5b. We specifically probed the idea of this type of mechanism in the presence of isotopic oxygen, focusing on desorption of either $H_2^{16}O$ (m/z = 18) or $H_2^{18}O$ (m/z = 20) with furfural and methylfuran. Appendix B Figure B-6 shows an enlarged view of the relevant spectra. We observe m/z = 18 at 320 K with furfural and methylfuran and no m/z = 20 at this temperature. This is consistent with the possibility of a bimolecular reaction mechanism, whereby one molecule of the alcohol is dehydrogenated to the aldehyde (- 2 H), while the other molecule is deoxygenated (- OH) and hydrogenated (+ H) to methylfuran and the remaining H and ¹⁶O form water. In addition, we have ruled out the methylfuran-producing pathway of furfuryl alcohol's reaction as a mode of furan production. Temperature-programmed desorption results following saturating exposures of methylfuran on both clean and ¹⁸O/Pd(111) are shown in Appendix B Figures B-7a and B-7b, respectively. There is no evidence for C-C cleavage to produce molecularly desorbing furan or methane from either the clean or oxygen-covered surface.

Density functional theory calculations have been employed by Pang, et al.³⁰ and Vorotnikov, et al.³¹ to establish detailed potential energy diagrams and reaction pathways. The first study used DFT to complement the TPD experiments (mentioned above), showing that furfuryl alcohol can decompose through a surface furfural intermediate, which then favors decarbonylation to CO and furan at the low coverages of the simulation (1/9 ML). The focus of the latter study by Vorotnikov, et al. was furfural conversion to furan, furfuryl alcohol, and methylfuran, which relates to catalytic hydrogenation of furfural

on supported catalysts. Under oxidizing conditions, or the presence of atomic oxygen in the present work, we do not expect the furfuryl alcohol or methylfuran pathways to be relevant. However, the production of furan from decarbonylation of furfural was observed on O/Pd(111). The adsorption of furan was calculated in flat, bent and upright geometries at varying coverages from low (1/16 ML) to high (1/4 ML); calculations of a >1/9 ML coverage of furan were unique to this study. In agreement with experiments,^{22,} ²⁶⁻²⁷ furan adsorbs nearly parallel to the surface at low coverage, but may adsorb with a tilt at higher coverages, as evidenced by a lack of coverage dependence of the adsorption energies for the bent and upright configurations.³¹ Vorotnikov, et. al. presented DFT calculated energies for various relaxed adsorption states of furan, furfural, furfuryl alcohol and methylfuran. A comparison of our experimental results with the previous DFT calculations in Appendix B Table B-3 suggests that interactions between adsorbates play a major role in observing the most interesting products. Density functional theory simulations of low-coverage intermediates seem to reasonably describe the low-coverage chemistry. However, some of the more interesting products are observed at high coverage; the TPD temperatures observed at high coverage for species like furan differ with the calculations at low coverage. This suggests the importance of detailed investigations of interactions between adsorbates.^{8, 52} Thus, accounting for neighboring atomic oxygen and higher coverages of adsorbates may be important in designing catalysts that operate with high surface coverages of adsorbates.

5.6 Conclusions

The surface chemistry of furan, furfural, and furfuryl alcohol on O/Pd(111) has been explored using TPD and HREELS. Furfuryl alcohol's O-H and C^{α}-H bonds sequentially undergo scission to form furfural, consistent with other multifunctional alcohol's decomposition pathways. Ring opening of furan proceeds through O-C^{α} scission and may be oxidized to a C₄-carboxylate or preferentially re-close to form furan at 340 K in an oxygen-assisted process. Furfural desorbs from two possible states: weakly bound $\eta^{1}(O)$ near 250 K or $\eta^{2}(CO)$ above 350 K. More furfural appears to desorb from an η^{1} orientation on O/Pd(111) than clean Pd(111), an effect of oxygen observed commonly for aldehydes.^{14, 53} Furfural also reacts with O_(a) to furoate, which may undergo decarboxylation to furan and CO₂ or deoxygenation back to furfural. At high coverages, the alcohol's deoxygenated product, methylfuran, is observed simultaneously with furfural near 320 K, possibly through a disproportionation reaction of two furfuryl alcohol molecules. Two partially oxidized products are observed in these reactions at high coverages following ring opening of furan. 2(5H)-Furanone (25HF) likely forms via closure of the carboxylate intermediate and maleic anhydride (MA) through an additional oxidation step of this intermediate. Temperature-programmed desorption isotope experiments on ¹⁸O/Pd(111) show incorporation of surface oxygen into furfural, H₂O, CO₂, CO, 25HF and MA products. Ring opening of furan in the presence of surface oxygen results in formation of partially oxidized products on Pd(111) in a minor pathway, which has not been reported previously.

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CHAPTER 6

Conclusions and Recommendations

6.1 Thesis Summary

This work has focused on determining oxygen's surface-level effects on multifunctional alcohol decomposition by comparing reactions of biomass probe molecules on $O/Pd(111)^{1-3}$ to previous results on clean $Pd(111)^{4-6}$ because catalytic oxidation reactions on transition metals usually involve participation of oxygen. Temperature-programmed desorption provided reaction product identification using mass spectrometry and reaction kinetics insight based on peak shapes and temperatures. High-resolution electron energy loss spectroscopy of the adsorbed molecules provided understanding of the reaction intermediates, their thermal stability and their adsorption structures. Surface investigations of the thermal oxidation chemistry of a range of multifunctional alcohols and aldehydes (1,2-propanediol, benzyl alcohol, benzaldehyde, furfuryl alcohol, furfural, furan) on O/Pd(111) were presented here. Reaction mechanisms were proposed for each molecule based on these TPD and HREELS experimental studies.

Overall trends observed for multifunctional alcohol reactions in the presence of surface oxygen are summarized here. The scission of alcohol O-H bonds was consistently observed prior to C^{α}-H scission based on isotopic studies with deuterium or oxygen-18 labeling, as well as observing alkoxides in HREELS. The presence of oxygen increased desorption of aldehyde intermediates from the surface compared to clean Pd(111). The desorption temperatures were often lower because they evolved from a more-weakly bound η^1 geometry, as was observed for benzaldehyde, furfural, glyoxal and methylglyoxal. Aldehydes were oxidized to surface carboxylates via nucleophilic attack; however, acids were not observed as desorption products. We propose this is a result of oxygen scavenging any available surface hydrogen before the carboxylate could be hydrogenated.

Two regimes were observed in TPD experiments based on the relative amounts of $O_{(a)}$ and reactant. When oxygen is in excess, the reactant tends toward complete decomposition (CO, CO₂), with

no molecular desorption as well as no H_2 production because oxygen scavenges H to form H_2O . However, when the concentration of $O_{(a)}$ is small compared to the reactant, a wider variety of products may be observed. For example, a high initial coverage of furfuryl alcohol resulted in partial oxidation products (furfural, 2(5H)-furanone, maleic anhydride), deoxygenated products (methylfuran) and decomposition (CO, H_2) products. Finally, co-adsorbed oxygen increases the coverage of multifunctional that proceeds toward decomposition, which often induced coverage effects, and thus influences decomposition activation barriers and desorption products. Promotion of the deoxygenation products may have resulted from higher coverages of intermediates. This was observed for ethylene and propylene from 1,2-propanediol as well as toluene and methylfuran from benzyl alcohol and furfuryl alcohol, respectively.

The latter half of this thesis work included studies of two types of multifunctional aromatic molecules, allowing us to determine if the various ring functionality (phenyl versus furyl) had overall effects on the reaction. Experiments conducted on ¹⁸O/Pd(111) the furfuryl and benzyl reactants reveal oxygen exchange between the surface and aldehyde (furfural, benzaldehyde) occurs through the process of carboxylate (furoate, benzoate) formation, which proceeds to isotopic aldehyde and CO_2 as well as isotopic CO. The observed isotopic scrambling has not been reported previously for reactions of aldehyde and alcohols on O-covered Pd surfaces, and suggests that the aromatic ring plays a strong role in moderating reactivity.

Some differences were observed between the reactions of the phenyl and furfuryl groups. Desorption temperatures of the furfuryl reactants were generally lower than the benzylic because of the difference in binding strength, i.e., furyl interacts more weakly with the surface than phenyl. For instance furan desorbed near 340 K following decarboxylation of furoate while benzene desorbed at 420 K after benzoate decomposed. As a result of furan being a heteroatomic molecule compared to benzene, the surface chemistry was altered on O/Pd(111) to include ring opening; this process proceeds through O-C^{α} scission and may be oxidized to a C₄-carboxylate or preferentially re-close to form furan at 345 K in an oxygen-assisted process. Ring opening of furan in the presence of surface oxygen results in formation of partially oxidized products on Pd(111) in a minor pathway, which has not been reported previously.

Surface oxygen may facilitate ring opening by site blocking from decarbonylation or stabilizing the ringopened intermediate.

6.2 Recommendations for Future Work

Thus far, a variety of multifunctional alcohols and aldehydes have been studied on a single crystal metal using surface science techniques. These findings have practical implications for catalyst design, where it is useful to understand the elementary steps of a reaction. Future work could include gas-phase reactor studies on supported Pd catalysts under reaction conditions. The goal in these studies would be testing hypotheses on technical catalysts at higher pressures based on the UHV-observed reaction mechanisms of this thesis. For example, UHV coverage effects trends for benzyl alcohol deoxygenation (chapter 4) may be observed at higher pressures of reactant over supported Pd catalysts.

In the furanic oxygenate studies of chapter 5, two partially oxidized products were observed in the reactions of furan, furfural and furfuryl alcohol at high coverages following the ring opening of furan. 2(5H)-Furanone likely forms via closure of the carboxylate intermediate and maleic anhydride through an additional oxidation step of this intermediate. This work could be extended to furan oxidation with O₂ over supported Pd catalysts, observing whether the novel oxidation mechanism is operable under realistic conditions. Catalyst design for new oxidation processes could follow this work if the partial oxidation products are observed. The expectation may be that ring-opened and partially-oxidized products such as 2(5H)-furanone will be observed. An alternative study could be reduction of the partially oxidized products, 2(5H)-furanone or maleic anhydride, with H₂ over heterogeneous catalysts. We might expect C=O scission and the formation of furan to occur. Additionally, we may suggest a bimetallic design for catalysts to oxidize large furanic molecules such as HMF to 2,5-furan dicarboxylic acid (chapter 1). In chapter 5we observed the furan ring interacting somewhat strongly with the Pd surface, evidenced by oxygen exchange in the furoate intermediate, ultimately producing isotopically-labeled furfural, CO₂ and CO. Strong ring-surface interactions could negatively impact reaction selectivities. For example, a

bimetallic Pd-Au catalyst would allow some Pd to activate molecular O_2 to $O_{(a)}$ while the more-noble metal counterpart, Au, would interact weakly with the furan ring.

The research presented in chapters 4 and 5 related to multifunctional aromatic molecules suggested that the alcohol may be facilely oxidized to the aldehyde, with oxygen inducing aldehyde desorption; further oxidation to a carboxylate and surface oxygen scrambling also occurs. The next steps in this work could include testing the underlying hypothesis that the pendant ring functionality will affect the rates of reaction, i.e., benzene has a stronger interaction with the Pd surface than furan. In order to determine the effect of the ring, gas phase reactor studies of benzyl alcohol and furfuryl alcohol oxidation on supported Pd catalysts with molecular oxygen will be conducted. A microkinetic analysis of these reactions is a systematic way to develop a consistent reaction mechanism and is useful for understanding selectivity, apparent activation energies, isotope effects and reaction orders. While exploring the oxidation versus decarbonylation pathways, this kinetic analysis could provide insight between the competing oxidation pathways to the aldehyde and acid as well. A quantitative model could be developed to understand the surface site distribution and coverages of reactants and products during multifunctional alcohol oxidation on Pd. There will be different molecules and competing reactions that proceed through different intermediates and might require different numbers of surface sites, etc. In situ DRIFT spectroscopy can be used to understand the adsorption of the alcohols and comparisons to HREELS experiments can be made. It might be useful to acquire RAIRS spectra of these reactions in situ under atmospheric catalytic conditions. This IR spectroscopy technique can gather vibrational spectra through multilayers of adsorbate, which is advantageous over the lack of HREELS sensitivity above monolayer coverage. The polarization dependence of the IR absorption can discriminate between adsorbed and gas or liquid phase molecules.

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APPENDIX A

Supporting Information for Chapter 4: Benzyl Alcohol Oxidation on Pd(111)



Figure A-1. Surface chemistry of benzyl alcohol on clean Pd(111), adapted from reference.¹



Figure A-2. Temperature-programmed desorption spectra of labeled (m/z = 110) and unlabeled (m/z = 108) benzyl alcohol and unlabeled benzaldehyde (m/z = 106) resulting from the same benzyl alcohol dose on ¹⁸O/Pd(111) as Figure 4-3b. The saturating dose corresponds to 0.05 ML CO, 0.017 ML C¹⁸O and 0.011 ML C¹⁶O₂, 0.017 ML C¹⁸O¹⁶O,0.005 ML C¹⁸O₂ desorption.



Figure A-3. High-resolution electron energy loss spectra comparing (a) a 1 Langmuir exposure of acrylic acid on O/Pd(111) to (b) a 2 Langmuir exposure of benzaldehyde on O/Pd(111). Spectra have been normalized to the elastic peak height and each scaled x25.



Figure A-4. High-resolution electron energy loss spectra from the same 2-Langmuir exposure of benzaldehyde on clean Pd(111) at 130 K (in Figure 4-5) and anneal briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.



Figure A-5. High-resolution electron energy loss spectra comparing Figure 4-6's 2-Langmuir exposure of benzyl alcohol-OD on O/Pd(111) (in blue) to Figure 4-5's 2-Langmuir exposure of benzaldehyde on O/Pd(111) (in red) at 130 K and annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height and scaled as indicated. δ is the symbol used for bending, either inplane (i.p.) and out-of-plane (o.o.p.), and v indicates a stretch.

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APPENDIX B

Supporting Information for Chapter 5: Oxidation of Furanic Oxygenates on O/Pd(111)



Figure B-1. Example TPD spectra for a saturating exposure of furan on clean Pd(111) at 130 K. The dose corresponds to 0.26 ML CO (m/z = 28). Experiment originally completed by Ormerod, et al. for furan at various coverages on Pd(111).¹



Figure B-2. High-resolution electron energy loss spectra of a 6 Langmuir furan exposure on clean (in black) Pd(111) (140-425 K) and O/Pd(111) (in blue). The O/Pd(111) experiment is the same as that depicted in Figure 5-2, with only a few additional temperatures shown here (140 K and 230 K).

aper priase.			
Mode	Furan	Furan clean	Furan IR
	clean	$Pd(111)^{1}$	vapor ²
	Pd(111)		
ring v(CH)	3100	3085	3140, 3167
ring v(C-O)	1700	1750	n/a
ring v(C-C)	1400	1445	n/a
v(C=C)	n.r.	n.r.	n/a
v(ring)	n.r.	1005	1384, 1491
δ(CH)	n.r.	1005	995, 1066
δ(ring)	n.r.	n/a	871
Y(CH)	750	750	n/a
Y(ring)	505, 530	540	n/a

Table B-1: Vibrational mode assignments (cm^{-1}) of furan adsorbed on O/Pd(111) compared to clean Pd(111) and in the vapor phase.

 δ =in-plane deformation v=stretch Y=wagging n.r. = not resolved n/a = not reported



Figure B-3. Temperature-programmed desorption spectra resulting from a saturating dose of furfural-d3 (C₄D₃OCHO) on (a) clean Pd(111) and (b) O/Pd(111) at 140 K. (a) Dose corresponds to 0.65 CO ML. (b) Dose corresponds to 0.75 CO ML. (c) Depiction of common m/z = 56 fragment for deuterated maleic anhydride and 2(5H)-furanone species. Peak deconvolutions were carried out to reduce contributions of the deuterated product fragments from the non-deuterated water products; D₂O's OD and DHO's OD fragment (m/z = 18) were subtracted from H₂O (m/z = 18), so the m/z = 18 signals reported are entirely due to H₂O desorption. The dotted lines below the water and hydrogen peaks are meant to guide the eye.

HREELS of Furfural

Comparisons of HREEL spectra from reactions of furfural on clean and O/Pd(111) are useful for elucidating the effects of oxygen. While TPD of furfural on clean Pd(111) has been carried out previously, vibrational spectroscopy studies in the present work are unique. At 140 K in Figure B-4, the spectra are similar between both surfaces, each with a furfural exposure of 2 Langmuir. Furfural is intact with evident ring wagging (550 cm⁻¹), C-H out-of-plane bending (750 cm⁻¹), ring stretching (900 cm⁻¹), aldehyde C-H stretching (2840 cm⁻¹), and ring C-H stretching (3075 cm⁻¹) while the aldehyde CO and ring CO stretching modes may be convolved in the 1600-1670 cm⁻¹ range. At 250 K the clean and O/Pd(111) spectra are most unique from each other, although peaks between 1000-1600cm⁻¹ are difficult to resolve in both. On O/Pd(111), strong C-H out-of-plane bending at 750 cm⁻¹ and some ring C-H stretching near 2900 cm⁻¹ signal a different intermediate. The presence of some aldehyde v(CH) near 2850 cm⁻¹ cannot be ruled out. However, a small peak at 1350 cm⁻¹, with a greater relative intensity to its clean Pd(111) counterpart, may be evidence of furoate, with this peak being assigned to v(OCO). The OCO deformation mode expected near 875 cm⁻¹ could be convolved in the shoulder in this scan. The peak at 1000 cm⁻¹ is assigned to C-H in-plane stretching, consistent with the furan ring being intact in the furoate intermediate. Unfortunately, at high coverages of multiple intermediates, it is difficult to be definitive about what is on the surface. The 1150 cm⁻¹ loss peak (small at 250 K in the clean and O/Pd spectra) is unique to the multifunctional aldehyde, i.e., it is not present in HREELS of furan alone, so we assign it to a combination of ring C-C stretching and complete ring stretching ³. Decarbonylation is evident on both surfaces by 350 K, consistent with the onset of desorption of CO from a saturated surface being < 370 K. The shift in v(CO) stretching frequency between clean and O/Pd(111) is similar to that of furan's mentioned previously (375 K in Figure 5-2). By 475 K molecular CO has desorbed from the surface, consistent with TPD peaks at 460 K on clean Pd(111)⁴ and 455 K on O/Pd(111) (Figure 5-3b); spectra look similar to the high-temperature furan results in Figure 5-2. Furan-derived decomposing carbonaceous species create stretching in the 750-840 cm⁻¹ range.



Figure B-4. High-resolution electron energy loss spectra of a high coverage 2-Langmuir furfural exposure at 140 K on clean (in black) and O/Pd(111) (in blue) and annealed briefly to the temperatures as noted. Spectra have been normalized to the elastic peak height.

Mode	2 L Furfural	2 L	Furfural IR
	clean	Furfural	Liquid ⁵
	Pd(111) 140	O/Pd(111)	_
	K	140 K	
ring v(CH)	2900-3050	2900-3050	3140
aldehyde v(CH)	2900	2840	2817
ring v(C-O)	1670	1670	n/a
aldehyde v(C=O)	1670	1670	1675, 1690
v(C=C)	n.r.	n.r.	1466, 1476
ring v(C-C)	1375	1375	n.r.
v(ring)	900	n.r.	n/a
δ(CH)	n.r.	1000	755, 770, 884
Υ (CH) out-of-plane bend	750	750	n.r.
Y(ring)	550	n.r.	n.r.
δ(ring)	n.r.	n.r.	505, 598, 630

Table B-2: Vibrational mode assignments (cm⁻¹) of furfural adsorbed on clean Pd(111), O/Pd(111), and compared to the liquid phase.

 δ =in-plane deformation v=stretch Y=wagging a=asymmetric s=symmetric n.r. = not resolved n/a = not reported



Figure B-5: Thermal desorption spectra focusing on maleic anhydride desorption that results from a saturating exposure of furan at 150 K on ¹⁸O/Pd(111) (same dose as Figure 5-1b). The dose corresponds to 0.15 ML C¹⁶O (m/z = 28), 0.15 ML C¹⁸O (m/z = 30), 0.0 ML C¹⁶O₂ (m/z = 44), 0.06 ML C¹⁶O¹⁸O (m/z = 46), and 0.02 ML C¹⁸O₂ (m/z = 48) desorption. The molecular structures of maleic anhydride drawn below the TPD are shown with orange oxygens in bold, corresponding to incorporation of a surface ¹⁸O. Its molecular desorption corresponds to m/z = 102, while the two other fragments desorbing in TPD (m/z = 54 and m/z = 56) are to the right with the arrow pointing down from the dash line in the direction of the particular fragment being represented by the mass ion.



Figure B-6. Temperature-programmed desorption spectrum resulting from a saturating dose of furfuryl alcohol on ¹⁸O/Pd(111) at 140 K, with focus on the desorption peak at 320 K. The mass labels relate as follows: furfural (m/z = 96), methylfuran (m/z = 82), $H_2^{16}O$ (m/z = 18) and $H_2^{18}O$ (m/z = 20). The furfuryl alcohol dose corresponds to 0.40 ML C¹⁶O desorption.

Methylfuran TPDs

On clean Pd(111), the decomposition of methylfuran is quite similar to that of furan, i.e., molecular desorption or decomposition to CO and H₂. In Figure B-7a methylfuran (m/z = 82) desorbs at 185 K and 295 K. Hydrogen desorbs in multiple peaks between 340-500 K and CO desorbs at 460 K. On the ¹⁸O/Pd(111) surface in Figure B-7b, methylfuran reacts to produce isotopic CO, CO₂ and H₂O. The desorption behavior of C¹⁸O¹⁶O, C¹⁸O₂ and C¹⁶O₂ above 350 K is similar to furan at high coverage (Figure 5-1b). There is no evidence for isotopic mixing or ring opening in methylfuran oxidation on Pd(111). CO₂ appears to result from surface C oxidation between 370-430 K. CO and H₂ are produced above 400 K as the result of ring decomposition.



Figure B-7: Thermal desorption spectra of methylfuran dosed at 150 K on clean and ¹⁸O/Pd(111). (a) The saturating dose on clean Pd(111) corresponds to 0.23 ML C¹⁶O desorption. (b) The saturating dose on ¹⁸O/Pd(111) corresponds to 0.14 ML C¹⁶O (m/z = 28), 0.10 ML C¹⁸O (m/z = 30), 0.001 ML C¹⁶O₂ (m/z = 44), 0.07 ML C¹⁶O¹⁸O (m/z = 46), and 0.02 ML C¹⁸O₂ (m/z = 48) desorption.

Table B-3. Comparison of adsorption energies (ΔE_{ads}) for furanic species calculated via the Redhead equation (1) for TPD experiments and DFT by Varotnikov, et al.⁶ Both the Pd(111) and O/Pd(111) surfaces are considered.

	experimental	TPD	TPD Pd(111)	DFTPd(111)	conformation/u
	coverage	O/Pd(111)	(eV)	(eV)	nit cell size
		(eV)			
furan	low	-0.77 ± 0.15		-(1.53-1.58)	flat/4 x 4
				-0.58	upright/4 x 4
				-1.03	bent/4 x 4
				-(1.35-1.39)	flat/3 x 3
				-0.55	upright/3 x 3
				-0.93	bent/3 x 3
	high	-0.48 ± 0.10		-(1.04-1.32)	flat/2 x 2
		-0.66 ± 0.13	-0.44 ± 0.09	-0.62	upright/2 x 2
		-0.88 ± 0.18	-0.73 ± 0.15	-0.93	bent/2 x 2
furfural	low			-(1.71-1.83)	flat/4 x 4
				-0.84	upright/4 x 4
				-(0.84-1.50)	bent/4 x 4
	high	-0.56 ± 0.11	-0.65 ± 0.13		
		-0.64 ± 0.13	-0.91 ± 0.18		
		-0.98 ± 0.20	-0.98 ± 0.20		
furfuryl	low			-(1.86-2.04)	flat/4 x 4
alcohol				-1.54	bent/4 x 4
	high	-0.60 ± 0.12	-0.64 ± 0.13		
		-0.65 ± 0.13	-0.70 ± 0.14		
methylfuran	low			-1.87	flat/4 x 4
	high	-0.51 ± 0.10	-0.48 ± 0.10		
		-0.73 ± 0.15	-0.77 ± 0.15		

Equation (1) was utilized to calculate adsorption energies from TPD peak temperatures.⁷ $\Delta E_{ads}(eV) = -0.0026T_{peak}/K \pm 20\% \qquad (1)$

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