THE INVESTIGATION OF THE ADSORPTION AND REACTION CHARACTERISTICS OF PALLADIUM OXIDE SURFACES

By

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To my family
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The adsorption and reaction of various molecules have been studied experimentally on oxidized Pd(111) surface under ultra-high vacuum conditions. Hydrogen, methanol, methane, ethane, propane, n-butane and n-pentane have been studied extensively as well as isotopes of hydrogen, propane and n-butane on the palladium oxide surfaces. Using UHV measurement techniques, the kinetics and physics of the interactions between these molecules and the PdO surface has been investigated.

When the hydrogen molecule is adsorbed on PdO(101) on cus-Pd site at low temperatures, it dissociates. During the temperature programmed desorption (TPD) experiment, it desorbs molecularly and recombinatively, additionally, it reacts with the surface and produces water. However, when deuterium is adsorbed under the same experimental conditions, the reaction products decrease significantly due to the effect of tunneling in hydrogen reactivity.

Methanol molecule is also adsorbed on the cus-Pd site as methoxy and reacts during TPD producing hydrogen, formaldehyde, methyl formate, water and carbon
dioxide depending on the coverage. As the coverage increases, the coupling reaction takes place more dominantly.

Methane, ethane, propane, n-butane and n-pentane (alkanes studied) are also adsorbed on to the cus-Pd site creating alkane sigma complexes. This alkane sigma complex results in a more strongly bound adsorbed species and it is the precursor for the reaction of the alkanes longer than ethane. Although methane and ethane both form the sigma complex, the kinetics favor desorption over reaction. Since the alkanes that react have both primary and secondary C-H bonds, selectivity analysis towards these bonds during the reaction on PdO(101) surface has also been investigated. The selectivity of C-H bond cleavage favors the primary bond in the case of propane activation on PdO(101) surface. n-Butane activation does not have preference to primary or secondary C-H bonds at high coverages, however at the limit of zero coverage, the reaction occur through the primary bond cleavage.
CHAPTER 1
INTRODUCTION

1.1 Motivation

Understanding the surface chemistry of late transition-metal (TM) oxides is central to many applications of oxidation catalysis. Oxides of late transition metals can be quite effective in promoting complete oxidation reactions due, at least in part, to the greater ease in reducing these oxides as compared with early TM oxides. Palladium oxide (PdO) occupies a special position among the late TM oxides due to its exceptionally high activity toward the complete oxidation of methane. In fact, the formation of bulk-like PdO is known to be responsible for the favorable performance of supported Pd catalysts in fuel-lean applications of methane oxidation[1]. Additionally, our recent findings show that PdO(101) can be very active towards alkanes with longer chain lengths. The high activity of PdO as a complete oxidation catalyst certainly motivates detailed investigations of the chemistry of PdO surfaces. More generally, clarifying the chemical properties of late TM oxides is important for understanding the catalytic behavior of transition metals in oxidizing environments, which includes applications of catalytic combustion, fuel cell catalysis, and pollution control systems.

Understanding the details of alkane activation on metal-based catalysts is especially important in advancing the efficiency and cleanliness of the applications of catalytic combustion along with transformation of saturated hydrocarbons to more useful forms. Since the initial C-H bond cleavage is the rate limiting step in this activation, respectable number [2-9] of studies has investigated the adsorption and activation of alkanes on transition metal surfaces[10]. However, relatively little work has been done on TM oxides since it has been expected that TM oxides would interact weakly with
alkanes. However, we investigated the adsorption of alkanes on palladium oxide and discovered that they have strong interactions with the oxide surface due to dative bonding and the creation of alkane σ-complexes with the oxide surface. We investigated the chemistry of alkanes with the carbon chains from C1 to C5. During our investigation it was determined that alkanes with chain lengths equal or longer than propane dissociate on the surface and react to produce CO$_2$ and H$_2$O. The alkane σ-complex was determined to be the precursor for the dissociation of the alkanes longer than C2 on the palladium oxide surface.

Investigating oxide chemistry under actual reaction conditions is complex and hard to analyze. In order to simplify the analysis, we utilize an ultra-high vacuum (UHV) environment that can isolate this complex process into more manageable steps. By studying the complex system in UHV, atomically clean surfaces can be prepared and maintained for the duration of the experiment. Under these conditions, studies can be carried out which focus on a particular step of the complex reactions or on a particular reactant. We utilize a variety of surfaces and reaction analysis methods under an UHV environment to evaluate binding energies, different product formation and reaction pathways on a PdO(101) thin film grown on a Pd(111) surface.

Significant amount of studies has been carried out on establishing high oxygen coverages on Pd and other transition metal surfaces under UHV conditions. Specifically for Pd, previous studies [11; 12] show that there are multiple oxidation phases of palladium under UHV conditions, however, for almost all of the tested adsorbates, the bulk-like PdO(101) oxide is the most reactive phase. For the experiment in this dissertation we exposed a Pd(111) sample to an atomic oxygen beam created by an RF
plasma source in order to oxidize the surface. This method has been proven to be very effective at creating thick, well ordered oxide films, which provides us an opportunity to study chemistry with minimal reaction attributed to surface defects.

Using an atomic oxygen beam is not the only way to oxidize a TM surface under an UHV environment. The simplest way of oxidizing a surface is to utilize a molecular oxygen beam, however this can only produce low oxygen coverages typically on the order of 0.25 monolayer (ML) on low index Pd(111) surface[13], while still maintaining an UHV environment. With this method, the coverage can be increased to 0.37ML when the exposure temperature is increased above 500K however, aggressive oxidants such as NO$_2$ and O$_3$ need to be used to produce higher oxygen coverages than those obtainable by molecular oxygen[13; 14]. In order to reach higher coverages than the ones that can be reached by aggressive oxidants, high pressure cells or atomic oxygen beams can be used[15; 16]. With an atomic oxygen beam, Pd surface can be oxidized in a control manor to produce oxygen surface coverages that were not previously possible, this results in studies being carried out under more real-like conditions.

The oxidation mechanism of a Pd(111) surface involves multiple steps and surface transformations. At temperatures below 80 K, only molecularly adsorbed oxygen is present on the surface. At temperatures between 80 K and 200 K oxygen dissociates and molecularly chemisorbs on Pd(111)[17]. By using the aggressive techniques mentioned above higher atomic oxygen coverages can be obtained leading to surface oxide, and eventually with increasing oxygen coverages, bulk like oxide phases develop[13; 16; 18].
As mentioned briefly above, previous studies[11] from our lab established that a high quality PdO(101) thin film can be grown on Pd(111) in UHV by oxidizing the metal at 500 K using an oxygen atom beam and then annealing to 675 K. Using experimental and simulated LEED patterns, it has been concluded that the surface structure of the PdO thin film deviates minimally from bulk-terminated PdO(101). With temperature programmed desorption (TPD) experiments, it has also been demonstrated that the PdO(101) thin film on Pd(111) is terminated by the stoichiometric surface in which half of the Pd atoms are coordinatively unsaturated (cus), corresponding to a cus-Pd atom density equal to about 35% of the surface density of Pd(111). The ability to generate a well-defined PdO(101) surface in UHV should provide new opportunities for conducting model surface science studies of PdO. Particularly, studies towards clarifying the reactivity of PdO(101) with respect to the species, which are important in commercial applications of Pd catalysis.

1.2 Ultra High Vacuum

Both the equipment employed and the experiments performed require very little to no interference from background gasses, therefore an ultra-high vacuum (UHV) chamber was utilized in order to perform the experiments mentioned in this dissertation. The UHV chambers utilized have a base pressures in the order of \(10^{-10}\) to \(10^{-11}\) torr, which require a series of pumps to be used continuously in order to reach and maintain these required pressures. As a first level of pumping, mechanical pumps which are oil-sealed rotary vane types are used. The main purpose of these mechanical pumps is rough pumping of the chamber volume and for lowering the operational pressure for turbomolecular or diffusion pumps to operate efficiently. Backed by the mechanical pump, turbomolecular pumps, which are molecular turbines that compresses gas by
momentum transfer,[19] can lower the chamber pressure down to obtain a $10^{-7} - 10^{-8}$ torr level. The diffusion pump, which operates via momentum transfer to the gas upon collision with its vapor jet stream[19], can also lower the chamber pressure down to a similar pressure range. Although these pumps can hold the chamber at UHV levels, the initial pump down also requires heating up the chamber walls for approximately two days in order to speed up the desorption of water molecules from the chamber walls. When the chamber cools down, UHV pressures of $10^{-10} - 10^{-11}$ torr can be obtained. Additional pumping is also required in order to have better control of the background gasses and to maintain UHV without turbomolecular pumps. These types of pumps are generalized as getter pumps and operate only in HV or UHV pressures. Getter style pumps operate by binding gas molecules to a surface[19] and therefore removing them from the chamber background. The sticking of the gas molecule to a surface can be achieved by cooling the surface (cryogenic pump), activating the gas molecule with a reactive metal (titanium sublimation pump (TSP)) or ionizing the gas (ion pump). Since their pumping speed varies with respect to the gasses that are being pumped, it is common to use these pumps in conjunction to each other in order to create uniform pumping of the background gasses in the chamber. The chamber utilized in these studies uses a TSP which pumps carbon oxides, oxygen and water at room temperature and is contained within a cryogenic housing which increases the sticking coefficients of hydrogen and nitrogen[19]. The UHV pressures enable sensitive measurement techniques to be employed in a clean and controlled environment with specialized equipment.
1.3 UHV Chamber and Equipment

In figure 1-1, the UHV chamber with its two levels separated is presented. This figure shows the equipment used during surface preparation and experimental measurement techniques. When a sample is to be experimented with, first its surface needs to be free of contaminants. In order to achieve cleanliness required for the UHV experiments, an ion source is used first. The Specs PU-IQE 11/35 model ion source that is connected to ultra-high purity Argon is used to knock off all of the unwanted adsorbates from the surface, this is known as ion bombardment. The ion source first charges the Ar gas and then accelerates the gas in a directed beam onto the sample surface. This creates a direct collision with the atoms on the sample surface and knocks them off the surface with direct momentum transfer. This can also damage the surface of the sample but it can rearrange and heal itself by annealing at high temperatures (1100K for Pd). Although Ar sputtering can clean the sample surface by itself, the annealing procedure puts the sample mount through unwanted stress. Therefore, oxidation of carbon species on the surface is used with the sputtering during the cleaning process. Desorption of the oxidized species occur at lower temperatures than the annealing after Ar sputtering, therefore the lifespan of the welds that hold the sample in place is prolonged. The oxidation of the sample surface is achieved by oxygen atoms created with Oxford Scientific RF plasma source coupled with Advanced Energy RFX-600 RF generator. The plasma source is also utilized for sample preparation during experiments if the oxide of the sample, such as PdO, is wanted. Additionally, a calibrated doser and metal evaporator may also be used in the sample preparation. The calibrated doser has its own pressure cell that can be controlled sensitively and a limited conductance to the UHV chamber that results in reproducible
gas delivery to the sample surface. If a metal is required to be delivered onto the sample, the metal evaporator is used. The evaporator uses a tungsten filament covered with the desired metal to be evaporated. By heating the tungsten filament, it is possible to evaporate the desired metal and thus exposing the sample surface to a beam of metal atoms. After sample preparation, the last stage of the experiment, the measurement step will take place. The details of the measurement techniques will be explained in the next section. Our system has a Specs EA10 hemispherical analyzer that can measure the intensity of charged particles. These charged particles can be photons excited by the Specs XR-50 X-Ray source or electrons excited by Specs PU-EQ 22 electron source or ions created by the ion source. Another analysis is to measure desorption species with the Hiden quadruple mass spectrometer. Additionally, surface structures of the prepared sample can be checked by Specs LEED 1000-A.

1.4 Experimental Techniques

1.4.1 Temperature Programmed Desorption and Reaction Spectroscopy

Our UHV system contains a variety of different surface science measurement techniques. The technique that is used the most is called temperature programmed desorption (TPD) or temperature programmed reaction spectrometry (TPRS). In this technique, upon preparation of the surface, the temperature of the sample is increased with a known rate, 1 K/s in every experiment reported in this dissertation, and the species that are desorbing from the surface are monitored by the mass spectrometer. If the monitored species are products of a surface reaction then this kind of spectra is called TPRS, if the species only desorb without reaction, this type of spectra is called TPD. Figure 1-2 shows an example of a TPD spectrum, in this case it is propane desorption from PdO(101) surface. When plotted, a TPD spectrum has temperature on
the X-axis and the rate of desorption on the Y-axis. The rate of desorption increases with increasing temperature and decreases as the species at that state runs out resulting in peaks in the TPD spectrum. The temperatures of the desorption spectra as well as its shape carries valuable information. Simply, as the binding energy of a molecule or an atom increases, the energy required for its desorption also increases therefore requiring higher temperatures to desorb. In figure 1-2, the species desorbing around 195 K is more strongly bound than the species desorbing around 130 K. More detailed explanation of alkane desorption spectra will be given in following chapters. It is also possible to further investigate the TPD spectra and actually estimate the kinetic parameters like binding energies. One method that is employed for this purpose is called Redhead’s analysis of TPD. Redhead’s analysis assumes that desorption process kinetics follow a power law given as;

$$\frac{r_d}{N_s} = -\frac{d\theta_A}{dt} = k_0\theta_A^n\exp\left(-\frac{E_A}{kT}\right)$$  (1-1)

Where $r_d$ is the rate of desorption, $N_s$ is the concentration of surface sites, $\theta_A$ is the coverage, $t$ is time, $n$ is the order of the desorption, $k_0$ is the pre-exponential factor, $E_A$ is the activation energy, $k$ is the Boltzmann’s constant and $T$ is the temperature. The derivation assumes constant heating rate and also direct measurement of $r_d$ from the experiment, both are valid for the experimental setup that was used[20]. By differentiating the power law expression and adding $\beta$ as heating rate, it is possible to derive the following equation;

$$k_0n\theta_A^{n-1}\exp\left(-\frac{E_A}{kT}\right) = \beta E_A/kT^2$$  (1-2)

Where $\theta_A$ is the coverage at the peak of the spectrum and $T$ is the peak temperature. With this equation, it is possible to calculate desorption energies from TPD spectra
given that the coverage is estimated. Additionally, this equation shows how the TPD spectra would behave with respect to initial coverage of the surface given that the desorption order is known. If the desorption is categorized as first order desorption, the TPD peak would increase with increasing coverage without any effect on the peak temperature, however for second order desorption, the peak temperature would shift with a change in coverage.

Other information that can be gathered from TPD is the surface coverage of the desorption species. Since the desorption rate is directly related to the initial coverage, one can easily correlate a spectrum with a known coverage to a spectrum with an unknown coverage and calculate the unknown surface coverage. Furthermore, surfaces with known coverages can be prepared with recipes found in the literature. The most common method to determine surface coverage is to adjust the surface temperature to limit the type of adsorption sites available for that species, therefore estimating the fraction of the sites as the coverage of the adsorbed species. For example, it is known that under an UHV environment oxygen adsorption on Pd(111) will terminate at 0.25ML at room temperature, as a result, the area under the desorption spectrum of oxygen adsorbed on Pd(111) at room temperature can directly be correlated to a coverage of 0.25ML. With the calculation correlation of the mass spec signal to the surface coverage, other oxygen spectra can be converted into surface coverage as well.

1.4.2 Beam Reflectivity Measurements

The beam reflectivity measurements (also called King & Wells measurements) are carried out by measuring the partial pressure of the residual exposure gas after it collides with the sample surface. In our study, the Pd(111) sample was placed in front of a calibrated doser that collimates the incident beam. The distance between the doser
and the sample is about 5mm and there is a shutter attached to the doser that can 
precisely start and stop the exposure. Quadruple mass spectrometer is used to 
measure background partial pressure of butane in these beam reflectivity 
measurements. The initial signal drop right after the shutter is opened is directly 
proportional to the initial sticking probability at that temperature and on the surface 
examined. As more of the surface sites are occupied with adsorbed molecules, the 
sticking probability decreases and finally plateaus out when there is no more adsorption. 
With the information this set of experiments give, it is possible to obtain the initial 
sticking probability of the gas that is introduced to the given surface at the given 
temperature. From these experiments, it is possible to calculate kinetic parameters 
other than the initial sticking probability such as dissociation energy and pre-factors.

1.4.3 X-Ray Photoelectron Spectroscopy

Another analysis method that is utilized to understand surface phenomenon is 
the X-ray photoelectron spectroscopy (XPS). Surface analysis by XPS is accomplished 
by irradiating the sample with mono-energetic soft X-rays and analyzing the energy of 
the emitted electrons\[21]. The x-rays used in our system are MgKα with an energy of 
1253.6 eV. This kind of energy limits the penetration of the photons to the order of 1-10 
micrometers. The incoming energy excites electrons from the surface and these 
electrons are collected and analyzed by the hemispherical energy analyzer to create a 
spectrum. The emitted electrons kinetic energy can be calculated with this formula;

\[ KE = h\nu - BE - \phi_s \]  

(1-3)

Where \( KE \) is the kinetic energy of the electron, \( h\nu \) is the energy of the photon, \( BE \) is the 
binding energy of the atomic orbital from which the electron originates and \( \phi_s \) is the
work function of the spectrometer[21]. The energy analyzer measures the kinetic energy of the emitted electrons, and since the rest of the variables in equation #.# are known, it is trivial to calculate binding energies directly from the measured spectra. However, after the sample is energized, in addition to photoelectrons, Auger electrons are also emitted due to energetic relaxation after the photoemission. The energy analyzer window is operated in the photoelectron range for the XPS, and can be changed with respect to the resolution desired. The smaller the window, the faster the scan is completed and additionally the total number of scans can also change the resolution of the spectrum greatly. The binding energy of the electron can be assumed to be the ionization energy of that atom, therefore when the electronic structure of an atom is affected, so is its XPS signal. For example, palladium XPS signal shifts to a higher binding energy when it is oxidized and PdO is created.

1.4.4 Auger Electron Spectroscopy

As it was mentioned above, after the photoelectron is emitted, an auger electron is also emitted due to relaxation. The same energy analyzer used for the XPS can also be used to conduct Auger electron spectroscopy (AES). To allow Auger electrons to travel into the analyzer, the pass energy is set to a lower value than the value for XPS. Since Auger electron energies does not depend on the initial beam for excitation, almost any kind of energy source with energies around 3-5 keV can be used for AES[21]. Since the energies of Auger electrons are lower than photoelectrons, the mean free path is also shorter, and therefore AES is more surface sensitive than XPS with the equipment we utilize in the lab.
1.4.5 Ion Scattering Spectroscopy

Another surface technique used in the lab is ion scattering spectroscopy (ISS). In this technique, ions with a set kinetic energy collide with the sample and the scattered ions are collected and measured with the energy analyzer[21]. The kinetic energies of the scattered ions differ due to the change in energy loss during collision with respect to the mass of the atom collided. With ISS, it is possible to determine the surface composition of a sample given that the atoms of the surface differ in mass, for example previous studies from our lab determined the oxygen concentration of the palladium oxide surface[11].

1.4.6 Low Energy Electron Diffraction

In addition to all these methods, we also utilize low energy electron diffraction (LEED) to determine the surface structures. LEED optics consists of an electron gun located in the middle of a fluorescent screen. The electrons are sent to the sample as a monochromatic beam and only the elastic scatters are accepted through the filters back on to the screen. If the sample has a well ordered crystalline surface, this creates an image represented with diffraction spots. An example of this can be seen in previous studies[11], where LEED images provides vital information on the surface structures of different oxidation states of palladium oxide.
Figure 1-1. The top view of the first and third level of the UHV chamber.
Figure 1-2. Example TPD spectra
CHAPTER 2
STRONG KINETIC ISOTOPE EFFECT IN THE DISSOCIATIVE CHEMISORPTION OF H₂ ON A PDO(101) THIN FILM

2.1 Motivation of Hydrogen Reactivity

Understanding the surface chemistry of late transition metal (TM) oxides is central to many applications of oxidation catalysis. Oxides of late transition metals can be quite effective in promoting complete oxidation reactions due, at least in part, to the greater ease in reducing these oxides compared with early TM oxides. Palladium oxide (PdO) occupies a special position among the late TM oxides due to its exceptionally high activity toward the complete oxidation of methane. In fact, the formation of bulk-like PdO is known to be responsible for the favorable performance of supported Pd catalysts in fuel-lean applications of methane oxidation.\[1-9; 22-24\] The high activity of PdO as a complete oxidation catalyst certainly motivates detailed investigations of the chemistry of PdO surfaces. More generally, clarifying the chemical properties of late TM oxides is important for understanding the catalytic behavior of transition metals in oxidizing environments, which includes applications of catalytic combustion, fuel cell catalysis and pollution control systems.

The interactions of H₂ with TM oxides are both scientifically interesting and important in several technological applications. The simplicity of H₂ makes it an ideal molecule for investigating atomistic details of σ-bond activation and subsequent chemical reactions on TM oxide surfaces. Furthermore, hydrogen oxidation is ubiquitous in the catalytic oxidation of hydrocarbons and other organic molecules, and is
a critical reaction in H₂ and methanol-powered proton-exchange-membrane fuel cells. In the present study, we examined the interactions of H₂ and D₂ with PdO(101) both experimentally and computationally, focusing particularly on characterizing the mechanisms for dissociative chemisorption.

Prior studies with RuO₂(110) provide key insights for understanding the basic mechanisms for H₂ adsorption and oxidation on late TM oxide surfaces.[25-29] Through a combination of UHV experiments and density functional theory (DFT) calculations, Wang et al. showed that H₂ can chemisorb molecularly on RuO₂(110) by forming a dative bond with a coordinatively unsaturated (cus) Ru atom.[25] The bonding in this adsorbed state is analogous to that in mononuclear H₂ σ-complexes that are known in organometallic chemistry.[30] In an H₂ σ-complex, the H₂ molecule acts as an electron donor and coordinates with the metal center of a TM compound, typically weakening the H-H intramolecular bond. The first studies of the H₂/RuO₂(110) system provide evidence that the molecularly adsorbed state serves as a necessary precursor to the dissociation of H₂ on RuO₂(110).[25-27] These workers report that the adsorbed H₂ precursor initially reacts with so-called bridging oxygen atoms (O₉br) to produce dihydride species (2H-O₉br) which subsequently decompose to yield bridging hydroxyl species (H-O₉br). The bridging oxygen atoms on RuO₂(110) have single coordination vacancies and form rows next to the cus-Ru rows. Key conclusions of these studies are that H₂ activation on RuO₂(110) occurs by a precursor-mediated mechanism and that cus-Ru sites must be available for this reaction to occur.

Subsequent investigations reveal additional details of the interactions between H₂ and RuO₂(110). In particular, Knapp et al. present evidence that gaseous H₂
molecules can dissociate directly on bridging oxygen atoms of RuO$_2$(110), rather than first chemisorbing molecularly on cus-Ru sites.[28; 29] Since the direct reaction is activated slightly relative to the gas-phase zero, this dissociation pathway should become more important at higher temperature, particularly when cus-Ru sites are occupied with adsorbed species. Studies by Knapp et al. also demonstrate that O$_{br}$ sites are needed for H$_2$ dissociation by both the precursor-mediated and direct pathways.[28; 29]

The PdO(101) surface shares common characteristics with RuO$_2$(110) with respect to molecule binding and reactions. Half of the surface Pd and O atoms of PdO(101) are coordinatively unsaturated and dominate the chemisorptive and reactive properties of this surface.[31-34] For example, small alkanes bind relatively strongly on PdO(101) by forming $\sigma$-complexes at cus-Pd sites,[35] and the resulting adsorbed states can act as precursors to alkane dissociation. For propane, the adsorbed $\sigma$-complex undergoes facile C-H bond cleavage at temperatures below 200 K.[32] A recent computational study by Blanco-Rey et al.[36] predicts that H$_2$ also forms $\sigma$-complexes on cus-Pd sites of PdO(101), and that dissociation can occur by multiple pathways involving hydrogen transfer to cus-O atoms. Overall, the results of prior studies demonstrate that adsorbed $\sigma$-complexes play a key role in the initial activation of saturated molecules on PdO(101) and RuO$_2$(110).

In the present study, we examined the dissociative chemisorption and oxidation of H$_2$ and D$_2$ on a PdO(101) thin film using temperature programmed desorption (TPD) and DFT calculations. We find that H$_2$ dissociation is highly facile on PdO(101), and occurs by a precursor-mediated mechanism wherein an adsorbed H$_2$ $\sigma$-complex serves
as the precursor to dissociation. We observe a strong kinetic isotope effect (KIE) for the dissociation reaction, with D$_2$ dissociating to a much lesser extent than H$_2$ during TPD. According to DFT, differences in zero-point energies are not responsible for the large KIE that we observe for the precursor-mediated pathway. We present evidence that H$_2$ dissociation on PdO(101) occurs predominantly by quantum-mechanical tunneling at low temperature, and that differences in tunneling rates produce large differences in the dissociation probabilities of H$_2$ vs. D$_2$.

2.2 Experimental Details

Previous studies[37; 38] provide details of the three-level UHV chamber utilized for the present experiments. The Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder that is held in thermal contact with a liquid nitrogen cooled reservoir. By bubbling gaseous helium through the liquid nitrogen reservoir, we obtained sample temperatures that are 10-15 K lower than previously achieved in our system. With the improved cooling, we can better resolve a TPD feature near 100 K that arises from the molecular desorption of H$_2$ (D$_2$) from the PdO(101) thin film. A type K thermocouple spot-welded to the backside of the crystal allows sample temperature measurements. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports maintaining or linearly ramping the sample temperature from 75 K to 1250 K.

Initially, sample cleaning consisted of sputtering with 600 eV Ar$^+$ ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to 923 K to desorb oxygen
and carbon oxides. As discussed previously,[11] we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in preparing the PdO(101) thin films used in this study. We considered the Pd(111) sample to be clean when we could no longer detect contaminants with X-ray photoelectron spectroscopy (XPS), obtained sharp low energy electron diffraction (LEED) patterns consistent with the Pd(111) surface, and did not detect CO production during flash desorption after oxygen adsorption.

A two-stage differentially-pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system.[37; 38] To produce a PdO(101) thin film, we expose a Pd(111) sample held at 500 K to an ~12 ML dose of gaseous oxygen atoms supplied in a beam, where we define 1 ML as equal to the Pd(111) surface atom density of $1.53 \times 10^{15}$ cm$^{-2}$. This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains ~3.0 ML of oxygen atoms and is about 12 Å thick.[12; 39] The structure of the PdO(101) surface is discussed in detail below.

We delivered H$_2$ (BOC 99.999%) and D$_2$ (Sigma-Aldrich 99.96%) to the sample surface using a calibrated beam doser with the sample located about 50 mm from the end of the doser to ensure uniform impingement of the gases across the surface. Due to the large sample-doser separation, the direct flux was only about 2.5 times higher than the background flux. After the H$_2$ (D$_2$) exposures, we collected TPD spectra by positioning the sample in front of a shielded mass spectrometer at a distance of about 10 mm and then heating at a constant rate of 1 K s$^{-1}$ until the sample temperature
reached 923 K. Because the PdO film decomposes when heated to 923 K, it was necessary to prepare a fresh PdO thin film for each adsorption/reaction experiment.

We estimate hydrogen and deuterium coverages by scaling integrated desorption spectra with TPD spectra obtained from saturated layers of atomic H or D prepared on Pd(111) at 75 K using H$_2$ or D$_2$. We assume that the H(D) atom layers saturate at a coverage of 1.0 ML.[40] Hydrogen and deuterium react with the PdO(101) surface to produce water during temperature programmed reaction spectroscopy (TPRS) experiments. To estimate the H$_2$O and D$_2$O desorption yields, we collected water TPD spectra from Pd(111) and assumed that a monolayer of water saturates at 0.66 ML on the metal surface.[41] We have previously used this approach to estimate H$_2$O coverages in a study of water adsorption on PdO(101).[12]

2.3 Experimental Results

2.3.1 Structure of the PdO(101) Thin Film on Pd(111)

Figure 2-1 depicts the structure of the stoichiometric PdO(101) surface that we examined in this study. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell of dimensions $a = 3.04$ Å and $b = 6.14$ Å, where the $a$ and $b$ lattice vectors coincide with the [010] and [101] directions of the PdO crystal, respectively. The PdO(101)-PdO surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the $a$ direction shown in Fig. 2-1. Thus, half of the surface O and Pd atoms are coordinatively unsaturated (cus) and likely to be more active than the fourfold coordinated atoms for binding adsorbed molecules. The areal density of each type of coordinatively-distinct atom of the PdO(101) surface is equal to 35% of the atomic
density of the Pd(111) surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML (monolayer), and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms. Given that the film contains ~3.0 ML of oxygen atoms, we estimate that the PdO(101) film on Pd(111) consists of between four and five layers and has a total thickness of ~12 Å. In a prior study,[11] we found that the PdO(101) structure aligns with the close-packed directions of the Pd(111) substrate, and would expand by 0.46% and 3.4% in the a and b directions to achieve commensurability with the metal substrate, which corresponds to unit cell dimensions of $a = 3.06 \, \text{Å}$ and $b = 6.35 \, \text{Å}$.

### 2.3.2 TPD Spectra as a Function of H₂ Coverage on PdO(101)

Figure 2-2 shows H₂ and H₂O TPD spectra obtained after exposing a PdO(101) thin film to various amounts of H₂ at a surface temperature of 75 K. Most of the hydrogen reacts with the surface to produce H₂O during TPD, while the remainder evolves as H₂ in multiple desorption peaks. The H₂O yield is about 76% of the total product yield, and the fractional yield of H₂O is nearly independent of the initial H₂ exposure. The maximum yield of desorbing species (H₂O + H₂) is equal to 0.33 ML of H₂, which corresponds to nearly one H₂ molecule per cus-Pd (or O) atom.

The reaction of hydrogen with PdO(101) produces multiple features in the H₂O TPD spectra. Most of the water desorbs in the sharp $\alpha_1$ peak that shifts from 350 to 337 K as the H₂O yield increases to its maximum value of 0.25 ML. The H₂O TPD spectra also exhibit broad features ($\alpha_2$ and $\alpha_3$) centered at about 420 and 540 K. The $\alpha_2$ feature overlaps the $\alpha_1$ peak, and extends from about 360 to 500 K, while the small $\alpha_3$ peak persists from ~500 to 700 K. Only about 0.03 ML of H₂O desorbs in the $\alpha_3$ feature. Our prior study of water adsorption on PdO(101)[33] helps to clarify the origins of the H₂O TPD features observed in the present work. In that study, we found that water desorbs
in a peak at 350 K for initial H$_2$O coverages below 0.175 ML, and that a second TPD feature at about 320 K emerges for coverages between 0.175 and 0.35 ML. According to DFT, the TPD peaks at 320 and 350 K originate from H$_2$O molecules that are chemisorbed on cus-Pd sites. The $\alpha_1$ TPD peak observed in the present study is thus consistent with desorption-limited water, implying that reactions between hydrogen and the oxide produce H$_2$O at relatively low temperature. Also, we previously observed water desorption at temperatures between 500 to 700 K after adsorbing H$_2$O on PdO(101), and attributed this feature to a small amount of water desorbing from surface defect sites.[33]

Contrary to the $\alpha_1$ and $\alpha_3$ peaks, a distinct $\alpha_2$ feature is not evident in TPD spectra obtained after adsorbing H$_2$O on PdO(101). One possibility is that the $\alpha_2$ feature originates from a reaction-limited process such as the disproportionation of hydroxyl groups (O$_{\text{cus}}$-H). If this is true, then the TPD data implies that multiple pathways for water production are available; a low-energy pathway(s) produces the desorption-limited water ($\alpha_1$ peak), while a higher energy pathway(s) causes water to evolve in the $\alpha_2$ peak. This situation is analogous to the behavior seen on RuO$_2$(110) when both on-top and bridging oxygen atoms are available for reaction with hydrogen.[27; 29] However, another possibility is that a fraction of the H$_2$O molecules bind strongly to oxygen vacancies or other reduced sites that result when H$_2$ molecules reduce the PdO surface, and ultimately desorb in the $\alpha_2$ peak.

The H$_2$ TPD spectra exhibit two main features centered at temperatures near 100 and 300 K, respectively. The high temperature feature has a complex shape that is indicative of multiple pathways for H$_2$ desorption. At low coverages, the maximum of the
high temperature feature is centered at ~305 K, while a new feature appears to emerge at ~260 K as the initial H₂ coverage increases. To clarify the origin of the high temperature feature(s), we obtained TPD spectra after co-adsorbing H₂ and D₂ on PdO(101). We observe substantial HD evolution only in the high temperature feature, and hence conclude that this TPD feature results from the recombinative desorption of atomic hydrogen. Studies of the adsorption of H₂ on RuO₂(110) also report an H₂ TPD feature near 300 K. While different interpretations have been offered, Knapp et al. present compelling evidence that the high temperature H₂ feature originates from the recombination of H atoms adsorbed on small metallic domains that exist on partially-reduced RuO₂(110) surfaces. As elaborated below, the high temperature H₂ feature observed in the present study also appears to be associated with defect sites within the PdO(101) thin film.

The low temperature H₂ TPD feature becomes evident only at high initial H₂ coverages, and shifts from about 115 to 93 K as the H₂ coverage approaches saturation. We attribute this TPD feature to the desorption of molecularly chemisorbed H₂. Experiments with co-adsorbed H₂ and D₂ support this assignment as they reveal negligible HD evolution in the low temperature TPD peak in contrast to the isotopic scrambling observed in the high temperature peak. Also, DFT calculations predict relatively strong binding of H₂ on cus-Pd atoms of the PdO(101) surface. As discussed below, the zero-point corrected binding energy of chemisorbed H₂ on PdO(101) agrees well with the value estimated from the TPD data. Finally, experimental and computational studies of H₂ adsorption on RuO₂(110) show that H₂ also chemisorbs
strongly on cus-Ru atoms, and desorbs during TPD at temperatures near 100 K.[25; 26; 29]

2.3.3 Reactivity of $D_2$ on PdO(101)

Experiments with $D_2$ reveal a strong kinetic isotope effect in the dissociation of dihydrogen on PdO(101). Figure 2-3 shows $D_2$ and $D_2O$ TPD spectra obtained after adsorbing various amounts of $D_2$ on the PdO(101) thin film at a surface temperature of 75 K. The $D_2$ and $D_2O$ TPD data are qualitatively similar to the TPD data obtained after $H_2$ adsorption in that similar desorption features appear in both sets of data; however, the product yields change significantly upon isotopic substitution. The most noticeable difference is that significantly more $D_2$ desorbs in the low temperature peak compared with $H_2$. We estimate that the desorption yield of the low temperature $D_2$ is about 67% of the total desorption yield ($D_2 + D_2O$) at saturation of the $D_2$ layer. The increase in the low temperature $D_2$ yield, relative to the $H_2$ data, is accompanied by a decrease in the $D_2O$ yield to about 19% of the total desorption yield, indicating a relationship between molecularly chemisorbed $H_2$ ($D_2$) and water production. Finally, we note that the maximum product yield corresponds to a total $D_2$ coverage of about 0.36 ML, which agrees well with the saturation coverage of $H_2$ on PdO(101) and is equivalent to approximately one $D_2$ molecule per cus-Pd atom.

We interpret the difference in product yields for $H_2$ vs. $D_2$ within the context of a precursor-mediated mechanism for $H_2$ ($D_2$) dissociation. We present further evidence that this mechanism is operable for the $H_2/PdO(101)$ system in the sections that follow. In the precursor-mediated mechanism, the molecularly chemisorbed state serves as the precursor for $H_2$ dissociation, and a kinetic competition between desorption and dissociation of the molecular precursor determines the net rate of dissociation. Within
this context, the yield data shows that the dissociation of chemisorbed H\(_2\) is strongly favored over desorption, but replacing H\(_2\) with D\(_2\) causes desorption to become dominant over dissociation. This difference reveals that kinetic isotope effects (KIE) strongly influence the relative rates of dissociation vs. desorption of the molecularly chemisorbed species, and indeed represents a significant change in the kinetic branching ratio. We explore the origin of the KIE in more detail in the computational section of this paper.

### 2.3.4 Desorption of Molecularly Chemisorbed H\(_2\) and D\(_2\)

The TPD data reveals that isotopic substitution influences the kinetics of H\(_2\) desorption in addition to H\(_2\) dissociation. For example, the high temperature desorption feature is centered at \(~260\) K for H\(_2\), but is centered at about \(305\) K for D\(_2\) when the adsorbed layers are saturated. The maximum yield in the high temperature feature is about 0.05 ML of H\(_2\) (D\(_2\)) for both molecules, which corresponds to only 14\% of the saturation coverage. The difference in peak temperatures indicates that kinetic isotope effects enhance the rates of recombinative desorption of hydrogen from PdO(101) compared with deuterium.

A similar enhancement is seen for desorption from the molecularly chemisorbed state. The low temperature TPD peak is centered at \(94\) K for H\(_2\) but appears at a higher temperature of \(105\) K for D\(_2\) when the molecular layers are saturated. Differences in both desorption pre-factors and activation energies can contribute to the shift in peak temperature for H\(_2\) compared with D\(_2\). To account for changes in both parameters, we computed desorption pre-factors using the transition state theory formula with vibrational frequencies determined by analysis of DFT results. These calculations yield average pre-factors of \(3.8 \times 10^{13}\) and \(1.8 \times 10^{14}\) s\(^{-1}\) for the desorption of molecularly
adsorbed H\textsubscript{2} vs. D\textsubscript{2} from PdO(101), respectively. With these pre-factors, the Redhead equation predicts binding energies of 29.1 and 33.5 ± 2.0 kJ/mol for molecularly chemisorbed H\textsubscript{2} and D\textsubscript{2} on PdO(101), respectively. Note that the difference in H\textsubscript{2} and D\textsubscript{2} binding energies would be overestimated if the same pre-factor was used in the Redhead equation. In contrast to H\textsubscript{2} (D\textsubscript{2}), the H\textsubscript{2}O and D\textsubscript{2}O peak shapes and temperatures are nearly identical in TPD spectra obtained for similar desorption yields of water. Thus, kinetic isotope effects appear to have little influence on the water desorption kinetics from PdO(101).

The characteristics of the low temperature D\textsubscript{2} TPD peak reveal that desorption of the molecularly adsorbed species cannot be described as a single first order process involving non-interacting adsorbates. As seen in Figure 2-3, the low temperature TPD peaks are broad and shift toward lower temperature with increasing D\textsubscript{2} coverage. Both of these characteristics are typical of a second-order desorption process involving non-interacting species. The low temperature D\textsubscript{2} peak may deviate from simple first order kinetics, at least in part, due to competing dissociation pathways for the adsorbed D\textsubscript{2}. For example, competitive dissociation can alter the shape of the desorption peak. However, the breadth of the D\textsubscript{2} desorption peak cannot be easily rationalized by considering only the effects of competing dissociation pathways. A more likely explanation is that desorption occurs from multiple local environments that result from the structural and compositional heterogeneity of the PdO(101) surface. Consistent with this interpretation, we have also reported broad TPD features in the desorption of molecularly adsorbed alkanes and O\textsubscript{2} from the PdO(101) film.[31; 32; 42]
2.3.5 Evolution of Product Yields for H₂ and D₂ on PdO(101)

The evolution of product yields with varying H₂ (D₂) coverage provides further insights for understanding the reactions of dihydrogen with the PdO(101) surface. Figures 2-4a and 2-4b show desorption yields of H₂O (D₂O), low temperature H₂ (D₂), and high temperature H₂ (D₂) as a function of the initial H₂ and D₂ coverages, respectively. As seen in Figure 2-4a, the H₂O yield increases nearly linearly with the initial H₂ coverage beyond a total H₂ coverage of ~0.1 ML (~29% of H₂ saturation). The H₂O yield reaches a value of 0.25 ML at saturation of the H₂ layer, which is equal to about 75% of the cus-Pd (or O) site density. The yield of low temperature H₂ exhibits a much slower increase, but does appear to increase continuously beyond a total H₂ coverage of 0.23 ML. In contrast, the yield of high temperature H₂ increases rather abruptly to a value of ~0.05 ML and remains largely unchanged as the initial H₂ coverage increases beyond about 0.15 ML.

The contrasting yield behavior provides evidence that H₂O and the high temperature H₂ product arise from distinct pathways. Specifically, the continuous rise in the H₂O yield implies that H₂ dissociation occurs readily on terraces of the PdO(101) surface, rather than being limited only to defect sites. In contrast, the abrupt saturation of the high temperature H₂ yield in addition to the relatively small quantities of this product suggests that defect sites mediate the hydrogen recombination reaction. Further support for this conclusion comes from observations that the H₂ TPD spectra obtained from Pd(111) closely overlap the high temperature TPD feature of H₂ evolving from the PdO(101) film. As mentioned above, a prior study demonstrates that a similar TPD feature results from H₂ recombination on metallic Ru domains located within RuO₂(110) films.[29] We thus conclude that the majority of the H₂O results from H₂
dissociation and oxidation on PdO(101) terraces, while the high temperature H$_2$ feature corresponds to hydrogen recombination at surface defects. As discussed below, we conducted additional experiments to help identify the types of defect sites that are responsible for the hydrogen recombination.

The yield behavior of deuterated products reveals the dramatic effect of isotopic substitution on the reactivity of dihydrogen toward PdO(101). The yield of low temperature D$_2$ remains small as the D$_2$ coverage initially increases, but begins to increase steadily with increasing D$_2$ coverage above about 0.1 ML. The low temperature D$_2$ yield reaches a value of 0.25 ML at saturation of the D$_2$ layer, which corresponds to ~70% of the adsorbed D$_2$. Similar to the behavior of H$_2$ (Fig. 2-4a), the high temperature D$_2$ yield rises relatively quickly but then remains steady at about 0.05 ML as the total D$_2$ coverage increases above ~0.1 ML. Interestingly, the yield of D$_2$O appears to track the high temperature D$_2$ yield, rising to 0.07 ML but then increasing only marginally above a D$_2$ coverage of 0.1 ML. Assuming that the high temperature D$_2$ originates from surface defects, the similar evolution of the D$_2$O and high temperature D$_2$ yields suggests that the D$_2$O is also associated with reaction at surface defect sites. Notice also that the low temperature D$_2$ yield begins to increase sharply once the D$_2$O yield effectively saturates. The implication is that D$_2$ molecules start to adsorb more rapidly on terraces once the defects saturate, and that desorption of the molecularly adsorbed D$_2$ precursor is strongly favored over dissociation on the terraces.

Overall, the evolution of product yields provides evidence that H$_2$ dissociates by at least two pathways on PdO(101), one of which is associated with defect sites and the other with terraces. Dissociation of H$_2$ is facile on both terraces and defects, with the
former pathway resulting in high fractional yields of H₂O and a continuous increase in the H₂O yield with increasing H₂ coverage. The dissociation of D₂ also appears to be facile on defects. Apparently, after D₂ dissociation at defect sites, the D atoms can either recombinatively desorb or react with the PdO surface to produce D₂O during TPD. The similar shapes of the D₂O and H₂O TPD curves indicate that water production follows similar pathways for both isotopes once the molecules dissociate on the surface.

The yield data further reveals that kinetic isotope effects strongly suppress the dissociation of D₂ on the PdO(101) terraces. The magnitude of the KIE is difficult to quantify since reaction at defect sites appears to be responsible for most of the D₂O that evolves. The ratio of the highest H₂O and D₂O yields provides a lower bound of 3.5 for the KIE, but the effect may be significantly greater. Finally, we note that the inverse relation between the H₂O (D₂O) yield and the low temperature H₂ (D₂) yield is entirely consistent with a precursor-mediated mechanism for dissociation on the PdO(101) terraces. In this mechanism, the molecularly adsorbed species serves as a common intermediate for both the desorption and dissociation pathways. Thus, large yields of low temperature D₂ are accompanied by small yields of D₂O and vice versa for hydrogen.

2.3.6 Reactivity of Partially Reduced PdO(101)

To further probe the role of surface defect sites, we studied the reactivity of D₂ on the PdO(101) thin film after partially reducing the surface using D₂. In these experiments, we collected D₂ and D₂O TPD spectra after D₂ adsorption at 75 K but terminated the TPD experiment at 550 K to avoid completely decomposing the PdO(101) film while ensuring that nearly all of the deuterium desorbs. We then repeated this procedure several times in an attempt to systematically increase the concentrations
of oxygen vacancies and other reduced sites that develop during PdO reduction. Each TPD experiment removed ~0.07 ML of oxygen atoms from the PdO film, which is equivalent to 20% of the cus-O atoms. Despite these attempts to enhance the surface reactivity, we find that the D$_2$ and D$_2$O TPD spectra are nearly identical for as many as five consecutive TPD experiments. Thus, the surface reactivity toward D$_2$ remains unchanged after removing the equivalent of 80% of the cus-O atoms and heating the PdO film to 550 K.

These partial reduction experiments demonstrate that any new sites resulting from the reductive treatments are inactive for D$_2$ dissociation. This finding seems to eliminate oxygen vacancies and metallic domains as the active sites. For example, if D$_2$ activation occurred selectively on metallic domains, then the surface concentration of these domains would need to remain at essentially the same value in order to activate the same quantity of D$_2$ in each experiment. Even if heating to 550 K facilitates surface re-oxidation via oxygen migration from the bulk, the concentrations of metallic domains and oxygen vacancies are likely to change during the reductive treatments. In contrast, the density of step edges could conceivably remain constant during the reductive treatments.

In other experiments, we examined the surface reactivity after subjecting the PdO(101) film to oxidative treatments such as O-atom exposure at elevated temperature and prolonged O$_2$ exposures, but these treatments caused only slight changes in the surface reactivity as well. We also considered the possibility that the atomic oxygen beam projects a non-uniform flux profile across the surface, leaving the perimeter of the crystal in metallic form. To test this possibility, we prepared the
PdO(101) thin film with the sample rotated at a highly glancing angle relative to the beam. As with the other treatments, this procedure had an immeasurable effect on the reactivity of the PdO film toward D₂. Since the variation of product yields with the H₂ (D₂) coverage (Fig. 2-4) supports the interpretation that D₂ activation occurs on a minority surface site(s), we conclude that the concentration(s) of these sites changes negligibly during the reductive and oxidative treatments that we examined. Although step edges may satisfy this condition, more detailed characterization of the surface structure is ultimately needed for identifying the active sites for D₂ dissociation on PdO(101).

2.3.7 Effect of Blocking cus-Pd Sites

The TPD data supports the idea that H₂ activation occurs by a mechanism wherein a molecularly chemisorbed state acts as a precursor to H₂ dissociation on the PdO(101) terraces. According to prior computational studies, the molecular precursor for H₂ dissociation on both RuO₂(110)[26] and PdO(101)[36] corresponds to H₂ molecules that are chemisorbed on coordinatively-unsaturated cation sites of these surfaces, forming adsorbed σ-complexes. If this interpretation is correct, then blocking access to the cus-Pd sites should be effective in suppressing the dissociation and hence subsequent oxidation of H₂ on the PdO(101) surface.

We have previously reported that O₂ chemisorbs relatively strongly on PdO(101) by binding to cus-Pd sites, reaching a saturation coverage of ~0.28 ML (O-atom basis).[31] The molecularly chemisorbed O₂ desorbs in two main features at about 120 K and 230 K during TPD, which suggests that O₂ binds in at least two distinct configurations on PdO(101). DFT calculations confirm that O₂ molecules strongly favor binding on cus-Pd sites over other sites. Specifically, DFT predicts that O₂ can bind as a
superoxy species to a single cus-Pd site, and can also form a more strongly-bound peroxy species by adopting a bidentate configuration along a cus-Pd row. Because formation of the bidentate species requires a pair of cus-Pd sites to be vacant, the O$_2$ layer saturates at a coverage that is less than the cus-Pd site density.

Shown in Figure 2-5 are H$_2$O TPD spectra obtained after adsorbing H$_2$ on a clean PdO(101) surface vs. PdO(101) that was pre-saturated with molecularly chemisorbed O$_2$. Note that we terminated the latter TPD experiment at 550 K to avoid the intense O$_2$ desorption peak that evolves during decomposition of the PdO(101) film. The TPD spectra in Figure 2-5 demonstrate that blocking the cus-Pd sites with O$_2$ strongly suppresses the production of H$_2$O after subsequent surface exposure to H$_2$. We also observe negligible H$_2$ desorption in our experiments with the O$_2$ pre-saturated surface. Thus, the H$_2$ and H$_2$O TPD data show that molecularly adsorbed O$_2$ hinders both H$_2$ adsorption and dissociation on PdO(101). We estimate that pre-saturating with O$_2$ causes the H$_2$O yield to decrease from 0.24 ML to ~0.05 ML, which is a decrease of ~80%. Since the O$_2$ layer saturates at only ~80% of the cus-Pd density, about 0.07 ML of cus-Pd sites is initially available for H$_2$ adsorption. This initial concentration of vacant sites is very close to the H$_2$O yield obtained from the O$_2$ pre-saturated surface (Fig. 2-5). Also, the D$_2$ yield data (Fig. 2-4b) suggests that hydrogen activation at defect sites accounts for approximately 0.07 ML of the water that is produced. Thus, a fraction of the ~0.05 ML of H$_2$O that evolves from the O$_2$ pre-covered surface may originate from the defect-mediated pathway, implying that blocking cus-Pd sites with O$_2$ suppressed H$_2$ activation on the PdO(101) terraces to an even greater extent than suggested by the data shown in Fig. 2-5. We note that the rising tail of the H$_2$O TPD peak indicates that a
large fraction of the water which forms on the $\text{O}_2$-saturated surface desorbs from defect sites during TPD. Overall, these experiments provide strong support for concluding that $\text{H}_2$ molecules chemisorbed on cus-Pd sites serve as necessary precursors for the dissociation of $\text{H}_2$ on PdO(101) terraces for the conditions studied here.

### 2.3.8 Influence of Surface Temperature on $\text{H}_2$ Dissociation

We examined the influence of the surface temperature on the dissociation of $\text{H}_2$ on PdO(101) to further test the hypothesis that reaction occurs by a precursor-mediated mechanism. Facile dissociation by a precursor-mediated mechanism typically arises when the apparent activation energy for dissociation is negative, in which case the dissociation probability and hence product yields decrease with increasing temperature. Figure 2-6 shows normalized $\text{H}_2\text{O}$ yields obtained after exposing the PdO(101) film to 0.1 L (Langmuir) of $\text{H}_2$ at surface temperatures ranging from 85 to 245 K. The maximum temperature for these experiments was chosen to be sufficiently below the $\text{H}_2\text{O}$ TPD peak temperatures in order to avoid $\text{H}_2\text{O}$ desorption during the $\text{H}_2$ exposures. Also, a 0.1 L $\text{H}_2$ exposure saturates the PdO(101) surface with $\text{H}_2$ at 75 K, and is thus high enough to effect measurable dissociation of $\text{H}_2$ at higher temperature. As seen in Figure 2-6, the $\text{H}_2\text{O}$ yield decreases by nearly a factor of two with increasing surface temperature from 85 to 245 K. Since hydrogen activation at defects also contributes to the measured $\text{H}_2\text{O}$ yields, the $\text{H}_2$ dissociation probability on terraces may decrease more sharply with temperature than suggested by the data. The contribution from defect sites complicates attempts to estimate kinetic parameters from the temperature-dependent data. As a rough approximation, we estimate that the apparent dissociation barrier is negative by a few kJ/mol. Overall, the temperature-dependent data supports the conclusion that $\text{H}_2$ dissociation on PdO(101) occurs predominantly by a precursor-
mediated mechanism up to at least 250 K, and that the apparent dissociation barrier for this pathway lies below the gas-phase zero.

2.5 Computational Results

The DFT calculations have been performed by our collaborators and have been published elsewhere. In short, the DFT results could not entirely explain the observed kinetic isotope effect and therefore some corrections were required. Below, these tunneling corrections can be found.

2.5.1 Tunneling Corrections

To assess the effects of tunneling on the dissociation rates of \( \text{H}_2 \) and \( \text{D}_2 \) on PdO(101), we computed rate coefficients using transition state theory (TST) and applied tunneling corrections that we determined using the one-dimensional Eckart barrier.\cite{43, 44} Using TST formulas, we write the rate coefficients for \( \text{H}_2 \) (\( \text{D}_2 \)) desorption and dissociation (reaction), \( k_d \) and \( k_r \), as the following:

\[
k_d(T) = \frac{k_B T}{h} \frac{q_d^{TS}}{q_{ad}} \exp\left(\frac{-\Delta E_d}{k_BT}\right) \tag{2-1}
\]

and

\[
k_r(T) = \Gamma(T) \frac{k_B T}{h} \frac{q_r^{TS}}{q_{ad}} \exp\left(\frac{-\Delta E_r}{k_BT}\right) \tag{2-2}
\]

where \( \Delta E_d \) and \( \Delta E_r \) represent the activation energies for desorption and dissociation, respectively, \( q_{ad} \) represents the partition function for \( \text{H}_2 \) adsorbed molecularly in the parallel configuration, and \( q_d^{TS} \) and \( q_r^{TS} \) represent the partition functions of the transition states for \( \text{H}_2 \) desorption and dissociation, less the contribution from motion along the reaction coordinates. The overall tunneling correction \( \Gamma(T) \) is the ratio of the quantum
mechanical barrier-crossing rate to the classical barrier-crossing rate as given by the equation,

$$\Gamma(T) = \frac{\exp(V_1 / k_B T)}{k_B T} \int_0^\infty \kappa(E) \exp(-E / k_B T) dE$$

(2-3)

where $V_1$ represents the barrier height and $\kappa(E)$ is the tunneling probability as a function of the energy $E$ associated with motion along the reaction coordinate.

For H\textsubscript{2} (D\textsubscript{2}) desorption and dissociation, the activation energies are $\Delta E_d = 32.5$ (36.6) kJ/mol and $\Delta E_r = 46.6$ kJ/mol, respectively. As discussed below, we find that the tunneling corrections better reproduce the experimentally-observed behavior when the Eckart potential is parameterized using the classical rather than ZPC dissociation barriers.

To estimate tunneling corrections, we calculated transmission rates through a one-dimensional Eckart barrier. Note that tunneling will have a negligible influence on the rates of H\textsubscript{2} and D\textsubscript{2} desorption since the barrier for molecular desorption is flat. The one-dimensional Eckart barrier may be represented by the equation;

$$V(s) = \frac{-As}{(1-s)} - \frac{Bs}{(1-s)^2}$$

(2-4)

where $s = -\exp(-2\pi x / L)$. Here, $x$ represents the distance along the reaction coordinate, $L$ represents the characteristic width of the barrier and $A$ and $B$ are constants given by the equations;

$$A = V_1 - V_2$$

(2-5)

and

$$B = (V_1^2 - V_2^2)$$

(2-6)
where $V_1$ and $V_2$ represent the forward and reverse barriers for $H_2$ dissociation. Based on the computed vibrational frequencies, we estimate a characteristic width\cite{44} of 2.7 Å for the DFT-derived dissociation barrier. Also, we set $V_1$ and $V_2$ equal to the classical energy barriers for dissociation and association determined with DFT. The specific values that we used are $V_1 = 46.6$ kJ/mol and $V_2 = 114.4$ kJ/mol for both $H_2$ and $D_2$. The transmission probability through the Eckart barrier\cite{44} may be written as

$$
\kappa(\xi) = 1 - \frac{\cosh(2\pi(a-b)) + \cosh(2\pi d)}{\cosh(2\pi(a+b)) + \cosh(2\pi d)} \quad (2-7)
$$

where $\pi a = \frac{(\alpha_1 \xi)^{\frac{1}{2}}}{\alpha_1^{\frac{1}{2}} + \alpha_2^{\frac{1}{2}}}$, $\pi b = \frac{(\alpha_1 (1+\xi) - \alpha_2)^{\frac{1}{2}}}{\alpha_1^{\frac{1}{2}} + \alpha_2^{\frac{1}{2}}}$ and $\pi d = \frac{\alpha_1 \alpha_2 - \frac{2\pi^2}{16}}{\alpha_1^{\frac{1}{2}} + \alpha_2^{\frac{1}{2}}}$ also, $\alpha_1 = \frac{2\pi V_1}{h\nu^*}$, $\alpha_2 = \frac{2\pi V_2}{h\nu^*}$ and $\xi = \frac{E}{V_1}$, where $\nu^*$ is the frequency associated with motion at the top of the barrier.

Our calculations suggest that tunneling is the dominant pathway for $H_2$ and $D_2$ dissociation on PdO(101) at the low temperatures at which these molecules dissociate during TPD (~100 K). For example, we estimate tunneling corrections of $2 \times 10^{10}$ and $6 \times 10^5$ for $H_2$ and $D_2$ dissociation at 100 K. In addition, the ratio of dissociation rate coefficients at 100 K is $k_r(H_2)/k_r(D_2) = 3.2 \times 10^4$. Thus, the tunneling calculations also predict a large KIE in the dissociation of $H_2$ on PdO(101), in agreement with our experimental observations. Figure 2-7 shows plots of $k_r$ and $k_d$ calculated as a function of the surface temperature for $H_2$ and $D_2$. For both molecules, the rate coefficient for dissociation is significantly larger than that for desorption at 85 K, but the $k_d$ curves
cross the $k_r$ curves due to a strong decrease in the tunneling correction with increasing temperature.

The higher values of $k_r$ compared with $k_d$ at low temperature suggest that dissociation should dominate over desorption for both H$_2$ and D$_2$. However, while the experimental data shows that the majority of the H$_2$ does dissociate prior to desorption at ~95 K, D$_2$ dissociates to only a limited extent during the TPD experiments. A plausible explanation is that the absolute rate coefficient for D$_2$ dissociation is very low at 85 K such that appreciable dissociation requires higher temperatures. Once a sufficiently high temperature is reached, the rate of D$_2$ desorption may exceed that for dissociation, causing most of the D$_2$ to desorb rather than dissociate. For example, the calculations predict that the rate coefficient for D$_2$ dissociation increases by a factor of ~20 with increasing temperature from 85 to 100 K, but the rate coefficient for D$_2$ desorption increases at a higher rate and is more than 3800 times that for dissociation at 100 K (Fig. 2-7). Defining the initial dissociation probability as:

$$S_o = \frac{k_r}{k_r + k_d} \quad (2-8)$$

We estimate that $S_o = 0.06$ at 100 K for D$_2$. Thus, the calculations suggest that the probability for D$_2$ dissociation becomes quite low near the temperatures for appreciable rates of desorption or dissociation of molecular D$_2$. In contrast, the dissociation probability for H$_2$ remains near unity for temperatures up to 100 K, which lies above the desorption temperature of molecularly chemisorbed H$_2$. We note that the rate coefficients exhibit similar qualitative behavior if the tunneling corrections are computed using the ZPC barriers rather than the classical barriers, but the $k_r$ and $k_d$ curves cross at higher temperature when the ZPC barriers are used to parameterize the Eckart
potential. The tunneling corrections based on the ZPC barriers are smaller than those determined using the classical barriers, but they remain very large at low temperature. Overall, the tunneling calculations provide a qualitatively consistent description of the KIE observed in the low temperature dissociation of H$_2$ and D$_2$ on PdO(101). We thus conclude that tunneling dominates the dissociation of H$_2$ on PdO(101) at low temperature and causes a large KIE for this reaction.

Our calculations imply that H$_2$ dissociation on PdO(101) occurs almost exclusively by tunneling at temperatures near 100 K. That is, at low temperature, nearly every reactive trajectory occurs by an H-atom penetrating the energy barrier to dissociation. In this case, a quantum mechanical treatment of the nuclear motion is needed to accurately predict the H$_2$ dissociation rates, which is beyond the scope of the present work. Indeed, tunneling corrections computed from a one-dimensional potential cannot be expected to provide quantitatively accurate values of the dissociation rate coefficient when tunneling is so dominant. Nevertheless, our one-dimensional tunneling calculations do offer a physically reasonable interpretation of the experimentally-observed behavior, namely, that tunneling is dominant in the low-temperature dissociation of H$_2$ on PdO(101) and that the large KIE observed experimentally arises from differences in H vs. D tunneling rates through the dissociation barrier rather than from zero-point energy differences. It is worth noting that the tunneling corrections decrease to values between one and ten as the temperature approaches 300 K, and should thus be more reliable in this temperature range.

2.6 Summary

We investigated the dissociative chemisorption and oxidation of H$_2$ and D$_2$ on a PdO(101) thin film using TPD experiments and DFT calculations. We find that H$_2$
dissociates readily on PdO(101) at temperatures below 100 K, and produces mainly
H$_2$O that desorbs above 350 K during TPD. We observe a small quantity of H$_2$
desorbing near 300 K which we attribute to hydrogen recombination at a surface defect
site(s). The experimental results demonstrate that H$_2$ (D$_2$) dissociation on PdO(101)
occurs by a precursor-mediated mechanism wherein H$_2$ molecularly chemisorbed on
cus-Pd sites serves as the precursor to dissociation. The precursor-mediated
mechanism is the dominant pathway for H$_2$ dissociative chemisorption up to at least 250
K. The data also reveals that a kinetic isotope effect strongly suppresses the
dissociation of D$_2$ on PdO(101) terraces, causing the kinetic branching to shift toward
desorption of the molecular D$_2$ precursor. The evolution of product yields with initial
coverage suggests that D$_2$ dissociation on PdO(101) is limited primarily to a surface
defect site(s), whereas H$_2$ dissociates readily on terraces as well.

DFT calculations support the experimental evidence that H$_2$ dissociates on
PdO(101) by a precursor-mediated pathway. According to DFT, H$_2$ forms a $\sigma$-complex
on PdO(101) by coordinating with a cus-Pd site and aligning its intramolecular bond
parallel to the cus-Pd rows. This parallel configuration has a ZPC binding energy of 32.5
kJ/mol, and is the only stable molecularly-chemisorbed state that we could identify. The
DFT calculations indicate that only a single pathway is viable for H$_2$ dissociation on
PdO(101) to generate stable products in the limit of low coverage. In this pathway, the
adsorbed H$_2$ molecule transfers an H-atom to a neighboring cus-O site, producing an O-
H species and an H-atom bound to a cus-Pd site.

Accounting for zero-point energy differences, DFT predicts apparent activation
energies of -0.6 and -3.3 kJ/mol for H$_2$ and D$_2$ dissociation on PdO(101), respectively.
The values of the apparent activation energies as well as their ordering (D$_2$ < H$_2$) are inconsistent with the experimental observations of facile H$_2$ dissociation and a KIE that strongly suppresses D$_2$ dissociation. By applying tunneling corrections to DFT-derived rate coefficients, we obtain a qualitatively consistent description of H$_2$ and D$_2$ dissociation on PdO(101). These calculations suggest that H$_2$ dissociation on PdO(101) is dominated by quantum-mechanical tunneling at low temperature, and that the large KIE originates from differences in the tunneling rates of H vs. D through the dissociation barrier. This finding may have implications for modeling H$_2$ dissociation as well as other hydrogen transfer reactions (e.g., C-H bond cleavage) on PdO surfaces.
Figure 2-1. Model representation of PdO(101) surface. (a) Top and (b) side view of the PdO(101) thin film structure. The red and gray atoms represent O and Pd atoms, respectively. Rows of threefold-coordinated (cus) Pd and O atoms are indicated. The a and b directions correspond to the [010] and [101] crystallographic directions of PdO.
Figure 2-2. TPD spectra of H₂ and H₂O. TPD spectra of H₂ (bottom) and H₂O (top) after exposing the PdO(101) surface to various quantities of H₂ at 75 K. The total desorption yield (H₂ + H₂O) is equal to 0.33 ML of H₂. A heating rate of 1 K s⁻¹ was used in each experiment.
Figure 2-3. TPD spectra of D$_2$ and D$_2$O. TPD spectra of D$_2$ (bottom) and D$_2$O (top) after exposing the PdO(101) surface to various quantities of D$_2$ at 75 K. The total desorption yield (D$_2$ + D$_2$O) is equal to 0.36 ML of D$_2$. A heating rate of 1 K s$^{-1}$ was used in each experiment.
Figure 2-4. Uptake curves of coverages calculated from the TPRS spectra. (a) TPD yields of H\textsubscript{2} desorbing in the low (~100 K) vs. high (~300 K) temperature peaks and H\textsubscript{2}O as a function of initial H\textsubscript{2} coverage, and (b) TPD yields of D\textsubscript{2} desorbing in the low (~100 K) vs. high (~300 K) temperature peaks and D\textsubscript{2}O as a function of initial D\textsubscript{2} coverage. In all cases, we prepared the initial H\textsubscript{2} (D\textsubscript{2}) coverage at a surface temperature of 75 K. Coverages are given in units of ML.
Figure 2-5. H₂O TPD spectra obtained after exposing clean PdO(101) and O₂ pre-covered PdO(101) to a saturation dose of H₂ at 75 K. The initial O₂ coverage was approximately 0.27 ML (O-atom basis) [31] in the experiment with pre-adsorbed O₂. A heating rate of 1 K s⁻¹ was used in each experiment.
Temperature dependence
$H_2 + PdO(101)$

Figure 2-6. TPD yield of H$_2$O as a function of the surface temperature (85 to 245 K) during H$_2$ adsorption. Prior to each TPD measurement, we exposed the PdO(101) surface to 0.1 L of H$_2$. The decrease in the H$_2$O yield with increasing surface temperature is characteristic of a precursor-mediated mechanism for H$_2$ dissociation in which the apparent activation energy is negative.
Figure 2-7. DFT-derived rate coefficients for desorption and dissociation, corrected for quantum mechanical tunneling using the one-dimensional Eckart potential, as a function of temperature for (a) D$_2$ and (b) H$_2$. The circular and triangular symbols represent the rate coefficients for dissociation ($k_r$) and desorption ($k_d$), respectively.
CHAPTER 3
MOLECULAR ADSORPTION OF SMALL ALKANES ON A PDO(101) THIN FILM:
EVIDENCE OF σ-COMPLEX FORMATION

3.1 Motivation of Small Alkane Study

The initial C-H bond activation of alkanes on metal-based catalysts has attracted widespread interest due to the desire to more effectively utilize saturated hydrocarbons as energy sources as well as feedstocks for chemical production. Because initial C-H bond cleavage is often a rate-determining step in the catalytic processing of alkanes, extensive efforts have been devoted toward understanding alkane adsorption in detail, with most studies focusing on clean transition metal surfaces [10]. In contrast, the interactions of alkanes with metal oxide surfaces have not been widely explored, largely because alkanes interact weakly with many oxide surfaces and are hence difficult to activate under ultrahigh vacuum (UHV) conditions. Palladium oxide (PdO) is an important exception as this material is highly active toward the complete oxidation of alkanes. In fact, prior studies conducted at commercially relevant pressures demonstrate that the formation of PdO is responsible for the exceptional activity of supported Pd catalysts in the catalytic combustion of natural gas in excess oxygen [1-9; 22-24]. This finding provides substantial motivation for studying the surface chemistry of PdO in detail. In particular, investigations with well-defined PdO surfaces provide opportunities for gaining insights into the mechanisms for alkane activation on transition metal oxides as well as clarifying the oxide surface properties that enhance C-H bond activation.

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In recent work, we observed that the initial C-H bond cleavage of propane is highly facile on a PdO(101) thin film grown on Pd(111) in UHV [32]. Our results demonstrate that the initial dissociation of propane on the PdO(101) surface occurs by a precursor-mediated mechanism in which a molecularly adsorbed state of propane acts as the precursor to initial C-H bond cleavage. Temperature programmed desorption (TPD) measurements reveal that the molecular precursor is strongly bound relative to physisorbed propane on Pd(111), leading us to suggest that dative bonding interactions contribute to the binding of the alkane precursor on PdO(101). In the present study, we examined the adsorption of methane, ethane and propane on PdO(101) both experimentally and computationally, and present further evidence that dative bonding strengthens the binding of small alkanes on PdO(101).

Dative bonding between alkane molecules and transition metal complexes is well known [45-47]. These bonding interactions produce compounds known as alkane σ-complexes that can serve as key intermediates in the initial C-H bond cleavage of alkanes by mononuclear transition metal compounds. Bond strengths for alkane σ-complexes are typically between 20 and 50 kJ/mol [45]. The dative bonding interaction that produces an alkane σ-complex generally involves electron donation from C-H σ bonds of the alkane molecule into empty d-orbitals of the metal center, and, in some cases, back-donation of electrons from filled d-orbitals of the metal into C-H σ* bonds. Among the few examples that have been reported, the adsorption of H₂ on RuO₂(110) provides the most comprehensive example of σ-complex formation on a solid surface [25; 26]. Recent work by Blanco-Rey et al. [36] as well as our group [48] also demonstrates that dihydrogen experiences relatively strong dative bonding on
PdO(101), which suggests the possibility that the surfaces of late transition metal oxides have properties that generally favor coordinate bond formation with saturated molecules.

While it is reasonable to expect that dative interactions would also influence the bonding of alkanes on transition metal or transition metal compound surfaces, clear evidence for such bonding is rather limited. For example, several studies have reported softening of C-H vibrational modes of alkanes upon adsorption on transition metal surfaces [49-58]. However, work by Fosser et al. [57] provides evidence that C-H mode softening can occur even when the attractive dispersion interaction dominates the alkane-surface binding. In this case, the dispersion interaction can bring the molecule close enough to the surface to cause charge flow from metal states into Rydberg molecular orbitals, resulting in C-H mode softening. Thus, the C-H mode softening seen on metal surfaces is not necessarily a consequence of the type of dative bonding that characterizes alkane $\sigma$-complexes.

Recent studies have established systematic trends in the desorption kinetic parameters for alkane molecules that are physically adsorbed on solid surfaces [59; 60]. As demonstrated in the present study, these trends provide a benchmark for comparison with systems in which dative bonding may affect the alkane-surface binding. At low coverage, straight chain alkane molecules adopt a flat-lying geometry when physisorbed on a close-packed surface [10]. This configuration maximizes the attractive interaction between the molecule and surface by allowing each CH$_n$ group to reside within the attractive region of the molecule-surface potential. In this simplified model, each CH$_n$ group contributes equally to the molecule-surface interaction, resulting
in alkane binding energies $E$ that increase linearly with the chain length $N$. Further, a plot of $E$ versus $N$ should have a zero intercept if each CH$_n$ group makes an additive contribution to the total binding energy.

Recently, Tait et al. [59; 60] reported extensive investigations of the desorption of physisorbed alkanes from MgO(100), Pt(111) and C(0001), and confirmed that the $E$ versus $N$ relationships are linear with zero intercepts. These workers developed a so-called inversion-optimization method to determine both the pre-factor and (coverage-dependent) activation energy for desorption from TPD spectra obtained at different initial coverages. A key finding from their analysis is that the pre-factors for desorption increase significantly with increasing chain length, which is consistent with earlier molecular dynamics simulations of alkane desorption [61; 62]. Compared with an analysis that assumes a molecule-independent pre-factor, the effect of the increasing pre-factors is to increase the slope of the $E$ versus $N$ curve, causing this curve to exhibit the expected zero intercept. In the context of transition state theory, the pre-factors for desorption increase with chain length because the densities of translational and rotational states of gaseous alkane molecules increase substantially with increasing molecular size, resulting in larger entropy changes upon desorption. Tait et al. [60] also report formulas, derived from transition state theory, that give limiting values of the desorption pre-factors for several alkanes as a function of the surface temperature. The minimum and maximum pre-factors correspond to adsorbed molecules that are fully mobile versus completely immobile, respectively. Overall, the work of Tait et al. [59; 60] provides important guidance in interpreting alkane TPD spectra, and identifying systems
that deviate from the systematic trends established for linear alkanes physisorbed on close-packed surfaces.

In the present study, we investigated the molecular adsorption of methane, ethane and propane on PdO(101) using TPD measurements and DFT calculations. The TPD results show that each of these small alkanes adsorb in a molecular state that is more strongly-bound than alkanes physically adsorbed on Pd(111), and that the \( E \) vs. \( N \) relationship has a non-zero intercept between 22 and 26 kJ/mol, which is consistent with dative bonding contributing to the alkane binding energy on PdO(101). DFT calculations predict that these small alkanes bind to coordinatively unsaturated (cus) Pd atoms through a donor-acceptor interaction, resulting in an adsorbed state that is analogous to an alkane \( \sigma \)-complex.

### 3.2 Experimental Details

Previous studies [37; 38] provide details of the three-level UHV chamber utilized for the present experiments. The Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder in thermal contact with a liquid nitrogen cooled reservoir. A type K thermocouple spot-welded to the backside of the crystal allows sample temperature measurements. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports maintaining or linearly ramping the sample temperature from 81 K to 1250 K. Initially, sample cleaning consisted of sputtering with 600 eV Ar\(^+ \) ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to
923 K to desorb oxygen and carbon oxides. As discussed previously [39], we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in preparing the PdO(101) thin films used in this study. We considered the Pd(111) sample to be clean when we could no longer detect contaminants with X-ray photoelectron spectroscopy (XPS), obtained sharp low energy electron diffraction (LEED) patterns consistent with the Pd(111) surface, and did not detect CO production during flash desorption after oxygen adsorption.

A two-stage differentially-pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system [37; 38]. To produce a PdO(101) thin film, we expose a Pd(111) sample held at 500 K to an ~12 ML dose of gaseous oxygen atoms supplied in a beam, where we define 1 ML as equal to the Pd(111) surface atom density of $1.5 \times 10^{15}$ cm$^{-2}$. This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains ~3.0 ML of oxygen atoms and is about 12 Å thick [11; 12]. The structure of the PdO(101) surface is discussed in detail below.

Alkanes were delivered to the sample from a calibrated beam doser at incident fluxes between $5 \times 10^{-4}$ and $5 \times 10^{-3}$ ML s$^{-1}$. We set the sample-to-doser distance to about 50 mm to ensure uniform impingement of the alkanes across the sample surface. After the alkane exposures, we conducted TPD experiments by positioning the sample in front of the mass spectrometer and then heating at a constant rate of 1 K s$^{-1}$ until the sample temperature reached 923 K. The PdO thin films completely decompose when heated to 923 K so it was necessary to prepare fresh PdO films for each alkane
adsorption experiment. In a few experiments with methane and ethane, we terminated the TPD experiments at a sample temperature of 550 K to avoid decomposition of the PdO film. The resulting TPD spectra differ negligibly from those obtained from fresh PdO films, most likely because methane and ethane dissociate to an immeasurable extent on PdO(101) (vide infra).

We estimated ethane and propane coverages by scaling integrated desorption spectra obtained from PdO(101) with integrated TPD spectra collected from monolayers of ethane and propane adsorbed on Pd(111) at 85 and 110 K, respectively, and assuming that these monolayers saturate at 0.237 ML vs. 0.205 ML on Pd(111). These values correspond to the saturation coverages of ethane and propane monolayers on Pt(111) as determined from calibrated molecular beam experiments by Carlsson and Madix [63]. Kao and Madix [64] have shown that the binding energies of ethane and propane are only slightly higher on Pd(111) compared with Pt(111) so it seems reasonable to assume that the monolayers saturate at the same coverages on each metal surface.

Since only low coverages of methane can be generated on Pd(111) at 85 K, we estimated methane coverages by scaling the mass spectrometer signals obtained from known gaseous flow rates generated with a calibrated leak. Our approach involves separately admitting methane and ethane into the UHV chamber using a calibrated leak and measuring mass spectrometer signals of these molecules. This procedure provides a relation between the ratio of CH$_4$ and C$_2$H$_6$ leak rates into the chamber and the corresponding ratio of mass spectrometer signals. We then collect a few CH$_4$ and C$_2$H$_6$ TPD spectra by facing the sample away from the mass spectrometer so that the
resulting signals represent background partial pressures. This approach simulates the conditions employed during the calibrated leak measurements. Using the absolute coverage of a saturated monolayer of C₂H₆ on Pd(111), we express the background TPD spectra of ethane in terms of absolute ethane coverage. Finally, with the ethane background TPD spectra given in units of ML s⁻¹, we use the relation between CH₄ and C₂H₆ flow rates and mass spectrometer signals to estimate the absolute methane coverages.

### 3.3 Results and Discussion

#### 3.3.1 Structure of the PdO(101) Thin Film on Pd(111)

Figure 3-1 depicts the structure of the stoichiometric PdO(101) surface that we examined in this study. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell of dimensions $a = 3.04$ Å and $b = 6.14$ Å, where the $a$ and $b$ lattice vectors coincide with the [010] and [101] directions of the PdO crystal, respectively. The PdO(101)-PdO surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the $a$ direction shown in Fig. 3-1. Thus, half of the surface O and Pd atoms are coordinatively unsaturated (cus) and likely to be more active than the fourfold coordinated atoms for binding adsorbed molecules. The areal density of each type of coordinatively-distinct atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML (monolayer), and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms. Given that the film contains ~3.0 ML of oxygen atoms, we estimate that the PdO(101) film on Pd(111) consists of between four and five layers and has a total...
thickness of ~12 Å. In a prior study [39], we found that the PdO(101) structure aligns with the close-packed directions of the Pd(111) substrate, and would expand by 0.46% and 3.4% in the $a$ and $b$ directions to achieve commensurability with the metal substrate, which corresponds to unit cell dimensions of $a = 3.06$ Å and $b = 6.35$ Å.

**3.3.2 Alkane TPD Spectra Obtained from Pd(111) and a PdO(101) Thin Film**

Figure 3-2 shows TPD spectra of methane, ethane and propane obtained after generating saturation coverages of these species on a PdO(101) thin film at 85 K. The ethane and propane TPD spectra each exhibit two broad peaks, labeled as $\alpha_1$ and $\alpha_2$, which are separated by about 65 K and 75 K, respectively. For methane, desorption appears to be too fast to appreciably populate the $\alpha_2$ state at 85 K. However, the broadening on the leading edge of the TPD peak suggests that methane molecules will populate the $\alpha_2$ state at temperatures sufficiently below 85 K. As reported previously, a fraction of the adsorbed propane molecules dissociates during the TPD measurements, and reacts with the PdO(101) surface to produce CO$_2$ and H$_2$O upon continued heating [33]. Neither methane nor ethane measurably dissociated during the TPD experiments.

Since the intensity of the $\alpha_2$ peak saturates for ethane and propane, we attribute this state to molecules adsorbed in the first layer rather than a multilayer. Further support for this interpretation is that the saturation coverages of ethane and propane on PdO(101) are similar to those of the alkane monolayers on Pd(111). Specifically, we estimate that the ethane and propane layers on PdO(101) saturate at coverages equivalent to 64% and 93% of the saturation coverages of these molecules physisorbed in monolayers on Pd(111). The coverages in the $\alpha_1$ and $\alpha_2$ states are nearly equal when the ethane and propane monolayers are saturated. Thus, the data indicates that the
alkane molecules studied populate two distinct states on PdO(101) at saturation of the monolayer.

The desorption data further reveals that small alkanes adsorbed in the $\alpha_1$ state on PdO(101) bind more strongly than alkanes physisorbed on Pd(111). The $\alpha_1$ peak temperatures for ethane and propane are 165 and 191 K, respectively, whereas ethane and propane desorb at lower temperatures (117 and 152 K) from Pd(111) (Figure 3-2). Similarly, the $\alpha_1$ peak for methane lies at 136 K, whereas, based on prior studies [60; 63], we estimate that methane would desorb from Pd(111) at about 70 K for the heating rate of 1 K/s employed in our experiments. In contrast to the $\alpha_1$ peaks, the $\alpha_2$ peak temperatures for ethane and propane are lower (100 and 120 K) than those for desorption from Pd(111). As discussed previously for propane [32], we attribute the $\alpha_2$ state to physically adsorbed molecules, and assert that a chemical bonding interaction provides extra stabilization for molecules adsorbed in the $\alpha_1$ state. This interpretation originates from the idea that physisorption bond strengths should be lower on an oxide than on the parent metal because the electric polarizability is generally smaller for the oxide. Accordingly, the weaker binding of alkanes in the $\alpha_2$ state on PdO(101) compared with Pd(111) suggests that dispersive interactions are primarily responsible for alkane binding in the $\alpha_2$ state. By the same argument, the stronger binding in the $\alpha_1$ state suggests that additional electrostatic interactions stabilize alkane molecules adsorbed in the $\alpha_1$ state beyond that expected for physisorption. Below we present evidence that a dative bonding interaction between alkane molecules and coordinatively unsaturated Pd atoms strengthens the binding of alkanes adsorbed on PdO(101).
3.3.3 TPD Spectra as a Function of Alkane Coverage

Figure 3-3 shows CH$_4$ and C$_2$H$_6$ TPD spectra obtained after preparing various alkane coverages on the PdO(101) thin film at 85 K. Similar to propane [32], the $\alpha_1$ and $\alpha_2$ states of C$_2$H$_6$ populate nearly sequentially with increasing coverage, and each state has approximately the same concentration of ethane at saturation of the layer. Both peaks are broad compared with TPD peaks for first-order desorption of non-interacting adsorbates, and both shift to lower temperature as the coverage increases (Fig. 3-3a). The $\alpha_1$ peak for methane is also broad and shifts to lower temperature with increasing coverage (Fig. 3-3b). These characteristics suggest that the alkanes encounter a distribution of local bonding environments on PdO(101). Variability in the alkane binding environments may arise from both intermolecular interactions and the heterogeneity of surface sites on PdO(101).

We analyzed the $\alpha_1$ TPD peaks for methane and ethane using the inversion-optimization method in an attempt to determine the pre-factors and activation energies for desorption from the $\alpha_1$ state. For methane, we find an optimum pre-factor of $10^{14.7}$ s$^{-1}$, and a binding energy that increases from about 40 to 44 kJ/mol as the coverage decreases from 0.08 ML. The desorption pre-factor for methane is slightly lower than the maximum value estimated for an immobile adsorbate. For ethane, however, the error between the experimental and calculated TPD curves continues to improve as the pre-factor decreases below the minimum value determined for a mobile adsorbate, which is physically unrealistic. We have reported a similar outcome of the inversion-optimization method in an analysis of a broad H$_2$O TPD feature obtained from PdO(101) [33]. As in that case, we conclude that ethane desorption from the $\alpha_1$ state cannot be fully described by a model based on the mean-field approximation due to the diversity
among local bonding environments. It is worth noting that we have not conducted experiments with isotopically-labeled species to eliminate the possibility that one of the alkane desorption peaks results from the recombination of an alkyl group and a hydrogen atom. However, we consider this possibility to be unlikely based on the low desorption peak temperatures as well as preliminary DFT calculations which predict significant barriers for the recombination reaction.

### 3.3.4 Alkane Binding Energy as a Function of Chain Length

Table 3-1 shows estimates of alkane binding energies on PdO(101) and Pd(111) for the molecules studied here. Since the inversion-optimization method could not provide optimum pre-factors for ethane and propane on PdO(101), we computed the alkane binding energies in the α₁ state using Redhead analysis with limiting values of the pre-factors, which we computed using the formulas suggested by Tait et al. [60]. Our analysis thus provides bounds on the alkane binding energies on PdO(101). Table 3-2 lists the minimum and maximum pre-factors determined for alkanes desorbing in the α₁ peak from PdO(101). For Pd(111), we computed the ethane and propane binding energies using Redhead analysis and the pre-factors reported by Tait et al. [60] for desorption from Pt(111) (Table 3-2). We find that the binding energies determined from this analysis are about 8% higher on Pd(111) compared with prior results for Pt(111) [60]. Kao and Madix have also reported higher binding energies of alkanes adsorbed on Pd(111) compared with Pt(111) [64]. For this reason, we assume that the methane binding energy on Pd(111) is also 8% higher than the value reported by Tait et al. [60] for Pt(111).

Our analysis suggests that the binding energy of each alkane is enhanced by a similar amount on PdO(101) compared with Pd(111). Based on the limiting pre-factors
for desorption, we estimate that the binding energy is higher on PdO(101) relative to Pd(111) by between 17 and 25 kJ/mol for methane, between 12 and 25 kJ/mol for ethane and between 13 to 27.5 kJ/mol for propane. In order to narrow these ranges, it would be necessary to determine optimum pre-factors for desorption for each alkane. For methane, we determined a pre-factor of $10^{14.7}$ s$^{-1}$ using the inversion-optimization method. In this case, the methane binding energy is about 23 kJ/mol higher on PdO(101) compared with Pd(111). As noted above, the optimum pre-factor for methane desorption from PdO(101) lies on the high end of the range of limiting values, which implies that adsorbed CH$_4$ is relatively constrained on PdO(101). This result is reasonable considering the heterogeneity of the PdO(101) surface as well as the more directional character of a dative bond compared with the dispersion interaction. An implication is that the desorption pre-factors for ethane and propane are also relatively high, and hence that the binding energies of these molecules on PdO(101) are well above the minimum values listed in Table 3-2, which would put the differences in ethane and propane binding on PdO(101) versus Pd(111) close to the value estimated for methane.

Figure 3-4 shows alkane binding energies on PdO(101) and Pd(111) plotted as a function of the alkane chain length up to $N = 3$. For Pd(111), the binding energies exhibit the expected linear increase with chain length and an intercept of nearly zero. The two sets of points shown for PdO(101) correspond to the binding energies computed using the minimum and maximum pre-factors for desorption evaluated at the peak desorption temperatures. For each set of pre-factors, the alkane binding energies increase linearly with chain length, and each $E$ vs. $N$ curve exhibits a non-zero intercept. The intercepts
are equal to 21.9 and 26.3 kJ/mol for the $E$ vs. $N$ lines determined for the maximum and minimum pre-factors, respectively. We emphasize that the $E$ vs. $N$ relations shown in Fig. 3-4 represent only two possibilities for alkanes on PdO(101) and that the actual behavior could differ from these limiting cases. However, as discussed above, adsorbed alkanes are probably more constrained on PdO(101) than on Pd(111). In this case, the pre-factors for desorption from PdO(101) will lie well above those for freely mobile adsorbates.

The non-zero intercepts seen in Fig. 3-4 suggest that the alkane binding energies on PdO(101) are higher than those on Pd(111) by an approximately constant amount. A possible explanation is that the dative bonding contribution to the total binding energy is nearly the same for each alkane, whereas the strength of the dispersion interaction increases with chain length in a manner similar to that for physisorbed alkanes. A dative bonding contribution that is roughly molecule independent is plausible because a CH$_n$ group must adopt a specific geometry to form an optimal dative bond with a surface Pd atom. Due to geometric differences between the alkane molecules and the PdO(101) surface, it is unlikely that more than one CH$_n$ group of each molecule can arrange into the ideal geometry for dative bonding.

3.3.5 DFT Calculations of CH$_4$ Adsorption

We used DFT to investigate the bonding of alkanes on the PdO(101) surface. Our main goal is to determine the extent to which dative bonding contributes to the alkane-surface interaction on PdO(101) vs. Pd(111). We emphasize that the optimized geometries and binding energies are likely to deviate from those of the actual adsorbed molecules due to neglect of dispersion interactions in the DFT calculations. Nevertheless, the DFT calculations reveal key differences in the dative bonding of
alkanes on PdO(101) vs. Pd(111), and thereby help to clarify the origins for the stronger binding that is observed on the oxide surface. The details of these calculations are reported elsewhere, and only the results will be mentioned in the summary of this chapter.

3.4 Summary

We investigated the molecular adsorption of methane, ethane and propane on a PdO(101) thin film using TPD and DFT calculations. The TPD data shows that alkanes adsorbed in the α₁ state on PdO(101) have higher binding energies than alkanes physisorbed on Pd(111). Based on an analysis of the TPD spectra using limiting desorption pre-factors, we estimate that the alkane binding energies on PdO(101) increase linearly with increasing chain length, but that the $E$ vs. $N$ relation has a non-zero intercept between about 22 and 26 kJ/mol. We attribute this constant offset to a dative bonding interaction that is similar in magnitude for each alkane, and suggest that the strength of the dispersion interaction with PdO(101) increases with alkane chain length for the molecules studied. We estimate that the formation of $\sigma$-complexes accounts for about 30% to 50% of the total binding energy of these small alkanes adsorbed on PdO(101).

DFT calculations predict that the alkanes bind on PdO(101) by forming coordinate bonds with cus-Pd atoms. The resulting adsorbed species are analogous to alkane $\sigma$-complexes in that the alkane-Pd coordination involves electron donation from C-H $\sigma$ bonds to the Pd center as well as back-donation from Pd $d$-states into localized anti-bonding states. According to DFT, methane and ethane achieve maximum binding energies on PdO(101) by adopting an $\eta^2$(H,H) configuration on top of a cus-Pd atom.
Propane also binds favorably in the $\eta^2$(H,H) configuration through the CH$_2$ group, and can attain a comparable binding energy by adsorbing in an $\eta^1$(2H) configuration along the cus-Pd row. The binding energies for alkanes in the $\eta^2$ configuration lie in a range from about 16 to 24 kJ/mol, which agrees well with the constant offsets estimated from TPD data. Because $\sigma$-complex formation weakens alkane C-H bonds, the DFT calculations suggest that the molecule-surface interaction may assist in the initial activation of C-H bonds on PdO(101). This finding is consistent with recent evidence that the strongly-bound molecular state of propane on PdO(101) serves as the precursor to initial bond cleavage [32]. Efforts are currently underway to study how surface modifications influence the coordinate bonding of alkanes on PdO(101) and the barriers for C-H bond cleavage.
Figure 3-1. Model representation of PdO(101) surface. (a) Top and (b) side view of the PdO(101) thin film structure. The orange and blue atoms represent O and Pd atoms respectively. Rows of threefold-coordinated (cus) Pd and O atoms are indicated. The a and b directions correspond to the [010] and [101] crystallographic directions of PdO.
Figure 3-2. TPD spectra of CH$_4$, C$_2$H$_6$ and C$_3$H$_8$. TPD spectra of CH$_4$, C$_2$H$_6$ and C$_3$H$_8$ obtained from a PdO(101) thin film (left) and TPD spectra of C$_2$H$_6$ and C$_3$H$_8$ obtained from Pd(111) (right) after exposing the surfaces to saturation doses of the alkanes at a substrate temperature of 85 K. The TPD spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 
Figure 3-3. TPD spectra of methane and ethane. (a) Ethane and (b) methane TPD spectra obtained from PdO(101) as a function of the initial alkane coverage prepared at a substrate temperature of 85 K. The TPD spectra were obtained using a constant heating rate of 1 K s⁻¹.
Figure 3-4. Binding energies of alkanes on PdO(101) and Pd(111) plotted as a function of alkane chain length. The open and solid circles correspond to binding energies on PdO(101) calculated using the minimum and maximum pre-factors, respectively (Table 3-2). The asterisk represents the binding energy computed for CH4 on PdO(101) using the optimum pre-factor of 1014.7 s⁻¹ determined from an inversion-optimization analysis of the CH4 TPD data.
Table 3-1. Binding energies of alkanes on Pd(111) and PdO(101) determined from Redhead analysis of the TPD spectra. Pre-factors reported by Tait et al. [65] were used to compute the binding energies on Pd(111). The columns labeled as “min” and “max” show alkane binding energies on PdO(101) determined using the minimum and maximum pre-factors discussed in the text. The final columns show differences between binding energies estimated for alkanes on PdO(101) and Pd(111).

<table>
<thead>
<tr>
<th>Chain length</th>
<th>Binding Energy (kJ/mol)</th>
<th>Pd(111)</th>
<th>PdO(101)</th>
<th>PdO(101) - Pd(111)</th>
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</thead>
<tbody>
<tr>
<td>C_{1}H_{2N+2}</td>
<td></td>
<td>min</td>
<td>max</td>
<td>Δ_{min}</td>
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<td>31.4</td>
<td>44.3</td>
<td>56.3</td>
<td>12.9</td>
</tr>
<tr>
<td>3</td>
<td>44.5</td>
<td>56.9</td>
<td>72.0</td>
<td>12.4</td>
</tr>
</tbody>
</table>
Table 3-2. Desorption pre-factors used in the Redhead analysis of the TPD spectra. The desorption pre-factors for alkanes on Pd(111) are taken from prior work by Tait et al. [65]. The columns labeled “min” and “max” are the minimum and maximum pre-factors evaluated at the peak desorption temperatures of alkanes from PdO(101) using formulas suggested for freely mobile vs. completely immobile adsorbed alkanes [65].

<table>
<thead>
<tr>
<th>Chain length ( C_NH_{2N+2} )</th>
<th>( \log_{10}(\text{prefactor (s}^{-1}) )</th>
<th>Pd(111)</th>
<th>PdO(101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N )</td>
<td></td>
<td>min</td>
<td>max</td>
</tr>
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CHAPTER 4
OXIDATION OF METHANOL ON A PDO(101) THIN FILM

4.1 Motivation of Methanol Reactivity

Understanding the surface chemistry of late transition metal (TM) oxides is central to many applications of oxidation catalysis that occur under oxygen-rich conditions, including the catalytic combustion of hydrocarbons, exhaust gas remediation in automobiles and catalytic oxidation in fuel cells. Under oxidizing conditions, various surface and bulk oxide phases can develop on late TM surfaces that can cause dramatic changes in catalytic properties. An example that is particularly relevant to the present study is the finding that bulk PdO is highly active for the complete oxidation of methane and that the formation of bulk-like PdO is responsible for the exceptional activity of supported Pd catalysts in the catalytic combustion of natural gas under fuel-lean conditions.[3] Consistent with these findings, we have recently shown that the activation and complete oxidation of H$_2$ and $n$-alkanes ($> C_2$) is highly facile on a PdO(101) thin film grown under ultrahigh vacuum (UHV) conditions.[32; 66] Both the ease of reduction of PdO and the availability of coordinatively unsaturated (cus) Pd atoms affords the PdO(101) surface with this high activity. In the present study, we investigated the oxidation of CH$_3$OH on PdO(101) in an effort to gain further insights into the chemical properties of this oxide surface.

Past surface science studies provide detailed information about the chemistry of methanol on clean and oxygen-modified transition metal surfaces.[55; 67-79] This prior work demonstrates that adsorbed oxygen atoms significantly enhance the chemical
reactivity of TM surfaces toward methanol, producing diverse oxidation chemistry. A critical role of the adsorbed oxygen atoms is to promote the initial deprotonation of methanol into the more strongly-bound methoxy intermediate. Madix and coworkers first showed that adsorbed oxygen atoms facilitate methanol deprotonation by acting as Bronsted bases that abstract the acidic H-atoms of adsorbed methanol molecules.[67; 70] The resulting methoxy groups react further on the surface, with the reaction selectivity depending on both the surface and the oxygen coverage. Recent studies of methanol oxidation on Au(111) show a dramatic effect of the oxygen coverage.[72] Complete oxidation of methanol is favored at high coverages of atomic oxygen on Au(111),[72; 73; 80] but the reaction selectivity shifts strongly toward methanol esterification at lower oxygen coverages.[72] Methanol reacts by several pathways on oxygen-covered Pd(111), including dehydrogenation to CH₂O and complete oxidation to CO₂ and H₂O.[76] Decomposition pathways on metal domains also produce CO and H₂. In addition to the products reported for methanol on oxygen-covered Pd(111), methyl formate is also observed as a product from methanol adsorbed on oxygen-covered Pd(100).[69]

Our previous work demonstrates that the PdO(101) surface has versatile chemical properties, and is likely to interact strongly with methanol. Most of this work has focused on the reactivity of PdO(101) toward saturated molecules. We find that PdO(101) readily activates alkanes and H₂ at low temperature, and that the resulting fragments undergo complete oxidation during continued heating.[32; 42; 66] The ability to activate sigma bonds is a characteristic of many transition metal surfaces that arises from the participation of d-electrons in the molecule-surface interaction. In addition,
however, we find that the bonding of water on PdO(101) is analogous to that seen on oxides in that the $\text{H}_2\text{O}$ molecule binds strongly to a cus-Pd atom through a donor-acceptor interaction.[33] Our results also provide evidence that $\text{H}_2\text{O}$-$\text{HO}$ dimers prefer to form along the cus-Pd rows, and that $\text{H}_2\text{O}$ dissociation occurs by proton transfer to a cus-O site. This finding demonstrates that the cus-O sites on PdO(101) can act as Bronsted bases that react with proton donors such as methanol. Taken together, these prior investigations show that PdO(101) has chemical properties that are characteristic of both transition metals and oxides, and thus that the PdO(101) surface is likely to react strongly with methanol.

4.2 Experimental Details

Previous studies[37; 38] provide details of the three-level UHV chamber utilized for the present experiments. The Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder that is held in thermal contact with a liquid nitrogen cooled reservoir. A type K thermocouple spot-welded to the backside of the crystal allows sample temperature measurements. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports maintaining or linearly ramping the sample temperature from 81 K to 1250 K. Initially, sample cleaning consisted of sputtering with 600 eV Ar$^+$ ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to 923 K to desorb oxygen and carbon oxides. As discussed previously,[11] we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in
preparing the PdO(101) thin films used in this study. We considered the Pd(111) sample to be clean when we could no longer detect contaminants with X-ray photoelectron spectroscopy (XPS), obtained sharp low energy electron diffraction (LEED) patterns consistent with the Pd(111) surface, and did not detect CO or CO\textsubscript{2} production during flash desorption after oxygen adsorption.

A two-stage differentially-pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system.[37; 38] To produce a PdO(101) thin film, we expose a Pd(111) sample held at 500 K to an \( \sim 12 \) ML dose of gaseous oxygen atoms supplied in a beam, where we define 1 ML as equal to the Pd(111) surface atom density of \( 1.53 \times 10^{15} \) cm\(^{-2}\). This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains \( \sim 3.0 \) ML of oxygen atoms and is about 12 Å thick.[11; 12] The structure of the PdO(101) surface is discussed in detail below.

We exposed our sample to CH\textsubscript{3}OH (Fisher Scientific, 99.9%) using a calibrated beam doser with the sample located about 50 mm from the end of the doser to ensure uniform impingement of the gases across the surface. We used several freeze-pump-thaw cycles to purify the methanol prior to admission into the UHV chamber. After the CH\textsubscript{3}OH exposures, we collected TPRS spectra by positioning the sample in front of a shielded mass spectrometer at a distance of about 10 mm and then heating at a constant rate of 1 K s\(^{-1}\) until the sample temperature reached 923 K. Because the PdO film decomposes when heated to 923 K, it was necessary to prepare a fresh PdO thin film for each adsorption/reaction experiment.
In initial TPRS experiments, we monitored a wide range of desorbing species to identify the main products that are generated from reactions of methanol on PdO(101). We specifically conducted TPRS experiments in which we monitored each mass between 1 to 100 amu using a short dwell time and a heating rate of 0.5 K s$^{-1}$. These experiments reveal that the only species desorbing from the PdO(101) sample after methanol adsorption at various coverages are H$_2$, H$_2$O, CH$_3$OH, CH$_3$O, CH$_3$OCHO, O$_2$ and CO$_2$. In subsequent TPR$S$ experiments, we monitored only mass fragments that allow these species to be readily distinguished, which includes m/z = 2, 18, 28, 30, 31, 32, 44, 60. The 60 amu trace is representative of the desorption rate of only methyl formate as none of the other products dissociates in the ionizer to yield an m/z = 60 fragment. The TPRS traces that we present for CH$_2$O and CH$_3$OH are obtained from the 30 and 31 amu traces, respectively, after correcting for fragmentation of relevant species in the ionizer. We used fragmentation patterns reported in the NIST database[81] to convert the mass-fragment TPRS traces into species TPRS traces. To assess the accuracy of this approach, we measured the fragmentation patterns of CH$_3$OH and CH$_3$OCHO and obtain excellent agreement with the data reported by NIST.

We estimate absolute product yields and coverages using similar procedures as described previously.[11; 31; 32; 39; 42] To estimate atomic oxygen coverages, we scale O$_2$ TPD spectra with desorption spectra obtained from Pd(111) covered with 0.25 ML of atomic oxygen prepared by exposing the surface to O$_2$ at 300 K.[39] Similarly, we estimate the H$_2$ and H$_2$O yields by scaling the corresponding desorption spectra to those obtained from monolayers of hydrogen and H$_2$O on Pd(111) and assuming that the atomic hydrogen and H$_2$O monolayers saturate at coverages of 1.0 ML[40] and 0.66
ML[41] on the Pd(111) surface, respectively. Investigations of H₂ and H₂O adsorption on PdO(101) attest to the accuracy of these scalings.[33; 42] We calibrated the CO₂ desorption yields by monitoring the production of CO₂ during CO oxidation on oxygen-covered Pd(111) and using a limiting amount of adsorbed atomic oxygen such that the CO₂ yield is equal to the initial atomic oxygen coverage. Prior work demonstrates that this procedure provides accurate estimates of the CO₂ yields.[33; 37] Finally, we estimate CH₃OH coverages by scaling integrated desorption spectra with TPD spectra obtained from a physically adsorbed monolayer of CH₃OH prepared on Pd(111) at 90 K and assuming a saturation coverage of 0.58 ML for the CH₃OH monolayer on Pd(111) as reported by Winograd et al.[82] As discussed below, we also used a different approach to estimate the methanol saturation coverage on Pd(111) and obtain excellent agreement with the value report by Winograd et al.[82]

We employ the procedure described by Ko et al.[83] to estimate the absolute yields of CH₃OCHO and CH₂O. These authors describe an approach for estimating normalization factors that can be used to scale mass spectrometer signal intensities obtained from various species to that obtained from one species. Ko et al. specifically applied this approach to products that evolve during the oxidation of methanol on oxygen-covered W(100).[83] The normalization factors take into account differences in ionization efficiencies, mass spectrometer gain, ion transmission and the fragmentation patterns of the parent molecules. In the present study, we referenced normalization factors reported by Ko et al.[83] to the methanol signal intensity and applied these factors to rescale the methyl formate and formaldehyde signals. We then estimate the absolute yields of methyl formate and formaldehyde by comparison with the absolute
yield of methanol determined using the method described above in which we assume that the CH$_3$OH monolayer on Pd(111) saturates at a coverage of 0.58 ML. To assess the accuracy of this approach, we rescaled the methanol signals using a normalization factor defined relative to H$_2$O, and then computed the methanol saturation coverage on Pd(111) based on our estimates of H$_2$O coverages on this surface, which we have previously found to give an accurate description of H$_2$O adsorption on PdO(101).[12] This calculation predicts the same methanol saturation coverage on Pd(111) as reported by Winograd et al.[82]

Finally, we performed XPS measurements using Mg K$_\alpha$ X-rays (h$_v$ = 1253.6 eV) with the sample oriented with its surface normal aligned with the axis of the hemispherical analyzer. In the XPS measurements, we operated the hemispherical analyzer in a retarding mode with a pass energy of 27 eV. We processed the XPS spectra by smoothing with ten-point adjacent averaging, followed by background subtraction using the Shirley method.

4.3 Experimental Results

4.3.1 Structure of the PdO(101) Thin Film on Pd(111)

Figure 4-1 depicts the structure of the stoichiometric PdO(101) surface that we examined in this study. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell of dimensions $a = 3.04$ Å and $b = 6.14$ Å, where the $a$ and $b$ lattice vectors coincide with the [010] and [101] directions of the PdO crystal, respectively. The PdO(101)-PdO surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the $a$ direction shown in Fig. 4-1. Thus, half of the surface O and Pd atoms are
coordinatively unsaturated (cus) and consequently more active than the fourfold coordinated atoms for binding adsorbed molecules. The areal density of each type of coordinatively-distinct atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML (monolayer), and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms. Given that the film contains ~3.0 ML of oxygen atoms, we estimate that the PdO(101) film on Pd(111) consists of between four and five layers and has a total thickness of ~12 Å. In a prior study,[11] we found that the PdO(101) structure aligns with the close-packed directions of the Pd(111) substrate, and would expand by 0.46% and 3.4% in the $a$ and $b$ directions to achieve commensurability with the metal substrate, which corresponds to unit cell dimensions of $a = 3.06$ Å and $b = 6.35$ Å.

4.3.2 CH$_3$OH Oxidation on PdO(101) at Low Coverage

Figure 4-2 shows TPRS spectra obtained after adsorbing ~0.10 ML of CH$_3$OH on the PdO(101) surface at 90 K. The data shown here is representative of the behavior observed at low methanol coverage. The TPRS data shows that CO$_2$ and H$_2$O are the main products that desorb during the experiment, and thus that the majority of the adsorbed CH$_3$OH is completely oxidized by the PdO surface at low methanol coverages. Hydrogen also desorbs in a broad feature centered at ~300 K that arises mainly from background adsorption.[84]

At low methanol coverage, water evolves in two features centered at 335 K and 450 K, while CO$_2$ desorbs in a single feature at 450 K. A small quantity of water (~0.03 ML) also desorbs in a broad shoulder that extends from 500 to ~650 K, which we have previously attributed to H$_2$O desorption from surface defects.[12] Based on prior studies,[12; 33; 42; 66] we attribute the H$_2$O feature at ~335 K to desorption-limited
water. The observation of desorption-limited water indicates that CH$_3$OH partially dehydrogenates on PdO(101) at low temperature (< 300 K), thus generating adsorbed H atoms that subsequently react with the surface to produce water during continued heating.

The concurrent desorption of H$_2$O and CO$_2$ at ~450 K is characteristic of the reaction-limited oxidation of an organic fragment. We have reported qualitatively similar behavior in TPRS experiments of alkane oxidation on PdO(101).[32; 66] From integration of the TPRS traces, we estimate that between 43% and 59% of the water desorbs in the reaction-limited feature at 450 K at the low initial CH$_3$OH coverages (≤ 0.12 ML) where complete oxidation is dominant. This estimate suggests that the reaction-limited CO$_2$ and H$_2$O result from the oxidation of an organic fragment with an H:C atomic ratio between 1.7 and 2.3. Note that it is not known if the H$_2$O desorbing from defects, above ~500 K, originates from H atoms that are produced mainly below the peak temperature for desorption-limited water or above this temperature. We considered both possibilities in our analysis and thus estimate the range of values stated above for the yield of reaction-limited H$_2$O. In particular, we decomposed the H$_2$O TPRS trace into regions between 250 and 380 K, 380 and 500 K and 500 to 700 K, where 380 K lies in the valley separating the main desorption maxima. We then considered that the reaction-limited H$_2$O yield corresponds to water desorbing either between 380 and 500 K or between 380 and 700 K, and that the balance of the water arises from H-atoms that are released from CH$_3$OH below the temperature at which desorption-limited water evolves.
4.3.3 CH$_3$OH Oxidation on PdO(101) at High Coverage

We find that partial oxidation dominates over the complete oxidation of methanol at high initial CH$_3$OH coverages. Figure 4-3 shows TPRS spectra obtained after adsorbing approximately 1.0 ML of CH$_3$OH on PdO(101) at 90 K. We estimate that about 0.60 ML of the CH$_3$OH desorbs during the TPRS experiment, with the remainder reacting on the surface to yield both complete and partial oxidation products. As seen in Fig. 4-3, the CH$_3$OH desorption trace exhibits a multilayer peak at 145 K and a broader peak at ~190 K. The top of the multilayer peak is omitted from Fig. 4-3 for clarity. The broad peak shifts from about 205 K to 190 K with increasing methanol coverage. Intermolecular interactions are likely responsible for the downshift observed in this case. For example, we find that methanol adsorbed in a monolayer on Pd(111) also desorbs in a peak near 190 K, with the desorption peak exhibiting a slight downshift with increasing coverage. Thus, the methanol TPD peak obtained from PdO(101) is consistent with the molecular desorption of CH$_3$OH from the first layer. The first-layer peak saturates at a methanol yield of about 0.30 ML, which is close to the 0.35 ML surface density of 3-fold or 4-fold Pd atoms (Fig. 4-1). Given that ~0.40 ML of methanol reacts on the surface at saturation of the monolayer (shown below), a plausible interpretation is that all of the CH$_3$OH adsorbed on cus-Pd sites reacts during the TPRS experiments, and that the first-layer methanol TPD peak originates from CH$_3$OH molecules adsorbed on the 4-fold Pd facet.

The TPRS data shown in Fig. 4-3 reveals that CH$_3$OH adsorbed in high coverages undergoes partial oxidation to methyl formate (CH$_3$OCHO) and formaldehyde (H$_2$CO) in addition to complete oxidation to CO$_2$ and H$_2$O. Desorption of H$_2$ and H$_2$O accompanies the evolution of methyl formate and formaldehyde in the high-coverage
experiments. We could detect no other partial oxidation products during TPRS, such as CO and formic acid. The partial oxidation products desorb over a relatively narrow temperature range from ~285 to 305 K, yielding overlapping TPRS peaks (Fig. 4-3). Among these products, CH₃OCHO desorbs first at ~285 K, followed by CH₂O at 295 K and H₂ at 305 K. Water also desorbs in a distinct peak that overlaps the sharp H₂ peak at 305 K. Note that desorption-limited H₂O evolves in a peak centered at 335 K when the methanol coverage is below ~0.1 ML (Fig. 4-2).

The narrow temperature range over which methyl formate and formaldehyde desorb suggests that a common intermediate or similar rate-determining step controls the rates at which these species are generated. Madix and coworkers have reported similar behavior in the oxidation of methanol on several oxygen-covered surfaces, including those of the coinage metals[67; 70] as well as Pd(100).[69] These workers have established that C-H bond cleavage of adsorbed methoxy groups is the rate-determining step in the partial oxidation of methanol in these systems. More recently, Xu et al.[72] have shown that C-H bond cleavage of adsorbed methoxy is also rate-determining in the esterification of methanol on oxygen-covered Au(111). In that case, CH₃OH and CH₃OCHO desorb simultaneously during TPRS after the adsorption of CH₃OD at low temperature, which demonstrates that the desorption of both products is determined by the rate of C-H bond cleavage of adsorbed CH₃O groups. Our results are consistent with these previous findings in that we also observe nearly concurrent desorption of the partially oxidized products (CH₃OCHO and CH₂O). However, we observe negligible desorption of CH₃OH over the temperature range for methyl formate.
and formaldehyde desorption, and thus conclude that the recombination of H-atoms and adsorbed methoxy groups is unfavorable on PdO(101) under the conditions studied.

4.3.4 Comparison of Products Obtained at Low vs. High Methanol Coverage

Figure 4-4 compares the H₂, H₂O and CO₂ TPRS spectra obtained during the low and high coverage experiments summarized in Figures 4-2 and 4-3. The close overlap of the CO₂ peaks demonstrates that the amount of CH₃OH which completely oxidizes reaches a saturation value at low methanol coverage (~0.12 ML) and remains steady with increasing coverage thereafter. The CO₂ peak obtained at high methanol coverage is slightly broader than the peak obtained at low coverage. This broadening may result from the greater extent of surface reduction that occurs prior to CO₂ desorption at high initial methanol coverage. As discussed above, the H₂O desorption trace obtained in the low coverage experiment exhibits two distinct peaks that arise from desorption and reaction-limited H₂O. The shapes and temperatures of these peaks agree well with those obtained previously in TPRS experiments of alkane oxidation on PdO(101).[32; 66] The H₂O trace obtained in the high coverage experiment also exhibits desorption and reaction-limited features. The reaction-limited H₂O feature obtained at high methanol coverage is less intense than that obtained in the low-coverage experiment, though the reaction-limited peaks are both centered at 450 K.

Compared with the reaction-limited peak, the desorption-limited H₂O feature obtained at high methanol coverage differs more significantly from that obtained at low methanol coverage. In particular, approximately twice the amount of H₂O evolves in the desorption-limited feature during the high vs. low coverage methanol experiments (~0.16 vs. 0.08 ML), and the desorption-limited H₂O feature obtained in the high-coverage experiment is clearly composed of distinct peaks centered at ~305 and 335 K.
Figure 4-4 also shows that the H$_2$O peak at 305 K evolves concurrently with the sharp H$_2$ peak seen in the high-coverage experiment, which suggests that the generation of these products involves similar steps or local environments. We elaborate on the possible origin of the H$_2$O peak at 305 K in the Discussion section. It is worth noting that we have previously found that the H$_2$O binding energy on PdO(101) is quite sensitive to the local H$_2$O coverage on the cus-Pd rows.[33] We found that adsorbed H$_2$O molecules increasingly encounter unfavorable configurations with increasing coverage, which causes the local binding energy to decrease and the H$_2$O TPD peak to broaden toward lower temperatures. In a similar way, water molecules produced at high methanol coverages may experience repulsive interactions with nearby CH$_3$O groups or other species.

The H$_2$O trace obtained at high methanol coverage also exhibits a peak at about 175 K, which coincides with the temperature range over which methanol desorbs (Fig. 4-3). This H$_2$O feature originates from reactions of methanol within the ionizer of the mass spectrometer and/or on the internal surfaces of the vacuum chamber. Separate measurements support this interpretation. For example, the methanol fragmentation pattern that we measure exhibits a larger H$_2$O signal than that reported in the NIST database. We also find that the relative intensity of the H$_2$O signal obtained from methanol is sensitive to the filament material used in the ionizer. In contrast, we find that the relative intensity of the H$_2$O peak at 305 K obtained in the methanol TPRS experiments is insensitive to the filament material. We also obtain good agreement with the reported fragmentation pattern of methyl formate; this observation demonstrates that the H$_2$O peak at 305 K does not originate from reactions of methyl formate in the
ionizer. While we did not conduct similar tests with formaldehyde, we believe that the tests conducted support our conclusion that the H$_2$O peak at 305 K originates from the desorption of H$_2$O from the PdO(101) surface, whereas the H$_2$O peak at 175 K is clearly an artifact associated with reactions of methanol within the mass spectrometer.

The appearance of a sharp H$_2$ peak indicates that hydrogen atoms encounter meta-stable binding environments on PdO(101) when they are released from adsorbed methanol (or methoxy) during the formation of methyl formate and formaldehyde at high methanol coverages. In prior studies, we found that H-atoms released during alkane decomposition on PdO(101) undergo negligible recombinative desorption, and instead are completely oxidized to H$_2$O that evolves in desorption and reaction-limited peaks.[32; 66] The H$_2$O features seen in our previous alkane experiments are analogous to the features obtained in the present study at low methanol coverages (Fig. 4-4). TPRS spectra obtained following H$_2$ adsorption on PdO(101) also exhibit a prominent desorption-limited H$_2$O feature at 335 K, and only a small recombinative H$_2$ desorption feature that is consistent with H atoms recombining at surface defect sites.[42] DFT calculations suggest that the strong preference for complete oxidation of adsorbed H-atoms arises largely from the stronger bonding of H atoms on cus-O sites compared with sites along the cus-Pd row of PdO(101). This stronger bonding also causes C-H and H-H bond dissociation of adsorbed alkanes and H$_2$, respectively, to preferably involve hydrogen transfer to cus-O sites.[42; 85]

In the present study, the sharp H$_2$ peak begins to appear only at relatively high methanol coverages, and is associated with the production of the partial oxidation products, methyl formate and formaldehyde. We assert that the preparation of high
methanol coverages on PdO(101) generates high concentrations of H-atoms along the cus-O sites that act to impede further hydrogen transfer to the cus-O sites, where the initially released H-atoms originate from O-H bond cleavage of methanol to produce CH$_3$O-Pd$_{cus}$ and HO$_{cus}$ groups. As a result of the cus-O site blocking, hydrogen atoms that are released during C-H bond cleavage at high methanol coverage are forced to bind on sites along the cus-Pd row. According to DFT calculations, recombinative desorption of H-atoms adsorbed on the cus-Pd row is facile due to their relatively weak binding.[42] Interestingly, C-H bond cleavage occurs readily even when all of the cus-Pd and cus-O atoms are occupied by adsorbed CH$_3$O groups and H atoms, respectively. We thus assert that C-H bond cleavage at high methanol coverages initially releases H-atoms to sites located between the Pd atoms of the cus-Pd row. Recent DFT calculations predict that H-atoms can adsorb into stable states between the cus-Pd atoms, though the binding is relatively weak.[42]

4.3.5 Variation of Product Yields with Methanol Coverage

Figure 4-5 shows the yields of carbon-containing reaction products obtained during TPRS as a function of the initial methanol coverage on PdO(101) prepared at 90 K. The methyl formate yield shown in Figure 4-5 is multiplied by a factor of two and thus represents the amount of adsorbed methanol that couples to produce methyl formate. The yield data shows that complete oxidation is the main reaction channel at low methanol coverages, while methanol esterification becomes dominant at high coverages (Fig. 4-5). The CO$_2$ yield rises sharply as the methanol coverage increases to ~0.12 ML, reaching a plateau value of 0.11 ML. Relatively small quantities of formaldehyde are also produced in the low coverage regime. The formaldehyde yield is ~0.03 ML when the CO$_2$ yield first plateaus at 0.11 ML. Methyl formate production is
negligible in the low-coverage regime, but initiates abruptly once the methanol coverage increases beyond 0.12 ML. This behavior reveals that the complete vs. partial oxidation channels dominate over distinct coverage regimes, separated at a methanol coverage equal to approximately one-third of the cus-Pd site density. The yields of methyl formate and formaldehyde begin to plateau as the methanol coverage passes ~0.50 ML. We estimate that ~0.40 ML of the adsorbed methanol is oxidized when the product yields have saturated, with methyl formate, formaldehyde and CO₂ accounting for ~52%, 22% and 26% of the methanol that reacts, respectively. Given that the cus-Pd atom density is equal to 0.35 ML, the yield data suggests that all of the methanol molecules which adsorb on cus-Pd sites undergo partial or complete oxidation under the conditions examined.

4.3.6 Adsorbate Characterization Using XPS

We also used XPS to characterize the decomposition of CH₃OH on PdO(101) as a function of the surface temperature at low vs. high methanol coverages. Changes in the O 1s spectrum are very challenging to interpret due to overlap between the O 1s and Pd 3p features as well as the dominance of the O 1s peak that arises from the PdO substrate. We thus considered only the C 1s spectra in our analysis. Fig. 4-6 shows C 1s XPS spectra obtained after adsorbing ~1 ML of CH₃OH on PdO(101) and then heating the surface to various temperatures, as specified in the figure. For 1.0 ML of methanol, we estimate that ~0.3 ML populates the multilayer while the remainder adsorbs in the first layer (Fig. 4-3).

At 90 K, the C 1s spectrum exhibits a large peak at 286.1 eV and a small feature centered at 292 eV. The main peak is rather broad with a FWHM of 3.0 eV. The binding energy of the main peak agrees well with the C 1s binding energy of 286.2 eV reported
by Levis et al.\cite{86} for methanol adsorbed in a monolayer on Pd(111). Levis et al. also report binding energies of 286.7 eV for the CH$_3$OH multilayer and 285.9 eV for CH$_3$O adsorbed on oxygen-covered Pd(111). The considerable width of the C 1s peak seen in Fig. 4-6 is thus consistent with the presence of a mixture of monolayer and multilayer CH$_3$OH and possibly CH$_3$O. The agreement between the C 1s binding energies for methanol adsorbed on Pd(111) and PdO(101) suggests that methanol (and methoxy) experiences similar bonding with both surfaces. Higher values of the C 1s binding energy have been reported for methanol adsorbed on other transition metal oxide surfaces. For example, the C 1s binding energy is reported to be 287.4 and 287.9 eV for methanol adsorbed on TiO$_2$(001)\cite{87} and CeO$_2$(111)\cite{88}, respectively. The small feature observed at 292 eV in the C 1s spectrum is consistent with carbonate species that are produced by the adsorption of CO or CO$_2$ from the background gas. Support for this assignment comes from separate measurements in which we observe a similar C 1s peak after exposing the clean PdO(101) surface to a hot filament. Carbon contamination develops during the XPS measurements due to the extended time that the sample is maintained at low temperature as well as the higher background pressure that results by operating the X-ray source.

After heating to 165 K to desorb the multilayer species, the main C 1s peak exhibits slight broadening mainly toward the high binding energy side, but is otherwise unchanged. Subsequent heating to 240 K causes first-layer CH$_3$OH to desorb (Fig. 4-3), while avoiding desorption of the oxidation products. The corresponding C 1s peak becomes broader than that obtained from the initial CH$_3$OH layer but remains centered at 286.1 eV. The slight broadening toward higher BE suggests that a fraction of the
methanol transforms to more highly oxidized species upon heating to 240 K. Overall, however, most of the methanol which remains on the surface undergoes an immeasurable change in oxidation state based on the close overlap of the C 1s peaks obtained at 240 K and those obtained before heating. Since the desorbing fraction of the adsorbed CH$_3$OH has been removed from the surface at 240 K (Fig. 4-3), the relative invariance of the C 1s binding energy suggests that most of the methanol remaining on the surface exists as methoxy species. Finally, the feature at 292 eV also intensifies slightly after heating to 240 K, indicating that the rate at which carbon contamination adsorbs on the sample increases after methanol desorbs from the first layer.

The C 1s spectrum changes most significantly after heating the sample to 350 K to desorb the partial oxidation products as well as a large portion of the desorption-limited H$_2$O. Heating to 350 K causes the main C 1s feature to broaden and shift to a higher binding energy of ~287.7 eV. The upward shift in the binding energy demonstrates that a large fraction of the remaining fragments becomes partially oxidized upon heating to 350 K. Spectral intensity is also evident near the original C 1s binding energy obtained from the CH$_3$OH layer, which suggests that a fraction of the methoxy groups did not oxidize during the experiment. The small feature centered at ~282.5 eV appears to correspond to noise that is accentuated by the background subtraction procedure.

We propose that adsorbed dioxymethylene (CH$_2$O$_2$) species are primarily responsible for the C 1s feature observed at 287.7 eV. This binding energy is consistent with reports for adsorbed dioxymethylene (CH$_2$O$_2$) as well as formate (CHO$_2$), and
indeed both of these species have been proposed as intermediates in the oxidation of methanol on oxygen-covered metal surfaces.[67; 76] Previous studies report C 1s binding energies of 287.7 eV and 288.2 eV for CH$_2$O$_2$ species adsorbed on oxygen-covered Cu(110)[89] and the CeO$_2$(111)[88] surface, respectively, where the CH$_2$O$_2$ species were generated by CH$_2$O adsorption in those cases. The C 1s binding energies of formate adsorbed on various oxide surfaces lie at least 1 eV higher (~289-290 eV) than the binding energy that we observe in the present study after heating the methanol layer.[87; 90-93] However, binding energies reported for formate adsorbed on metal surfaces (~287-288 eV) are close to the C 1s peak position seen in our experiments.[89; 94] We are thus unable to make an unambiguous peak assignment based only on the available C 1s data. Recall that the H$_2$O TPRS data reveals that about half of the hydrogen from adsorbed methanol evolves in the desorption-limited H$_2$O feature at low initial CH$_3$OH coverages, which implies that partial oxidation up to ~350 K produces an adsorbed species with a H:C ratio of about two. Based on this observation as well as additional quantification of the product yields, which we elaborate below, we conclude that the C 1s peak near 287.7 eV arises primarily from adsorbed CH$_2$O$_2$. At higher temperatures, the CH$_2$O$_2$ species most likely convert to formate prior to completely dehydrogenating to produce CO$_2$. Overall, the C 1s data demonstrates that the partial oxidation of high coverages of CH$_3$OH or CH$_3$O occurs to only a limited extent below 240 K, but occurs more readily between 240 and 350 K. After heating to 350 K, the majority of the organic fragments that remain adsorbed are more highly oxidized than CH$_3$OH or CH$_3$O.
A key issue is whether the formation of CH$_2$O$_2$ is limited by the surface temperature or the adsorbate coverage. To address this question, we collected C 1s spectra after generating a low CH$_3$OH coverage and then heating to various temperatures. Fig. 4-7 compares C 1s spectra for CH$_3$OH coverages of ~0.18 and 1.0 ML on PdO(101) obtained at the preparation temperature of 90 K and after heating to 350 K. The C 1s spectrum obtained from the low CH$_3$OH coverage exhibits a broad feature that appears to consist of separate features centered at 286.1 eV and 287.7 eV, consistent with adsorbed CH$_3$OH/CH$_3$O and CH$_2$O$_2$, respectively. Thus, a large portion of the adsorbed CH$_3$OH is partially oxidized at a temperature as low as 90 K when the initial CH$_3$OH coverage is low. In contrast, we observe a narrower C 1s peak centered at 286.1 eV from the high coverage CH$_3$OH layer after preparation at 90 K, which is consistent with the presence of only CH$_3$OH and possibly CH$_3$O species. After heating to 350 K, the C 1s spectra obtained from the low and high coverage layers overlap closely, both exhibiting maxima at ~287.7 eV. The C 1s data thus demonstrates that CH$_3$OH oxidation to CH$_2$O$_2$ is intrinsically facile on PdO(101), but that this reaction is inhibited at high CH$_3$OH coverages.

4.4 Discussion

We find that the complete oxidation of methanol is favored on PdO(101) at low methanol coverages, while partial oxidation reactions become dominant at high coverage. The availability of cus-O sites appears to play a key role in determining the branching between the complete and partial oxidation pathways. In particular, we present evidence that cus-O sites are required for the irreversible formation of a CH$_2$O$_2$ species which acts as an intermediate in the complete oxidation of methanol on PdO(101). At low methanol coverage, cus-O sites are present in sufficient
concentrations to accommodate the transformation of adsorbed CH$_3$OH to the CH$_2$O$_2$ intermediate. At high methanol coverages, the reaction selectivity shifts toward partial oxidation because hydrogenation of cus-O sites renders these sites effectively inactive for CH$_2$O$_2$ formation. Desorption of the partially oxidized products as well as H$_2$O partially restores the ability of the surface to accommodate CH$_2$O$_2$ formation due to the regeneration of vacant cus-O sites, thus returning the selectivity toward favoring complete oxidation.

4.4.1 Complete Oxidation of Methanol

Dioxymethylene has been proposed as an intermediate during the oxidation of methanol on oxygen-covered metal surfaces,[76] and has been identified spectroscopically.[88; 89; 95] In the present study, evidence for the CH$_2$O$_2$ species comes firstly from the C 1s spectra obtained after methanol adsorption at low-coverage and after heating a high-coverage layer, where we observe C 1s binding energies that agree with previously reported values for adsorbed CH$_2$O$_2$. The H$_2$O TPRS spectra obtained at low methanol coverage provide additional evidence of CH$_2$O$_2$ formation as they reveal that the adsorbed CH$_3$OH molecules release roughly half of their H-atoms below ~400 K. The implication is that the reaction-limited H$_2$O feature originates from an intermediate with an H:C ratio of two, which is consistent with CH$_2$O$_2$.

The evolution of product yields with increasing methanol coverage further supports the idea that the irreversible formation of CH$_2$O$_2$ is a key step toward complete oxidation of methanol on PdO(101). We find that the maximum yield of CO$_2$ occurs when the methanol coverage increases to ~0.12 ML, and remains steady with increasing coverage thereafter. A coverage of 0.12 ML is equal to roughly one third of the cus-O density. Thus, the maximum CO$_2$ yield is obtained when roughly three cus-O
atoms are available for each CH$_3$OH molecule to accommodate the formation of CH$_2$O$_2$. This behavior suggests that the overall stoichiometry of CH$_2$O$_2$ formation may be represented by the equation,

$$\text{CH}_3\text{OH- Pd}_{\text{cus}} + 3\text{O}_{\text{cus}} \rightarrow \text{Pd}_{\text{cus}}\text{-OCH}_2\text{-O}_{\text{cus}} + 2\text{HO}_{\text{cus}} \quad (1)$$

where our depiction of the dioxymethylene species assumes a bidentate configuration in which one end of the molecule binds to a cus-Pd site while the other end binds to the adjacent cus-O site.

The pathway toward CH$_2$O$_2$ is certain to occur in multiple steps. Most likely, the initial decomposition step of adsorbed CH$_3$OH involves transfer of the acidic H-atom to a cus-O site, resulting in CH$_3$O-Pd$_{\text{cus}}$ and HO$_{\text{cus}}$ moieties. Methoxy formation in this case may be represented by the following equation,

$$\text{CH}_3\text{OH(ad)} + \text{O}_{\text{cus}} \rightarrow \text{CH}_3\text{O(ad)} + \text{HO}_{\text{cus}} \quad (2)$$

where we use the symbol “(ad)” to indicate that a species is bound on top of a cus-Pd atom. Subsequently, C-H bond cleavage of the methoxy group and C-O$_{\text{cus}}$ bond formation would produce the dioxymethylene species, where these reactions may occur in a concerted process. The formation of the C-O$_{\text{cus}}$ bond requires a vacant cus-O site adjacent to the CH$_3$O-Pd$_{\text{cus}}$ species. The C-H bond cleavage step could involve H-atom transfer directly to a second cus-O site or to a site along the cus-Pd row. These reactions may be represented by the following equations,

$$\text{CH}_3\text{O(ad)} + 2\text{O}_{\text{cus}} \rightarrow \text{Pd}_{\text{cus}}^-\text{OCH}_2\text{-O}_{\text{cus}} + \text{HO}_{\text{cus}} \quad (3)$$

$$\text{CH}_3\text{O(ad)} + * + \text{O}_{\text{cus}} \leftrightarrow \text{Pd}_{\text{cus}}^-\text{OCH}_2\text{-O}_{\text{cus}} + \text{H}^* \quad (4)$$

In reaction (4), we assume that an H-atom is transferred to a site located between cus-Pd atoms, which we represent with the symbol “*”. Recall from the discussion above
that hydrogen transfer to sites between cus-Pd atoms can explain the observation of CH$_3$O dehydrogenation when the cus-Pd and cus-O sites are saturated with adsorbed species. While reaction (4) is viable, an H-atom released onto the cus-Pd row is likely to bond rapidly with the nearest vacant cus-O site, thus yielding an HO$_{\text{cus}}$ group as in reaction (3). Due to the high H-O$_{\text{cus}}$ bond strength, we speculate that formation of HO$_{\text{cus}}$ groups is effectively irreversible with respect to hydrogenation of the CH$_2$O$_2$ species to CH$_3$O, and that the HO$_{\text{cus}}$ groups ultimately transform to H$_2$O. Our data also suggests that the CH$_2$O$_2$ species are relatively stable on PdO(101) such that these species only undergo complete oxidation during heating, rather than transforming to other oxygenates that desorb. Moreover, dehydrogenation of the CH$_2$O$_2$ groups appears to occur only during the evolution of the reaction-limited CO$_2$ feature above ~400 K. Our interpretation thus asserts that complete oxidation is strongly favored when enough cus-O sites are available to accommodate the irreversible formation of CH$_2$O$_2$. This process requires enough cus-O sites to participate in C-O$_{\text{cus}}$ bond formation and to bind the H-atoms that are released during CH$_3$OH dehydrogenation to CH$_2$O$_2$.

According to the stoichiometric equation (1), the cus-O sites are able to accommodate the irreversible transformation of the all of the adsorbed CH$_3$OH molecules to CH$_2$O$_2$ up to a methanol coverage of ~0.12 ML. Above 0.12 ML, the excess methanol molecules begin to react by pathways that yield gaseous CH$_3$OCHO and CH$_2$O. Notice that, on average, CH$_3$O groups would be separated by two cus-Pd sites when the CH$_3$O coverage is equal to one third of the cus-Pd density. Additional CH$_3$O groups would thus bind on cus-Pd sites that are adjacent to other CH$_3$O groups, which is a necessary condition for methoxy groups to couple.
4.4.2 Partial Oxidation of Methanol

Characteristics of our TPRS data allow us to elicit several details about the mechanisms governing methyl formate and formaldehyde production on PdO(101). Firstly, the narrow temperature range over which CH$_3$OCHO and CH$_2$O desorb points toward a common rate-determining step or reaction intermediate in the formation of these species. Similar behavior reported for several other surfaces[67; 69; 72; 76] has been shown to arise from the rate-determining C-H bond cleavage of adsorbed CH$_3$O groups, resulting in adsorbed CH$_2$O species. In the present study, we find that the methyl formate peak temperature remains invariant with increasing methanol coverage, which implies that a first order process controls the methyl formate desorption rate. This observation is consistent with CH$_3$O dehydrogenation to adsorbed CH$_2$O acting as the rate-controlling step for CH$_3$OCHO and CH$_2$O production on PdO(101), in agreement with behavior reported for methanol oxidation on coinage metals.[67; 70; 72] Finally, the appearance of a sharp H$_2$ desorption peak only when methyl formate and formaldehyde are produced is a strong indication that the formation of these species involves hydrogen transfer from CH$_3$O groups to sites on the cus-Pd rows.

Taking these observations into account, we propose that the following reactions can describe the formation of CH$_3$OCHO and CH$_2$O on PdO(101),

\[
\begin{align*}
\text{CH}_3\text{O(ad) + *} & \rightarrow \text{CH}_2\text{O(ad) + H*} & (5) \\
\text{CH}_3\text{O(ad) + CH}_2\text{O(ad)} & \rightarrow \text{CH}_3\text{OCH}_2\text{O(ad) + Pd}_{\text{cus}} & (6) \\
\text{CH}_3\text{OCH}_2\text{O(ad) + *} & \rightarrow \text{CH}_3\text{OCHO(g) + H* + Pd}_{\text{cus}} & (7) \\
\text{CH}_2\text{O(ad)} & \rightarrow \text{CH}_2\text{O(g) + Pd}_{\text{cus}} & (8)
\end{align*}
\]
In this scheme, dehydrogenation of CH$_3$O(ad) first produces a CH$_2$O(ad) group via reaction (5) in which a H-atom is transferred to a site located between cus-Pd atoms. Due to the presence of a neighboring HO$_{\text{cus}}$ group, we consider that the CH$_2$O(ad) group interacts only weakly with the adjacent cus-O atom and is thus distinct from the CH$_2$O$_2$ species discussed above. Most likely, CH$_2$O(ad) rather than CH$_2$O$_2$ groups form at high methoxy coverages because high concentrations of HO$_{\text{cus}}$ groups prevent C-O$_{\text{cus}}$ bond formation. According to the proposed reaction scheme, a CH$_2$O(ad) group can desorb as CH$_2$O(g) or react with a CH$_3$O group to produce an CH$_3$OCH$_2$O(ad) species which subsequently dehydrogenates to produce methyl formate. This pathway for methyl formate production is analogous to that discussed by Wachs and Madix for methanol on oxygen-covered Ag(110).[67] Based on the above discussion, we assert that reaction (5) is the rate-determining step since this reaction produces the CH$_2$O(ad) species which serves as the common intermediate for methyl formate and formaldehyde formation. Reaction (5) is also first-order in the CH$_3$O(ad) coverage which is consistent with the invariance of the methyl formate peak temperature with increasing methanol coverage.

4.4.3 Water and Hydrogen Production

We lastly consider reactions leading to the desorption of H$_2$ and H$_2$O. Essential features are that only H-atoms adsorbed on the cus-Pd row can recombine to H$_2$, and that an H$_2$O formation reaction regenerates vacant cus-O sites. The generation of vacant cus-O sites is necessary to explain the observation of complete oxidation at high methanol coverages, as elaborated below. The following reactions provide a viable representation of the formation of H$_2$ and H$_2$O,

$$H^* + Pd_{\text{cus}} \rightarrow H(\text{ad}) + * \quad (9)$$
$H^* + H(\text{ad}) \rightarrow H_2 (g) + * + Pd_{\text{cus}}$ \hspace{1cm} (10)

$H(\text{ad}) + HO_{\text{cus}} \leftrightarrow H_2O_{\text{cus}} + Pd_{\text{cus}}$ \hspace{1cm} (11)

$2HO_{\text{cus}} \leftrightarrow H_2O_{\text{cus}} + O_{\text{cus}}$ \hspace{1cm} (12)

$H_2O_{\text{cus}} + Pd_{\text{cus}} \rightarrow H_2O(\text{ad}) + v$ \hspace{1cm} (13)

$H_2O(\text{ad}) \rightarrow H_2O(g) + Pd_{\text{cus}}$ \hspace{1cm} (14)

where the symbol “v” represents an oxygen vacancy along the cus-O row. Here, reactions (9) and (10) depict a pathway for the recombinative desorption of H$_2$, where a key feature is the requirement of a vacant cus-Pd site to allow H-atoms to come in close enough proximity to recombine. This aspect of the hydrogen association reaction can explain the observation that H$_2$ desorption begins to occur only after a large quantity of methyl formate has desorbed.

Steps (11) to (14) represent proposed reactions leading to H$_2$O desorption. Steps (11) and (12) depict separate processes that could produce an H$_2$O$_{\text{cus}}$ species, while steps (13) and (14) show a pathway by which the H$_2$O$_{\text{cus}}$ intermediate transforms to a more stable H$_2$O(\text{ad}) species that desorbs. In this scheme, we assume that the H$_2$O$_{\text{cus}}$ species is the intermediate to water evolution. Previous investigations present evidence that an analogous H$_2$O$_{\text{cus}}$ species is an intermediate in the oxidation of H$_2$ on RuO$_2$(110).[25; 26] We emphasize, however, that direct evidence of this species on PdO(101) is unavailable and thus that other intermediates may mediate H$_2$O formation instead. This detail is not critical to the present discussion. The important characteristics are that one of the H$_2$O formation reactions regenerates vacant cus-O sites, and that H$_2$O desorption occurs from cus-Pd sites. Similar to H$_2$ desorption, the requirement that H$_2$O desorbs from the H$_2$O(\text{ad}) state has the effect that H$_2$O desorption will begin to
occur at appreciable rates only after vacant cus-Pd sites are generated by the desorption of methyl formate and formaldehyde.

4.4.4 Product Evolution at High Methanol Coverage

The reactions discussed here can explain key aspects of the trends in product evolution that we observe at high methanol coverage. This can be best understood by considering the reactions that occur when the cus-Pd sites are initially saturated with methanol. In this case, methoxy formation via reaction (2) would saturate the cus-Pd and cus-O sites with CH$_3$O groups and H-atoms, respectively. The conversion of CH$_3$O to CH$_2$O$_2$ would be unable to occur due to the presence of H-atoms on the cus-O sites, which is consistent with the C 1s spectra discussed above. Thus, CH$_3$O groups would initially transform to methyl formate and formaldehyde via reactions (5) to (8). As methyl formate and formaldehyde desorb, vacant cus-Pd sites are continuously regenerated and the desorption of both H$_2$ and H$_2$O becomes possible according to reactions (9) to (14). If the energetics favor H$_2$ and H$_2$O desorption, then the H$_2$ and H$_2$O desorption rates would increase sharply as methyl formate and formaldehyde vacate cus-Pd sites. Thus, the proposed site requirements offer a plausible explanation for the emergence of relatively sharp H$_2$ and H$_2$O TPRS peaks at a temperature that is only 10 to 20 K above that for formaldehyde and methyl formate desorption, respectively.

Finally, our data shows that a similar quantity of methanol is completely oxidized during TPRS at initial CH$_3$OH coverages above ~0.12 ML, and that CH$_2$O$_2$ formation is facile at low coverage but only begins to occur at high coverages after a large portion of the H$_2$O desorbs. This behavior suggests that H$_2$O desorption regenerates vacant cus-O sites that subsequently react with the remaining CH$_3$O(ad) groups to produce CH$_2$O$_2$ and HO$_{\text{cus}}$ groups. According to the stoichiometric equation (1), the complete
conversion of 0.11 ML CH₃O groups to CH₂O₂ requires 0.22 ML of cus-O sites. From integration of the H₂O TPRS spectra, we estimate that ~0.18 ML of H₂O desorbs between 250 and 400 K when the methanol coverage is high enough to maximize the product yields. If H₂O formation occurs exclusively by HO cus disproportionation (reaction (12)), then 0.18 ML of cus-O sites would be produced as H₂O desorbs between 250 and 400 K. This estimate lies close to cus-O site concentration needed to produce 0.11 ML of CH₂O₂, and thus supports concluding that H₂O desorption regenerates vacant cus-O sites that can transform a fraction of the remaining CH₃O groups to CH₂O₂. We do not exclude the possibility that H₂O is also produced by reaction (11) in which case other processes for cus-O site regeneration would need to occur to account for CH₂O₂ production through the assumed stoichiometry for this reaction. For example, oxygen vacancies could be replenished with oxygen atoms from subsurface layers of the PdO film. Such processes should become more probable as the extent of surface reduction increases due to H₂O desorption. A key point is that regeneration of a large fraction of the cus-O sites can explain the finding that the CO₂ yield remains constant as the methanol coverage increases into the regime where partial oxidation reactions become dominant.

Surface reduction caused by the initial desorption of H₂O could influence the chemical transformations of adsorbed methoxy on PdO(101), especially considering that approximately half of the cus-O atoms evolve in the desorption-limited H₂O peak when the product yields are saturated. However, the TPRS spectra do not exhibit features that can be clearly attributed to reactions at reduced sites. For example, the reaction-limited H₂O and CO₂ TPRS peaks exhibit similar characteristics (peak
temperature, shapes) for all of the methanol coverages investigated, even though the amount of lattice oxygen that is removed prior to the evolution of these products varies significantly over the range of initial methanol coverages that we studied. The main change that we observe is that the reaction-limited CO\(_2\) and H\(_2\)O TPRS peaks broaden slightly as the initial methanol coverage is increased (Fig. 4-4). Furthermore, since methanol decomposition on metallic Pd surfaces produces CO and H\(_2\),\[69; 76\] it is reasonable to expect that reactions of methanol on reduced sites of PdO(101) would also generate CO and H\(_2\). For example, Mullins et al.\[88\] find that the reaction selectivity of methanol on CeO\(_2\)(111) surfaces shifts from CH\(_2\)O and H\(_2\)O production on the fully oxidized surface toward CO and H\(_2\) production as the ceria surface is progressively reduced. In the present study, we observe only CO\(_2\) and H\(_2\)O evolution after the release of desorption-limited water from PdO(101) for all initial methanol coverages investigated. Thus, reduced sites appear to have an insignificant influence on the product selectivity and desorption kinetics under the conditions studied. Reduced surface sites could, however, be important in other chemical reactions on PdO(101) or under different reaction conditions. Future studies using scanning tunneling microscopy should be particularly helpful for clarifying the coupling between reduction and possibly re-oxidation of the PdO surface and chemical transformations of adsorbed species.

4.4.5 Comparison Between Methanol and Alkane Oxidation

To conclude the discussion, it is instructive to compare the reactivity of methanol with that of alkanes on the PdO(101) surface. Recently, we have found that \(n\)-alkanes dissociate on PdO(101) at low temperature and that the resulting fragments are completely oxidized at higher temperatures during TPRS.\[32; 66\] The reaction-limited CO\(_2\) peak observed in the alkane studies evolves at nearly the same temperature as
that seen here during methanol oxidation. Our work shows that the formation of
adsorbed alkane σ-complexes facilitates initial C-H bond cleavage, resulting in
adsorbed alkyl groups. The relative yields of desorption to reaction limited H₂O that
evolves during TPRS further indicates that the resulting alkyl groups remain stable up to
~400 K, at which point they are completely oxidized by the surface. Based on the CO₂
yields, we estimate that 0.70 ML of oxygen atoms from the PdO(101) thin film are
incorporated into the CO₂ and H₂O products that evolve during TPRS after saturating
the surface with n-butane. [66] We observed even higher yields of CO₂ and H₂O in
experiments in which we cycled the adsorption and desorption of n-butane on PdO(101)
to generate higher coverages of butyl groups. These findings demonstrate that the
amount of oxygen that is incorporated into the CO₂ and H₂O products can greatly
exceed the 0.35 ML concentration of cus-O sites. For comparison, we estimate that a
maximum of 0.40 ML of oxygen atoms is removed from the PdO film due to oxidation of
adsorbed methanol.

These results demonstrate that the ability of the PdO film to release oxygen
atoms does not limit the complete oxidation of methanol at high coverages. The results
thus imply that adsorbed methoxy groups are less stable on PdO(101) than the alkyl
groups that we have studied. For instance, even when cus-O sites are unavailable for
hydrogen transfer, methoxy groups are not stable enough to remain on the PdO(101)
surface up to the temperatures at which oxygen atoms from within the PdO film become
sufficiently mobile to fully oxidize adsorbed organics. Instead, it is more favorable for the
methoxy groups to transform to methyl formate and formaldehyde via reactions that
involve H-atom transfer to the cus-Pd row. It is worth noting that we conducted initial
TPRS experiments after preparing layers of co-adsorbed methoxy and propyl groups on PdO(101), but did not observe new products such as those which could result from cross-coupling reactions. Indeed, our results demonstrate that the oxidation selectivity of PdO(101) toward adsorbed organics is determined by a delicate balance among several rate processes.

4.5 Summary

We investigated the oxidation of methanol on a PdO(101) thin film using TPRS and XPS. We find that complete oxidation is highly favored at CH₃OH coverages below ~0.12 ML, with nearly all of the adsorbed methanol molecules oxidizing to CO₂ and H₂O during TPRS. As the methanol coverage increases from 0.12 ML to ~0.50 ML, the CO₂ yield remains steady while the desorption yields of methyl formate and formaldehyde increase to saturation values. At high methanol coverage, methyl formate and formaldehyde constitute ~70% of the total yield of reacted methanol. Methanol begins to desorb from the surface only as the yields of methyl formate and formaldehyde first start to plateau at a methanol coverage of ~0.50 ML. This behavior suggests that all of the methanol molecules that adsorb on cus-Pd sites are oxidized by the surface during TPRS, and that the desorbing methanol originates from CH₃OH molecules that bind to the 4-fold Pd facet after methanol saturates the cus-Pd sites.

The availability of cus-O sites appears to be decisive in determining the branching between the partial and complete oxidation of methanol on PdO(101). Our data suggests that the irreversible transformation of adsorbed methanol to a bidentate CH₂O₂ species causes complete oxidation to dominate at low methanol coverages. According to XPS, the conversion of CH₃OH to CH₂O₂ is intrinsically facile on PdO(101), and occurs to a significant extent at temperatures as low as 90 K when the
methanol coverage is low. We present evidence that this reaction is irreversible when three cus-O atoms are available for each CH₃OH molecule. Once cus-O sites become the limiting reactant for CH₂O₂ formation, adsorbed methoxy groups begin to dehydrogenate by pathways that yield methyl formate and formaldehyde. Comparison with previous studies of alkane oxidation demonstrates that methoxy groups are less stable on PdO(101) than the alkyl groups that we have studied (n-C₃-C₅), and transform to methyl formate and formaldehyde rather than surviving to the higher temperatures (> 400 K) at which the PdO surface rapidly oxidizes adsorbed alkyl groups and CH₂O₂. Finally, this study serves to illustrate the diverse chemical properties of the PdO(101) surface. In particular, the present results reveal that the PdO(101) surface can efficiently promote the types of acid-base reactions that occur on many oxides and oxygen-covered metal surfaces, while also exhibiting a high propensity for σ-bond activation which is a characteristic of many transition metals.
Figure 4-1. Model representation of PdO(101) surface. (a) Top and (b) side view of the PdO(101) thin film structure. The red and gray atoms represent O and Pd atoms, respectively. Rows of 3-fold coordinated (cus) Pd and O atoms are indicated. The a and b directions correspond to the [010] and [101] crystallographic directions of PdO.
Figure 4-2. TPRS spectra of CH$_3$OH, H$_2$, CH$_3$OCHO, CH$_2$O, H$_2$O and CO$_2$ obtained from a PdO(101) thin film after adsorbing ~0.10 ML of CH$_3$OH at a substrate temperature of 90 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 

TPRS
CH$_3$OH + PdO(101)
$T_s = 90$ K
$[\text{CH}_3\text{OH}]_o = 0.10$ ML
Figure 4-3. TPRS spectra of CH$_3$OH, H$_2$, CH$_3$OCHO, CH$_2$O, H$_2$O and CO$_2$ obtained from a PdO(101) thin film after adsorbing ~1.0 ML of CH$_3$OH at a substrate temperature of 90 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$.
Figure 4-4. H₂, H₂O and CO₂ TPRS spectra obtained after adsorbing 0.1 ML and 1 ML of CH₃OH on a PdO(101) surface at 90 K. The TPRS spectra were obtained using a constant heating rate of 1 K s⁻¹.
Figure 4-5. Yields of carbon-containing desorption products obtained as a function of the initial methanol coverage on PdO(101). The yields were estimated from integrated TPRS spectra obtained after adsorbing methanol on a PdO(101) thin film at 90 K. Multiplying the methyl formate yield by two causes each data set to represent the quantity of methanol that reacts to the specified products.
Figure 4-6. XPS C 1s spectra obtained from PdO(101) surface after adsorbing ~1.0 ML of CH$_3$OH at 90 K and heating to the temperatures indicated.
Figure 4-7. XPS C 1s spectra obtained from PdO(101) after adsorbing 0.18 ML and 1.0 ML of CH$_3$OH at 90 K. The top of the graph shows C 1s spectra obtained after heating the methanol layers to 350 K.
5.1 Motivation of the Propane Selectivity Study

Alkane activation by transition metals has attracted considerable interest due to the desire to more effectively utilize these abundant natural resources as energy sources and to develop improved processes to convert alkanes to more valuable chemicals. A significant challenge in this area is the development of catalysts that afford both high activity and precise selectivity toward the initial C-H bond activation of low molecular-weight alkanes. Catalysts capable of selectively activating the primary C-H bonds of alkanes are particularly interesting since the thermodynamic preference is the cleavage of secondary or tertiary C-H bonds. Moreover, selective activation of the CH$_3$ groups would offer flexibility in developing synthetic processes for directly transforming alkanes to value-added products such as 1-alkenes and primary alcohols.

Alkane activation on transition-metal surfaces has been widely investigated,[10] but only a few studies have focused on characterizing regioselectivity in the initial C-H bond cleavage. On transition metal surfaces, the initial C-H bond selectivity tends to follow the thermodynamically preferred route, at least for the systems that have been investigated in detail. For example, molecularly adsorbed propane exhibits an energetic preference for 2$^\circ$ C-H bond cleavage on Pt(110),[96] Ir(111)[97] and Ru(0001),[98] with the activation energies for 1$^\circ$ vs. 2$^\circ$ C-H bond cleavage scaling with the homolytic bond dissociation energies; 412 kJ/mol for 1$^\circ$ C-H bonds, 404 kJ/mol for 2$^\circ$ C-H bonds.

A version of this chapter was previously published in the Journal of the American Chemical Society titled as "High Selectivity for 1$^\circ$ C-H Bond Cleavage of Propane $\sigma$-Complexes on the PdO(101) Surface" and reprinted with the permission from (J. F. Weaver, C. Hakanoglu, A. Antony and A. Asthagiri, J. Am. Chem. Soc., 2011, 133, 16196-16200) Copyright © (2011) American Chemical Society.
Computational studies also report a preference for 2° C-H bond cleavage in the activation of propane on molybdenum oxides[99] and a binary Fe-Sb oxide,[100] which are representative of catalysts used in applications of propane ammoxidation. Likewise, several metal oxide clusters exhibit a preference for 2° C-H bond activation of propane in the gas-phase.[101; 102] A recent investigation of alkane activation by the gas-phase MgO** ion is an exceptional case in which 1° C-H bond cleavage of both propane and n-butane is preferred.[103]

In prior work we have found that propane activation is highly facile on the PdO(101) surface, with initial C-H bond cleavage occurring readily in ultrahigh vacuum (UHV) below 200 K.[32] Our results reveal that propane activation on PdO(101) occurs by a precursor-mediated mechanism wherein a molecularly adsorbed state acts as a precursor for initial C-H bond cleavage and a kinetic competition between desorption and dissociation of the precursor determines the net dissociation probability. We have presented evidence based on experimental measurements as well as density functional theory (DFT) calculations that alkanes form σ-complexes on PdO(101) by bonding with coordinatively unsaturated (cus) Pd atoms at the surface, and that these complexes act as precursors for initial C-H bond activation.[34; 66] DFT calculations show clearly that dative bonding with the cus-Pd atoms significantly weakens the C-H bonds, making them easier to cleave. Finally, our experimental results show that the propyl groups generated during propane activation remain stable on the surface up to at least 400 K, at which point these species are completely oxidized by the PdO surface to produce CO₂ and H₂O which desorb.[32] Although partial oxidation products are more desirable, the stability of propyl groups on PdO(101) over a wide temperature range (~200 K) may
provide opportunities for steering the chemistry toward more valuable products. Overall, the alkane/PdO(101) system is ideally suited for investigating fundamental aspects of the activation of alkane σ-complexes and the oxidation chemistry of the resulting alkyl groups.

In this paper, we report results of a combined experimental and computational study of C-H bond selectivity in the low-temperature activation of propane on the stoichiometric PdO(101) surface. Differences in the reactivity among propane isotopologues reveal a strong preference for 1° C-H bond cleavage of propane on PdO(101), with the overall selectivity for generating 1-propyl groups equal to 90% at surface temperatures below 200 K. DFT calculations confirm that 1° C-H bond cleavage is the preferred pathway for propane activation on PdO(101), and predict that this selectivity arises from greater stabilities of both the initial state and the transition state for 1° vs. 2° C-H bond cleavage. According to DFT, stabilization of the transition structures arises largely from a substituent polarization mechanism, an effect which is analogous to the influence of alkyl substituents in determining the stability of gas-phase alkyl anions.

5.2 Experimental Details

Previous studies[37; 38] provide details of the three-level UHV chamber utilized for the present experiments. The Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder that is held in thermal contact with a liquid nitrogen cooled reservoir. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports maintaining or linearly ramping the sample temperature from 81 K to
1250 K. Initially, sample cleaning consisted of sputtering with 600 eV Ar$^+$ ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to 923 K to desorb oxygen and carbon oxides. As discussed previously,[11] we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in preparing the PdO(101) thin films used in this study.

A two-stage differentially-pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system.[37; 38] To produce a PdO(101) thin film, we expose a Pd(111) sample held at 500 K to an ~12 ML dose of gaseous oxygen atoms supplied in a beam, where we define 1 ML as equal to the Pd(111) surface atom density of $1.53 \times 10^{15}$ cm$^{-2}$. This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains ~3.0 ML of oxygen atoms and is about 12 Å thick.[11; 12] The structure of the PdO(101) surface is discussed in detail below.

We studied the reactivity of C$_3$H$_8$ (Matheson, 99.993%), (CH$_3$)$_2$CD$_2$ (Isotec, 98 atom% D), (CD$_3$)$_2$CH$_2$ (Isotec, 98 atom% D) and C$_3$D$_8$ (Isotec, 99 atom% D), denoted as propane-$d0$, $d2$, $d6$ and $d8$, respectively, on the PdO(101) surface using temperature programmed reaction spectroscopy (TPRS). Each gas was delivered to the sample surface through a molecular beam doser and was used at the purity supplied by the vendor. After the propane exposures, we collected TPRS spectra by positioning the sample in front of a shielded mass spectrometer at a distance of about 10 mm and then
heating at a constant rate of 1 K s\(^{-1}\) until the sample temperature reached 923 K. Because the PdO film decomposes when heated to 923 K, it was necessary to prepare a fresh PdO thin film for each adsorption/reaction experiment. We monitored the desorption of propane, water, CO\(_2\) and O\(_2\) since prior studies show that these are the only products to evolve from propane-covered PdO(101) during TPRS.[32; 34] The majority mass fragment of the propane fragmentation pattern corresponds to the ethyl radical, and the mass-to-charge ratio of this fragment is equal to \(m / z = 29, 31, 32\) and 34 for C\(_3\)H\(_8\), (CH\(_3\))\(_2\)CD\(_2\), (CD\(_3\))\(_2\)CH\(_2\) and C\(_3\)D\(_8\), respectively. We estimate absolute coverages and desorption yields using procedures described previously.[32; 34; 66; 104] We determined the absolute propane coverages from TPD experiments of propane on Pd(111), and calculated CO\(_2\) desorption yields by performing TPRS experiments of CO oxidation on oxygen-covered Pd(111).

5.3 Results and Discussion

5.3.1 Structure of Stoichiometric PdO(101)

A model representation of the stoichiometric PdO(101) surface that we investigated in this study is shown in Figure. 5-1. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell, where the \(a\) and \(b\) lattice vectors coincide with the [010] and [101] directions of the PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the \(a\) direction shown in Fig. 5-1. Thus, half of the surface O and Pd atoms are coordinatively unsaturated (cus). The side view of PdO(101) shows that the coordinative environment associated with each cus-Pd atom resembles a square planar Pd complex with a
coordination vacancy directed away from the surface and three oxygen ligands, one of
which is a cus-O atom. The areal density of each type of coordinatively-distinct atom of
the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface.
Hence, the coverage of cus-Pd atoms is equal to 0.35 ML (monolayer), and each
PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms.

5.3.2 Reactivity of Propane Isotopologues on PdO(101) Studied with TPRS

Figure 5-2 shows TPRS traces for propane and mass 44 amu (CO\textsubscript{2}) obtained in
separate experiments in which we adsorbed different propane isotopologues on
PdO(101) at 85 K. In these experiments, we initially populated the molecular precursor
state (\(\alpha_1\) state) to approximately the saturation coverage (\(~0.09\) ML) where the total
coverage of the adsorbed precursor is equal to the amount of molecular precursor
which desorbs plus the amount which dissociates and evolves as CO\textsubscript{2} and H\textsubscript{2}O. The
TPRS traces are presented in units of absolute desorption rates, as determined using
established procedures. [32; 34; 85] This scaling allows direct comparisons to be made
among the TPRS traces obtained from the different propane isotopologues. An
exception is that the peaks seen below 250 K in the 44 amu traces arise from propane
desorption and have not been rescaled to the propane desorption rates. Instead, each
44 amu trace was rescaled to represent the CO\textsubscript{2} desorption rate, while only the traces
labeled as “propane” are proportional to the propane desorption rates.

Molecularly adsorbed propane desorbs in the two main features centered at 130
and \(~195\) K, which we denote as the \(\alpha_2\) and \(\alpha_1\) states, respectively. We have previously
shown that the more strongly-bound \(\alpha_1\) state corresponds to a propane \(\sigma\)-complex(s)
and that this state serves as the precursor for initial C-H bond activation. [32; 34; 66] We
note that the total initial coverages in the $\alpha_1$ state were within 0.01 ML for the TPRS data represented in Fig. 5-2. The initial coverage in the $\alpha_2$ state exhibits greater variability because it is challenging to ensure saturation of the $\alpha_1$ state without partially populating the $\alpha_2$ state. The presence of different amounts of propane in the $\alpha_2$ state has a negligible influence on the activation of propane adsorbed in the $\alpha_1$ state.[32]

The TPRS traces reveal a significant kinetic isotope effect (KIE) in the low-temperature activation of propane on PdO(101). Comparing the data obtained from C$_3$H$_8$ and C$_3$D$_8$, it may be seen that the amount of propane desorbing in the $\alpha_1$ peak is considerably lower for C$_3$H$_8$ than C$_3$D$_8$, while the CO$_2$ yield is proportionally higher. This difference reveals that complete deuteration suppresses the initial bond activation of propane and thus shifts the kinetic branching toward desorption of the molecular precursor. Based on the CO$_2$ yields, we estimate that approximately 41% of the C$_3$H$_8$ molecules (~0.037 ML) initially adsorbed in the $\alpha_1$ state undergo dissociation, and that the dissociation yield for C$_3$H$_8$ is about 2.7 times greater than that of C$_3$D$_8$ when the $\alpha_1$ state is initially saturated.

The data further reveals that propane-$d_2$ is more reactive than propane-$d_6$ under the conditions examined in the TPRS experiment. In particular, the larger CO$_2$ peak as well as the smaller $\alpha_1$ peak obtained from propane-$d_2$ compared with propane-$d_6$, clearly demonstrates that the dissociation probability of propane-$d_2$ is higher than that of propane-$d_6$ for the conditions studied. In fact, the results show that the reactivity of propane-$d_2$ is very similar to that of C$_3$H$_8$, while the reactivity of propane-$d_6$ is close to, although slightly higher than, that of C$_3$D$_8$. Thus, selectively deuterating the $1^\circ$ C-H bonds has a more pronounced effect on the reactivity than does deuteration at the
secondary position. The difference in reactivity between propane-$d_2$ and $d_6$ indicates that cleavage of $1^\circ$ C-H bonds is mainly responsible for the KIE observed upon complete deuteration to $C_3D_8$ and is therefore the favored pathway for the initial dissociation of propane on PdO(101).

Figure 5-3 shows the propane dissociation yield, determined from TPRS experiments, as a function of the initial coverage in the $\alpha_1$ state for each propane isotopologue. The dissociation yield represents the quantity of adsorbed propane which dissociates during TPRS, and is equal to one third of the measured CO$_2$ yield. The data shows that the relative differences in reactivity are similar among the propane isotopologues for all of the initial coverages that we investigated, which span about 20% to 100% of the $\alpha_1$ saturation coverage. This comparison demonstrates that the preference for $1^\circ$ C-H bond cleavage persists down to low initial coverages of the propane $\sigma$-complexes, and must therefore arise primarily from the intrinsic interaction between propane and the PdO(101) surface; intermolecular interactions appear to have only a small influence on the bond selectivity. For each isotopologue, the dissociation yield as a function of the $\alpha_1$ propane coverage is well-approximated by a linear function over the range of coverages studied. The linear relations serve a practical purpose in analyzing the dissociation data as they provide a convenient way for estimating the dissociation yields of the various isotopologues as a function of the initial coverage.

5.3.3 Kinetic Model for Precursor-Mediated Dissociation

To quantify the C-H bond selectivity, we analyzed our data within the context of a kinetic model developed by Weinberg and Sun,[96] after modifying the model to more accurately represent the experimental conditions employed in our study. The model
describes the kinetics for the precursor-mediated dissociation of an alkane on a solid surface, where a molecularly-adsorbed state of the alkane serves as the precursor for dissociation and a kinetic branching between desorption and dissociation determines the net dissociation probability. The following reactions represent the elementary steps that are considered in this model,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3(\text{g}) & \leftrightarrow \text{CH}_3\text{CH}_2\text{CH}_2(\text{ad}) & \tilde{k}_d \\
\text{CH}_3\text{CH}_2\text{CH}_2(\text{ad}) & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2(\text{ad}) + \text{H}(\text{ad}) & \tilde{k}_{1H} \\
\text{CH}_3\text{CH}_2\text{CH}_2(\text{ad}) & \rightarrow (\text{CH}_3)_2\text{CH}(\text{ad}) + \text{H}(\text{ad}) & \tilde{k}_{2H}
\end{align*}
\]

The first step represents the reversible adsorption of propane into the molecularly-adsorbed precursor state where \( \tilde{k}_d \) represents the rate coefficient for desorption. The remaining steps represent the dissociation of adsorbed propane by either 1\(^\circ\) or 2\(^\circ\) C-H bond cleavage with the rate coefficients for these steps denoted as \( \tilde{k}_{1H} \) and \( \tilde{k}_{2H} \), respectively. We use the symbol \( \tilde{k}_i \) to represent an apparent rate coefficient which takes into account the statistical factor for reaction \( i \), and the symbol \( k_i \) to represent an intrinsic rate coefficient which excludes the statistical factor. This notation is useful for distinguishing the apparent and intrinsic rate coefficients for 1\(^\circ\) and 2\(^\circ\) C-H bond cleavage of propane for which the statistical factors are equal to six and two, respectively. From these definitions, one obtains the relations;

\[
\tilde{k}_{1H} = 6k_{1H} \quad (5-1)
\]

and

\[
\tilde{k}_{2H} = 2k_{2H} \quad (5-2)
\]

130
According to the model, the dissociation probability of $\text{C}_3\text{H}_8$ in the limit of zero adsorbate coverage may be written as:

$$S_0 = \frac{\bar{k}_r}{(\bar{k}_r + \bar{k}_d)} \quad (5-3)$$

where $\bar{k}_r = \bar{k}_{1H} + \bar{k}_{2H}$ and the molecular adsorption probability is set equal to unity in this expression. A molecular adsorption probability of unity is reasonable for propane molecules that impact the surface with thermal kinetic energies. We define a branching ratio for $\text{C}_3\text{H}_8$ dissociation as:

$$f_0 = \frac{\bar{k}_r}{\bar{k}_d} \quad (5-4)$$

and note that

$$f_0 = \frac{S_0}{1 - S_0} \quad (5-5)$$

Thus, estimates of $S_0$ allow calculation of the branching ratio $f_0$.

The main goal of the analysis is to quantify the probabilities for $1^\circ$ vs. $2^\circ$ C-H bond cleavage from experimental measurements of the dissociation probabilities of various propane isotopologues. Weinberg and Sun define apparent probabilities for $1^\circ$ vs. $2^\circ$ C-H bond cleavage as $\bar{p}_1$ and $\bar{p}_2$, respectively, where:

$$\bar{p}_1 + \bar{p}_2 = 1 \quad (5-6)$$

The apparent probability $\bar{p}_1$ is equal to the branching probability

$$\bar{p}_1 = \frac{\bar{k}_{1H}}{(\bar{k}_{1H} + \bar{k}_{2H})} \quad (5-7)$$

and thus represents the conditional probability for the $1^\circ$ C-H bond cleavage of propane, given that propane reacts. The quantity $\bar{p}_1$ is also equal to the fraction of 1-propyl fragments that result from the dissociative chemisorption of propane. The definition of $\bar{p}_2$ follows from that of $\bar{p}_1$. 
A few assumptions must be made to estimate the branching probability for $1^\circ$ C-H bond cleavage from the kinetic model. The first assumption is that secondary kinetic isotope effects are negligible compared with primary KIEs in the C-H bond cleavage of adsorbed propane. The analysis also neglects differences in the rate coefficients for desorption among the molecularly-adsorbed propane isotopologues. In support of this assumption, we find that the desorption temperatures of $C_3H_8$ and $C_3D_8$ from Pd(111) differ by less than 3.5 K. Finally, the analysis assumes that the ratios of rate coefficients $\bar{k}_{1H}/\bar{k}_{2H}$ and $\bar{k}_{1D}/\bar{k}_{2D}$ are equal. This approximation is also reasonable because one can expect that the changes in zero-point energies are very similar for $1^\circ$ vs. $2^\circ$ C-H bond cleavage of propane.

With the approximation that $\bar{k}_{1H}/\bar{k}_{2H} \approx \bar{k}_{1D}/\bar{k}_{2D}$, the branching ratio for propane-$d_2$ may be written as

$$f_2 = \tilde{p}_1f_0 + \tilde{p}_2f_8$$

where $f_0$ and $f_8$ represent the branching ratios for the initial dissociation of propane-$d_0$ and $d_8$, respectively. Similarly, the branching ratio for propane-$d_6$ is given by the expression,

$$f_6 = \tilde{p}_1f_8 + \tilde{p}_2f_0$$

Given estimates of the branching ratios for propane-$d_0$, $d_2$ and $d_8$, equation (5-8) and the relation $\tilde{p}_1 + \tilde{p}_2 = 1$ can be solved simultaneously to determine the probability $\tilde{p}_1$ for different initial propane coverages. Because we collected data for propane-$d_6$ as well, we can obtain separate estimates of $\tilde{p}_1$ from equation (5-9) for comparison with the values obtained from equation (5.8).
We emphasize that the branching ratios derived from the kinetic model apply to conditions in which propane dissociation on PdO(101) occurs at constant surface temperature and in the limit of zero coverage.[96] In contrast, propane dissociation during TPRS occurs over a range of surface temperatures (~35 K) and propane coverages. As such, rigorously applying the model to estimate the dissociation fraction obtained from TPRS measurements would require integration of the mole balance equations over temperature and coverage, as appropriate for the experimental conditions, and thus requires knowledge of how the rate coefficients depend on both the temperature and the coverages of propane molecules and propyl groups. To circumvent this difficulty, we treat the measured dissociation fractions as average branching probabilities, denoted as $\langle S \rangle$, and conducted the analysis presented above using these averaged quantities.

Table 5-1 shows estimates of the dissociation fractions for each isotopologue as a function of coverage as well as the branching probabilities for $1^\circ$ C-H bond cleavage determined separately from the $d2$ vs. $d6$ datasets using equations (5-8) and (5-9). To estimate the dissociation fractions as a function of coverage, we calculated the dissociation yields from the regression lines shown in Figure 5-3 and divided these yields by the total coverage of propane in the $\alpha_1$ state. We limited the analysis to initial propane coverages from 0.05 to 0.09 ML since the measurement uncertainty is higher at lower coverages. The values of $\tilde{p}_1$ vary only slightly with propane coverage in the $\alpha_1$ state. From the $d2$ data, we estimate that $\tilde{p}_1$ increases from 84% to 88%, while the $d6$ data predicts a small decrease from 92% to 91% for initial propane coverages.
increasing from 0.05 to 0.09 ML. Considering experimental uncertainty, the values of $\tilde{p}_1$ are effectively invariant over the range of propane coverages considered.

Importantly, the values of $\tilde{p}_1$ determined from the $d2$ vs. $d6$ data are in excellent agreement; the $\tilde{p}_1$ values agree to within better than 3% at the saturation coverage of 0.09 ML. The good agreement between the $\tilde{p}_1$ values lends confidence to the analysis and the validity of the assumptions of the kinetic model. From the analysis, we estimate that the apparent probability for $1^\circ$ C-H bond cleavage is equal to 90% when the $\alpha_1$ state is initially saturated. Thus, 90% of the adsorbed propane molecules that dissociate on PdO(101) do so by $1^\circ$ C-H bond cleavage. The apparent probabilities for $1^\circ$ and $2^\circ$ C-H bond cleavage take into account the fact that propane has six $1^\circ$ C-H bonds and only two $2^\circ$ C-H bonds. Intrinsic probabilities for $1^\circ$ vs. $2^\circ$ C-H bond represent the conditional probabilities for breaking a single $1^\circ$ vs. $2^\circ$ C-H bond, irrespective of the number of each type of bond in the propane molecule. The intrinsic and apparent probabilities are related by the equation,

$$\tilde{p}_1/\tilde{p}_2 = 3p_1/p_2,$$

(5-10)

where $p_1 + p_2 = 1$ and $\tilde{p}_1 + \tilde{p}_2 = 1$. Solving these equations simultaneously gives $p_1/p_2 = 2.85$ and an intrinsic probability for $1^\circ$ C-H bond cleavage of $p_1 = 74\%$. Thus, the intrinsic probability for $1^\circ$ C-H bond cleavage of propane on PdO(101) is nearly three times greater than that for $2^\circ$ C-H bond cleavage for the reaction conditions that we investigated. We conducted DFT calculations to determine the factors that are responsible for the preference for $1^\circ$ C-H bond cleavage in the activation of propane on PdO(101).
5.4 Summary

We conducted TPRS experiments using propane isotopologues to investigate regioselectivity in the initial C-H bond activation of propane on the PdO(101) surface. Our experiments reveal a significant kinetic isotope effect in the C-H(D) bond cleavage of propane on PdO(101) such that the dissociation yield of C$_3$H$_8$ is 2.7 times higher than that of C$_3$D$_8$ during TPRS at temperatures between ~150 to 200 K. Experiments using (CH$_3$)$_2$CD$_2$ and (CD$_3$)$_2$CH$_2$ further demonstrate that deuteration of the methyl groups is largely responsible for the KIE observed upon complete deuteration of propane, and thus that propane activation on PdO(101) occurs preferentially by 1° C-H bond cleavage. By analyzing the dissociation data within the context of a precursor-mediated kinetic model, we estimate that 90% of the propane molecules which dissociate on PdO(101) during TPRS do so by 1° C-H bond cleavage. As far as we know, the present study is the first to report a strong preference for 1° C-H bond cleavage in the initial dissociation of a molecularly-adsorbed alkane on a solid surface. Future studies of the interactions of alkanes with the PdO(101) surface may provide opportunities for identifying factors which promote the 1° C-H bond cleavage of alkanes on transition-metal oxides.
Figure 5-1. Model representation of PdO(101) surface. (a) Top and (b) side view of the PdO(101) thin film structure. The orange and blue atoms represent O and Pd atoms, respectively. Rows of 3-fold coordinated (cus) Pd and O atoms are indicated. The a and b directions correspond to the [010] and [101] crystallographic directions of PdO.
Figure 5-2. TPRS spectra of 44 amu and the majority propane mass fragment obtained from PdO(101) after saturating the $\alpha_1$ state of molecularly adsorbed propane at a substrate temperature of 85 K. The initial coverage of propane in the $\alpha_1$ state was equal to ~0.09 ML in each experiment. The spectra were obtained in separate experiments using C$_3$H$_8$ (d0), (CH$_3$)$_2$CD (d2), (CD$_3$)$_2$CH (d6) and C$_3$D$_8$ (d8). The reaction-limited desorption of CO$_2$ produces the peak at 465 K in the 44 amu traces, while the features below 250 K arise from molecular propane desorption. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 
Figure 5-3. Dissociation yield (ML) versus the initial coverage of propane $\sigma$-complexes ($\alpha_1$ state) on PdO(101) as determined from TPRS experiments at an initial surface temperature of 85 K. The propane dissociation yield is equal to one third of the CO2 desorption yield and is estimated from the CO2 TPRS data. Data is shown for the dissociation of $C_3H_8$ (d0), $(CH_3)_2CD_2$ (d2), $(CD_3)_2CH_2$ (d6) and $C_3D_8$ (d8) and the dashed lines represent linear fits to each dataset.
Table 5-1. Dissociation yields of propane isotopologues, determined from TPRS measurements, as a function of the initial coverage of propane $\sigma$-complexes ($\alpha_1$ state) on PdO(101). The dissociation yield is equal to the amount of propane which dissociates divided by the total amount of propane initially adsorbed in the $\alpha_1$ state. The dissociation yields of $\text{C}_3\text{H}_8$ (d0), $(\text{CH}_3)_2\text{CD}_2$ (d2), $(\text{CD}_3)_2\text{CH}_2$ (d6) and $\text{C}_3\text{D}_8$ (d8) are given in the columns labeled as $\langle S_0 \rangle$, $\langle S_2 \rangle$, $\langle S_6 \rangle$ and $\langle S_8 \rangle$, respectively. The table also shows values of the apparent probability for $1^\circ$ C-H bond cleavage, $\tilde{p}_1$, that are determined separately using the propane-d2 and d6 data. The final column shows the percent difference between the $\tilde{p}_1$ values determined from the d2 and d6 datasets.

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<th>Propane coverage (ML)</th>
<th>$\langle S_0 \rangle$</th>
<th>$\langle S_2 \rangle$</th>
<th>$\langle S_6 \rangle$</th>
<th>$\langle S_8 \rangle$</th>
<th>$\tilde{p}_1$ (d2)</th>
<th>$\tilde{p}_1$ (d6)</th>
<th>% difference</th>
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</tr>
<tr>
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SELECTIVITY IN THE INITIAL C-H BOND CLEAVAGE OF n-BUTANE ON PdO(101)

6.1 Motivation of the n-Butane Selectivity Study

Understanding the mechanisms governing alkane C-H bond cleavage on transition metal oxide surfaces is essential to the development of catalysts that efficiently promote chemical transformations of alkanes for energy and environmental applications as well as chemical synthesis. Among the transition metal oxides studied, palladium oxide (PdO) is an exceptional catalyst for promoting the dissociation and complete oxidation of alkanes. For example, many investigations establish that the formation of PdO layers is responsible for the high activity of oxide-supported Pd catalysts in applications of the catalytic combustion of natural gas.[1-9; 24] Consistent with these findings, we have shown that the activation and complete oxidation of n-alkanes (> C2) is facile on a PdO(101) surface under ultrahigh vacuum (UHV) conditions.[32; 66; 105] Recent in situ studies have also shown that the PdO(101) facet develops preferentially during the oxidation of Pd(111) and Pd(100) surfaces and that the formation of PdO(101) coincides with increased rates of methane oxidation during reaction at millibar pressures.[106] These findings provide strong evidence that alkane chemistry on PdO(101) plays a key role in practical applications of oxidation catalysis by Pd. More generally, fundamental investigations with PdO(101) provide an opportunity to gain new insights into the mechanisms governing alkane chemistry on oxide surfaces. Of particular interest in this regard is to clarify factors which control both the activity and selectivity of transition metal oxide surfaces toward alkane C-H bond cleavage.

In prior work, we have shown that the activation and complete oxidation of propane and n-butane is highly facile on PdO(101), with initial C-H bond cleavage
occurring below about 250 K under UHV conditions.[32; 66] We have presented evidence from both experiments and density functional theory (DFT) calculations that alkanes form σ-complexes on PdO(101) by datively bonding with coordinatively unsaturated (cus) Pd sites, and that the σ-complexes act as necessary precursors for initial C-H bond cleavage.[32; 35; 66; 105; 107] DFT calculations demonstrate clearly that dative bonding weakens the Pd-coordinated C-H bonds of alkanes on PdO(101), making these C-H bonds easier to cleave. Finally, following the initial C-H bond cleavage, the alkane fragments are completely oxidized by the PdO(101) surface to produce CO₂ and H₂O which desorb at temperatures above 350 K during temperature programmed reaction spectroscopy (TPRS) experiments.

More recently, we have reported both experimental and computational results which show that propane exhibits a strong preference to dissociate on PdO(101) by 1° C-H bond cleavage. We estimate that 90% of the propane molecules which dissociate on PdO(101) during TPRS experiments do so through cleavage of a 1° C-H bond, with the C-H bond selectivity remaining invariant with the initial propane coverage over the range studied.[85] Such high selectivity toward 1° C-H bond cleavage is generally unexpected since the energy required for homolytic cleavage of a 1° C-H bond is about 12 kJ/mol higher than that for a 2° C-H bond. Consistent with the relative stability of alkane C-H bonds, Weinberg and coworkers[96; 98; 108] have shown that 2° or 3° C-H bond cleavage is preferred over 1° C-H bond cleavage in the activation of alkanes on the Pt(110), Ir(111) and Ru(0001) surfaces.

Dispersion-corrected DFT calculations reproduce the experimentally-observed preference for 1° C-H bond cleavage of propane on PdO(101) and also predict an
activation energy for C-H bond cleavage that agrees quantitatively with experimental estimates.[107] The calculations predict that propane undergoes heterolytic C-H bond cleavage on PdO(101) by transferring a positively-charged H-atom to a cus-O atom of the surface, thus affording an HO_{cus} group and a 1-propyl group bound to a cus-Pd atom. The calculations predict that the intrinsic energy barrier is lower for 1° vs. 2° C-H bond cleavage because the 1-propyl transition structure adopts a charge distribution that better stabilizes the negatively charged C-atom at the reaction site. A similar effect (substituent polarization) has been invoked to explain the higher stability of gas-phase 1- vs. 2-alkyl anions.[109; 110] While propane activation on PdO(101) appears to be the only example in which an adsorbed alkane dissociates preferentially by 1° C-H bond cleavage on a solid surface, detailed investigations of alkane activation on transition metal oxide surfaces are sparse. An interesting issue will be to determine if the heterolytic nature of the C-H bond cleavage process causes 1° C-H bond cleavage to be the preferred route for alkane activation on other oxides and polar surfaces.

In the present study, we used TPRS and beam reflectivity measurements to investigate the kinetics and selectivity of the initial C-H(D) bond cleavage of n-butane isotopologues on the PdO(101) surface. We find that n-butane exhibits a strong preference to dissociate by 1° C-H bond cleavage on PdO(101) in the limit of zero coverage, but observe a nearly equal preference for 1° vs. 2° C-H bond cleavage for n-butane dissociation during TPRS experiments at moderate to high n-butane coverages. Using a model for precursor-mediated dissociation, we estimate apparent kinetic parameters for n-butane activation on PdO(101), including kinetic parameters for the selective cleavage of 1° vs. 2° C-H bonds.
6.2 Experimental

Details of the three level UHV chamber utilized during these experiments are given elsewhere.[37; 38] Briefly, the Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder that is held in thermal contact with a liquid nitrogen cooled reservoir. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports maintaining or linearly ramping the sample temperature from 81 K to 1250 K. Initially, sample cleaning consisted of sputtering with 600 eV Ar⁺ ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to 923 K to desorb oxygen and carbon oxides. As discussed previously,[39] we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in preparing the PdO(101) thin films used in this study. We considered the Pd(111) sample to be clean when we could no longer detect contaminants with x-ray photoelectron spectroscopy, obtained sharp low energy electron diffraction patterns consistent with the Pd(111) surface, and did not detect CO production during flash desorption after oxygen adsorption.

A two-stage differentially-pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system.[37; 38] To produce a PdO(101) thin film, we expose a Pd(111) sample held at 500 K to an ~12 ML dose of gaseous oxygen atoms supplied in a beam, where we define 1 ML as equal to the Pd(111) surface atom density.
of $1.53 \times 10^{15}$ cm$^{-2}$. This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains $\sim3.0$ ML of oxygen atoms and is about 12 Å thick[12; 39]. The structure of the PdO(101) surface is discussed in detail below.

We studied the reactivity of n-C$_4$H$_{10}$ (Airgas, 99.99%), n-(CD$_3$)$_2$(CH$_2$)$_2$ (Aldrich, 98 atom% D) and n-C$_4$D$_{10}$ (Aldrich, 98 atom% D), denoted as butane-$d_0$, -$d_6$ and $d_{10}$ respectively, on the PdO(101) surface using temperature programmed reaction spectroscopy (TPRS) and beam reflectivity measurements utilizing King and Wells technique.[111] We collected TPRS spectra after butane exposures by positioning the sample in front of a shielded mass spectrometer at a distance of about 10 mm and then heating at a constant rate of 1 K s$^{-1}$ until the sample temperature reached 923 K. Because the PdO film decomposes when heated to 923 K, it was necessary to prepare a fresh PdO thin film for each adsorption/reaction experiment. We monitored the desorption of butane, water, CO$_2$ and O$_2$ since prior studies show that these are the only products to evolve from butane-covered PdO(101) during TPRS.[33; 66] The majority mass fragment of the butane fragmentation pattern corresponds to the propyl radical, and the mass-to-charge ratio of this fragment is equal to $m/z = 43$, 46 and 50 for butane-$d_0$, butane-$d_6$ and butane-$d_{10}$ respectively. We estimate absolute coverages and desorption yields using procedures described previously.[32; 35; 66] We determined the absolute butane coverages from TPD experiments of n-butane on Pd(111), and calculated CO$_2$ desorption yields by performing TPRS experiments of CO oxidation on oxygen-covered Pd(111).

We conducted beam reflectivity measurements to investigate the kinetics of n-butane dissociation on PdO(101) in the limit of zero coverage. In these experiments, the
sample surface is exposed to a n-butane molecular beam while the n-butane partial pressure is simultaneously measured using a mass spectrometer. The instantaneous partial pressure is directly proportional to the rate at which n-butane molecules reflect from the surface, and thus provides a direct measure of the adsorption rate, as described below. The calibrated molecular beam doser used in these experiments has been described previously.[37; 112] Briefly, the beam doser consists of a custom-designed end cap that is sealed against a 0.25" tube by a VCR gasket that contains a 10 μm pinhole. The upstream end of the tube is connected to a gas reservoir (~250 ml) in which the n-butane partial pressure is maintained at a constant value of about 0.25 Torr. This arrangement provides a constant gas flow rate through the doser. The end cap of the doser is terminated by a glass microcapillary array which collimates the molecular beam emanating from the doser.[113] The entire doser assembly is mounted on a linear translator to allow the doser-to-sample distance to be adjusted and a mechanical shutter positioned at the end of the doser is used to control the gas exposure to the surface.

Figure 6-1 shows representative King and Wells traces obtained during n-butane beam exposures under the conditions indicated in the figure. In these experiments, the sample is positioned about 5 mm from the end of the doser to ensure that the sample surface intercepts a large fraction of the beam. The King and Wells experiment is initiated by monitoring the n-butane partial pressure obtained before admitting the n-butane beam into the UHV chamber. After about 63 sec, the beam is admitted into the chamber but the shutter is interposed in the beam path to establish a steady-state partial pressure when net adsorption onto the sample surface is negligible. After about
83 sec, the shutter is removed from the beam path and the n-butane beam impinges upon the sample surface. Adsorption of the beam molecules onto the sample surface causes the n-butane partial pressure to fall below the steady-state value measured when adsorption is negligible, and the initial decrease in partial pressure is directly proportional to the adsorption rate of n-butane in the limit of zero n-butane coverage, i.e., the initial adsorption rate. One can estimate the initial adsorption probability \( S_i \) from the King and Wells trace using the equation

\[
 fS_i = (P_{ss} - P_i)/(P_{ss} - P_o)
\]  

(6-1)

where \( f \) is the intercepted fraction of the beam by the sample, \( P_{ss} \) is the steady state partial pressure obtained when the net adsorption rate equals zero, \( P_i \) is the partial pressure obtained when n-butane is initially impinging on the sample surface and \( P_o \) is the baseline partial pressure or equivalently the partial pressure that would be obtained if all the n-butane molecules emanating from the beam source were to adsorb on the sample surface. After about 183 sec, the shutter is interposed into the beam path and the gas flow through the doser is then terminated after ~203 sec by evacuating the gas line using a turbomolecular pump. For the experiment conducted at 325 K on PdO(101) (black curve, Fig. 1), the partial pressure rapidly increases after the initial decrease and returns to a steady value during the remainder of the beam exposure, indicating that the net adsorption rate becomes zero due to saturation of the adsorbed layer or other processes that render the surface inactive toward additional n-butane adsorption. Notice, however, that the steady state partial pressure is higher in our experiments when the shutter is open vs. closed. We find that this difference is caused by a change in the effective n-butane pumping speed and appears to originate from a change in the
fraction of the beam that adsorbs directly onto the LN₂-cooled sample support-structure when the shutter is opened vs. closed.

We conducted beam reflectivity experiments with clean Pd(111) to obtain estimates of the intercepted fraction $f$ and the steady state partial pressure in the limit of zero net adsorption $P_{ss}$. After completing a King and Wells experiment with the PdO(101) film, we decomposed the film by heating the sample above 923 K without changing the sample position. We then conducted King and Wells measurements by impinging the n-butane beam onto clean Pd(111) held at 90 and 400 K. In the experiments performed at 90 K, the n-butane partial pressure abruptly decreases when the shutter is opened and remains at a constant value for the duration of the beam exposure to the surface due to the formation of a stable n-butane multilayer (blue curve, Fig. 6-1). We assume that the n-butane adsorption probability is equal to unity for adsorption at 90 K. With this assumption, we estimated the intercepted fraction of the beam for each King and Wells experiment using the equation given above. We find a value of $f = 0.44 \pm 0.02$ for the experiments conducted in this study.

After each measurement at 90 K, a King and Wells measurement was also conducted at 400 K to quantify the steady state partial pressure obtained in the limit of zero net adsorption when the shutter is open. The net adsorption rate is zero under these conditions because the surface temperature of 400 K is much higher than the n-butane desorption temperature obtained in TPD (~195 K) from Pd(111)[66] and the low-energy n-butane molecules dissociate to a negligible extent on clean Pd(111) at the conditions employed. As seen in Figure 6-1, the partial pressure increases upon exposing the n-butane beam to clean Pd(111) held at 400 K (red curve), and reaches a
steady value that is identical to that observed in experiments conducted under conditions when measurable quantities of n-butane adsorb on the sample. Thus, to calculate the initial adsorption probability of n-butane from the King and Wells traces, we set the value of $P_{ss}$ equal to the shutter-open, steady state partial pressure obtained in the measurements of n-butane reflection from Pd(111) at 400 K. As an example, we estimate an initial adsorption probability of 0.612 from the King and Wells trace shown in Figure 6-1 for n-butane adsorption on PdO(101) at 325 K. We estimate an uncertainty of about ±0.05 in the initial adsorption probabilities determined from the King and Wells measurements. In this study, we report estimates of the initial dissociation probabilities of each n-butane isotopologue as a function of the surface temperature as determined from King and Wells measurements, and estimate kinetic parameters for initial C-H(D) bond cleavage from this data. Lastly, we note that the total quantity of n-butane molecules that adsorb or undergo reaction with the surface during a King and Wells measurement is proportional to the area between the n-butane partial pressure trace obtained during adsorption and the partial pressure in the limit of zero net adsorption.[111; 114] We find that the yields of dissociated n-butane correspond to a significant fraction of the maximum coverage of n-butane $\sigma$-complexes on PdO(101), and thus conclude that n-butane dissociation occurs on the terraces of PdO(101), as expected.[66]

6.3 Results and Discussion

6.3.1 Structure of Stoichiometric PdO(101)

A model representation of the stoichiometric PdO(101) surface that we investigated in this study is shown in Figure 6-2. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms fourfold coordinated with
oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell, where the \( a \) and \( b \) lattice vectors coincide with the [010] and [\( \bar{1}01 \)] directions of the PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the \( a \) direction shown in Figure 6-2. Thus, half of the surface O and Pd atoms are coordinatively unsaturated (\( \text{cus} \)). The side view of PdO(101) shows that the coordinative environment associated with each \( \text{cus} \)-Pd atom resembles a square planar Pd complex with a coordination vacancy directed away from the surface and three oxygen ligands, one of which is a \( \text{cus} \)-O atom. The areal density of each type of coordinatively-distinct atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface. Hence, the coverage of \( \text{cus} \)-Pd atoms is equal to 0.35 ML (monolayer), and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms, where we define 1 ML as equal to the surface atom density of Pd(111).

### 6.3.2 Reactivity of Butane Isotopologues on PdO(101) Studied with TPRS

Figure 6-3 compares \( n \)-butane and \( \text{CO}_2 \) TPRS traces obtained in experiments in which a given \( n \)-butane isotopologue was adsorbed on PdO(101) at 90 K up to a coverage that exceeds the saturation coverage of the first layer. As reported previously, the desorption of \( n \)-butane from PdO(101) produces a complex TPD trace when the first layer is saturated.[66] Briefly, \( n \)-butane desorption from the monolayer on PdO(101) produces a broad TPD feature with distinct rate maxima (\( \alpha_2 \) and \( \alpha_1 \)) at temperatures of \( \sim 148 \) and 212 K for \( n \)-butane-\( d_0 \). The desorption of \( n \)-butane from the multilayer produces the sharp peak at 110 K, which is truncated in Figure 6-3 to accentuate the higher temperature features. We have previously shown that \( n \)-butane molecules
adsorbed in the $\alpha_1$ state correspond to adsorbed $\sigma$-complexes and that these species act as precursors to the initial dissociation of n-butane on PdO(101). During TPRS, a fraction of the n-butane molecules adsorbed in the $\alpha_1$ state dissociate via C-H bond cleavage and are oxidized completely by the surface at higher temperature. The resulting CO$_2$ and H$_2$O products desorb in reaction-limited peaks above 450 K, and a fraction of the H$_2$O evolves in a desorption-limited peak at 350 K (not shown). Because CO$_2$ is the only carbon-containing reaction product, the amount of n-butane molecules that dissociate during TPRS is equal to one fourth of the CO$_2$ desorption yield. From the present experiments, we estimate that n-butane-$d_0$ saturates the $\alpha_1$ state at a coverage of 0.073 ML, and that 73% of these species dissociate during TPRS when the state is initially saturated. These values agree to within 15% of previously reported values of the $\alpha_1$ saturation coverage of 0.085 ML and the dissociated fraction of 64%.[66] The differences appear to arise from experimental error in estimating the absolute n-butane coverage.

The saturation coverage of the n-butane $\alpha_1$ state corresponds to about 21% of the cus-Pd site density on PdO(101), suggesting that saturation occurs when one n-butane molecule is present for every four to five cus-Pd atoms. The saturation coverage is also equivalent to about 0.83 C atoms per cus-Pd atom, which agrees well with the saturation coverage of the propane $\alpha_1$ state reported previously.[32] According to dispersion-corrected DFT (DFT-D3) calculations, the favored n-butane $\sigma$-complex on PdO(101) corresponds to an $\eta^1$ complex in which the n-butane molecule adopts a trans geometry and aligns along the cus-Pd row.[107] The $\eta^1$ complex forms H-Pd dative bonds with adjacent cus-Pd atoms of the surface, with one of the bonds forming at a
CH₃ group and the other forming at the next closest CH₂ group, i.e., at the C₁ and C₃ positions of carbon backbone (Figure 6-4). Since the formation of an η¹ n-butane complex on PdO(101) requires at least two adjacent cus-Pd atoms, statistics predicts that the n-butane molecules will not close pack along the cus-Pd row when the adsorbates are immobile and adsorb randomly. The reason is that a fraction of the neighboring adsorbed molecules will be separated by fewer than the minimum number of sites needed to accommodate an adsorbed molecule, thus creating “stranded” sites within the layer. Interestingly, the saturation coverage of 0.83 C atoms per cus-Pd atom lies between the values of the maximum coverages (i.e., jamming densities) of randomly-adsorbed, linear dimers and tetramers on a line of sites (86% vs. 80%),[115] which is consistent with the interpretation that n-butane molecules in the α₁ state align along the cus-Pd row and occupy multiple binding sites.

Our TPRS experiments with different n-butane isotopologues reveal a significant kinetic isotope effect (KIE) in the dissociation of n-butane on PdO(101). Comparing the n-butane d₀ and d₁₀ TPRS results, the CO₂ desorption yield is larger for the n-butane d₀ compound, while the α₁ desorption yield is proportionally lower. This result demonstrates that complete deuteration suppresses dissociation of the adsorbed n-butane precursor, and thereby shifts the kinetic branching away from dissociation and toward molecular desorption. Indeed, the inverse relation between the α₁ n-butane and CO₂ desorption yields provides further evidence that the α₁ state serves as a necessary precursor for the initial dissociation of n-butane on PdO(101). We estimate a dissociated fraction of ~40% for n-butane-d₁₀ on PdO(101) at saturation of the α₁ state, and thus a
KIE of about 1.8 between the $d_0$ and $d_{10}$ species based on the dissociation yields obtained during TPRS.

It is worth noting that the $\alpha_1$ peaks appear at increasing temperatures as the extent of deuteration increases for the n-butane isotopologues that we investigated; the $\alpha_1$ peak temperatures are equal to 235, 222 and 212 K for the $d_{10}$, $d_6$ and $d_0$ compounds, respectively (Figure 6-3). This trend appears to arise predominantly from the inverse relation between the desorption and dissociation yields of the molecular precursor(s), rather than from an intrinsic KIE in the molecular desorption process. For example, we obtain desorption maxima at 193 and 188 K in TPD experiments of n-butane-$d_0$ and $d_{10}$ from Pd(111), respectively, which corresponds to only a 5 K difference in peak temperature in contrast to the 23 K difference observed for the $\alpha_1$ peaks obtained from n-butane-$d_0$ vs. $d_{10}$ on PdO(101). While n-butane $\sigma$-complexes do interact more strongly with PdO(101) than n-butane molecules that are physisorbed on Pd(111), a 23 K difference in peak temperature is difficult to reconcile by considering kinetic isotope effects alone and the shifts in peak temperature are opposite for n-butane-$d_0$ vs. $d_{10}$ on Pd(111) compared with PdO(101). We thus assert that the $\alpha_1$ desorption peak not only diminishes in intensity as more n-butane molecules dissociate on PdO(101) during TPRS but also shifts to lower temperature. The downshift in peak temperature occurs in part because the desorption peaks at lower temperature have a greater influence on the $\alpha_1$ peak position when the $\alpha_1$ peak is small. An additional possibility is that n-butane $\sigma$-complexes adsorbed in multiple environments or configurations contribute to the $\alpha_1$ TPD peak and that the more strongly-bound $\sigma$-complexes among this population have a higher probability of dissociating during TPRS.
TPRS experiments with the partially-deuterated n-butane-$d_6$ compound provide insights for understanding the origin of the KIE as well as the initial bond selectivity of n-butane on PdO(101). As seen in Figure 6-3, the CO$_2$ and $\alpha_1$ desorption yields obtained from the n-butane-$d_6$ species lie between those determined for the $d_0$ and $d_{10}$ compounds, but are closer to the yields obtained from the $d_0$ species. We estimate that the dissociated fraction of n-butane-$d_6$ is equal to 64% when the $\alpha_1$ state is initially saturated. Relative to the dissociated fraction of n-butane-$d_0$, we estimate KIEs of 1.1 and 1.8 for the dissociation of n-butane-$d_6$ and $d_{10}$ on PdO(101), respectively. This result suggests that deuteration of the methylene groups is largely responsible for the KIE observed upon complete deuteration of n-butane, and thus that n-C$_4$H$_{10}$ preferentially dissociates via secondary C-H bond cleavage during TPRS when the $\alpha_1$ state is initially saturated. The analysis presented below actually predicts that primary and secondary C-H bond cleavage are nearly equally probable for n-butane dissociation on PdO(101) during TPRS at moderate to high n-butane coverage. The C-H bond selectivity of n-butane on PdO(101), as determined from TPRS results, differs from previous results which show a strong preference for primary C-H bond cleavage in the low temperature dissociation of propane on PdO(101).[85]

Figure 6-5 shows CO$_2$ desorption yields determined from TPRS results as a function of the initial n-butane coverage in the $\alpha_1$ state for each isotopologue, where the initial coverages range from about 0.025 to 0.075 ML. Each dataset is well approximated by a linear function over the range of coverages investigated. The linear functions aid in quantifying the bond selectivity, but should be viewed as approximations since the relation between the dissociation yield and the initial coverage is not
necessarily linear. As elaborated below, the relative differences in reactivity among the n-butane isotopologues remains approximately invariant with the n-butane coverage for the coverages that we investigated using TPRS. While the reactivity at low n-butane coverages (< 0.02 ML) is difficult to quantify with TPRS, it is clear from Figure 6-5 that the linear fits extrapolate to positive, non-zero intercepts for each isotopologue. This behavior indicates that the relations between the product yield and n-butane coverage deviate from the linear functions when the n-butane coverage is sufficiently low. Below, we show that the initial C-H bond selectivity at moderate n-butane coverages is different from that estimated in the zero coverage limit from King and Wells measurements.

Before presenting the King and Wells results, we discuss the approach that we have taken to quantify the C-H bond selectivity from the dissociation yields determined from TPRS experiments.

**6.3.3 Quantification of Bond Selectivity**

To quantify the C-H bond selectivity, we analyzed our data within the context of a kinetic model developed by Weinberg and Sun,[96] after modifying the model to more accurately represent the experimental conditions employed in our study. The model describes the kinetics for the precursor-mediated dissociation of an alkane on a solid surface, wherein a molecularly-adsorbed state of the alkane serves as the precursor for dissociation and a kinetic branching between desorption and dissociation determines the net dissociation probability. The following reactions represent the elementary steps that are considered in the model,

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 (g) & \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 (\text{ad}) \quad k_d \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 (\text{ad}) & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 (\text{ad}) + \text{H(ad)} \quad k_{1H}
\end{align*}
\]
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \text{ (ad)} \rightarrow \text{CH}_3\text{CHCH}_2\text{CH}_3 \text{ (ad)} + \text{H(ad)} \quad k_{2H} \]

The first step depicts the reversible adsorption of \( n \)-butane into the molecularly-adsorbed precursor state where \( k_d \) represents the rate coefficient for desorption. The remaining steps represent the dissociation of adsorbed \( n \)-butane by either \( 1^\circ \) or \( 2^\circ \) C-H bond cleavage with the rate coefficients for these steps denoted as \( k_{1H} \) and \( k_{2H} \), respectively. These “apparent” rate coefficients implicitly take into account the different number of \( 1^\circ \) vs. \( 2^\circ \) C-H bonds in the \( n \)-butane molecule. According to the model, the total probability for dissociative chemisorption of \( n \)-butane (\( d_0 \)) in the limit of zero coverage is given by:

\[
S_0 = \frac{\alpha(k_{1H}+k_{2H})}{k_{1H}+k_{2H}+k_d} = \frac{\alpha k_{r0}}{k_{r0}+k_d}
\]  

(6-2)

where \( \alpha \) is the molecular adsorption probability and \( k_{r0} = k_{1H} + k_{2H} \). The quantity \( k_{r0} \) represents an effective rate coefficient for the initial dissociation (“reaction”) of \( n \)-butane-\( d_0 \). By analogy, the effective dissociation rate coefficients for the \( d_6 \) and \( d_{10} \) species are given by the equations:

\[
k_{r6} = k_{1D} + k_{2H}
\]  

(6-3)

and

\[
k_{r10} = k_{1D} + k_{2D}
\]  

(6-4)

where \( k_{1D} \) and \( k_{2D} \) represent the rate coefficients for primary and secondary C-D bond cleavage, respectively. These definitions assume that the rate coefficients for primary and secondary C-H(D) bond cleavage are independent of one another, e.g., \( k_{1D} \) is the same for both \( n \)-butane-\( d_6 \) and \( d_{10} \). In the analysis, we also assume that the desorption rate coefficients and molecular adsorption probabilities are the same for the different \( n \)-butane isotopologues. We define a branching ratio for isotopologue \( d_j \) as
\[ f_j = \frac{k_r}{k_d} \]  \hspace{1cm} (6-5)

where the branching ratio is related to the dissociation probability by the equation,

\[ f_j = \frac{s_j}{\alpha - s_j} \]  \hspace{1cm} (6-6)

The main goal of the analysis is to quantify the probabilities for \(^1\)\(^\circ\) vs. \(^2\)\(^\circ\) C-H bond cleavage from experimental measurements of the reactivity of different \(n\)-butane isotopologues. Toward this end, one may define the apparent probability for \(^1\)\(^\circ\) C-H bond cleavage \(p_1\) as equal to a kinetic branching probability by the equations,

\[ p_1 = \frac{k_{1H}}{k_{1H} + k_{2H}} \approx \frac{k_{1D}}{k_{1D} + k_{2D}} \]  \hspace{1cm} (6-7)

The quantity \(p_1\) represents the probability for \(^1\)\(^\circ\) C-H bond cleavage, given that \(n\)-butane reacts, and is also equal to the fraction of the butyl products that are \(^1\)-butyl groups.

Equation (6-7) assumes that the relation \(k_{1H}/k_{2H} \approx k_{1D}/k_{2D}\) is valid. This approximation is reasonable because one can expect that the zero-point vibrational energy differences between the initial state and transition state are similar for \(^1\)\(^\circ\) and \(^2\)\(^\circ\) C-H(D) bond cleavage. The branching ratio for the \(d_6\) isotopologue may thus be written as,

\[ f_6 = \frac{k_{1D}}{k_d} + \frac{k_{2H}}{k_d} = p_1 f_{10} + p_2 f_0 \]  \hspace{1cm} (6-8)

Finally, since

\[ p_1 + p_2 = 1 \]  \hspace{1cm} (6-9)

the probability for \(^1\)\(^\circ\) C-H bond cleavage can be expressed in the terms of branching ratios by the following equation,

\[ p_1 = \frac{f_0 - f_6}{f_0 - f_{10}} \]  \hspace{1cm} (6-10)
To estimate $p_1$ values from the TPRS data, we equate the dissociated fraction obtained during a TPRS experiment with a dissociation probability $\langle S_j \rangle$ that is “averaged” over the range of temperature and coverage that the n-butane precursors react and desorb during TPRS. We then use the $\langle S_j \rangle$ values to calculate branching ratios and $\langle p_1 \rangle$ values as a function of the initial n-butane coverage. We have recently employed this same approach to estimate apparent probabilities for 1° C-H bond cleavage of propane on PdO(101) based on TPRS data.[85] We set the molecular adsorption probability equal to unity when calculating $\langle f_j \rangle$ values from the dissociated fractions $\langle S_j \rangle$ determined from the TPRS data. This assumption considers that the initial n-butane coverage in the $\alpha_1$ state is established when the n-butane layer is being prepared at 90 K, rather than by a competitive process wherein weakly-bound species either convert to the $\alpha_1$ state or desorb as the sample warms during the TPRS measurement.

Figure 6-6 shows the computed values of $\langle p_1 \rangle$ as a function of the initial coverage of n-butane in the $\alpha_1$ state on PdO(101). We used the linear fitting functions (Figure 6-5) to estimate dissociation fractions needed to calculate $\langle p_1 \rangle$ values at given n-butane coverages. According to the analysis, the branching probability for 1° C-H bond cleavage is equal to 49% when the $\alpha_1$ state is initially saturated, and remains approximately constant as the coverage decreases from 0.075 to about 0.03 ML. The $\langle p_1 \rangle$ values appear to increase as the coverage decreases below 0.03 ML, but the experimental uncertainty is higher for the TPRS data that we obtained at low coverage. Nevertheless, an increase in the 1° C-H bond selectivity with decreasing n-butane coverage is consistent with the findings of our beam reflectivity measurements, as discussed below. The C-H bond selectivity in the dissociation of propane on PdO(101)
also remains constant as the initial propane coverage decreases from saturation to moderate values, but propane exhibits a stronger preference than n-butane to undergo primary C-H bond cleavage on PdO(101) at the coverages investigated using TPRS. We have reported a branching probability of 90% for 1° C-H bond cleavage of propane on PdO(101) during TPRS.[85] Overall, we find that n-butane exhibits a nearly equal preference for 1° vs. 2° C-H bond cleavage when the initial coverage in the molecular precursor state lies in a range from about 40% to 100% of the saturation value.

6.3.4 Initial Dissociation Probabilities of n-Butane on PdO(101)

Figure 6-7 shows initial adsorption probabilities determined from King and Wells measurements for n-butane-\( d_0 \), \( d_6 \) and \( d_{10} \) on PdO(101) as a function of the surface temperature over a range from 150 to 450 K. The King and Wells experiments performed above ~280 K provide a direct measure of the initial dissociation probability \( S_j \) of n-butane on PdO(101), with negligible contributions from non-reactive, molecular adsorption. The reason is that the molecular desorption rate of n-butane is significantly higher than the beam flux (~0.05 ML/s) at temperatures above ~280 K, and thus only the molecular species which dissociate on the surface contribute to the adsorption rate measured using the King and Wells method at these temperatures. At temperatures below about 280 K, the initial adsorption probability obtained from the King and Wells experiments contains contributions from both non-reactive and dissociative adsorption.

The King and Wells measurements reveal that the initial dissociation probability \( S_j \) of n-butane on PdO(101) decreases with increasing surface temperature from ~300 to 450 K. For example, the dissociation probabilities of n-butane-\( d_0 \) at temperatures of 300 and 450 K are equal to 0.74 to 0.20, respectively. The decrease of \( S_j \) with
increasing temperature is indicative of a facile mechanism for precursor-mediated,
dissociative chemisorption wherein the activation energy for dissociation is less than
that for desorption of the molecularly adsorbed precursor. We have reported similar
kinetics for the initial dissociation of propane on PdO(101) at surface temperatures
between 250 and 350 K.[32]

The measurements conducted below ~280 K provide information about how the
probability for non-reactive, molecular adsorption depends on the surface temperature.
As seen in Figure 6-7, the initial adsorption probability decreases sharply with
increasing surface temperature from 150 to ~215 K, but remains approximately constant
at a value of 0.78 over the temperature range from ~215 to 280 K. Notice that the $\alpha_1$
TPD peak of n-butane from PdO(101) (Figure 6-3) spans the same temperature range
(~200 to 280 K) over which the initial adsorption probability remains constant at 78%.
This behavior suggests that the probability for adsorption into the $\alpha_1$ state is less than
unity for n-butane molecules incident on the surface with low kinetic energies. An
adsorption probability below unity is surprising in this case since the molecular
adsorption of alkanes is typically non-activated and the incident kinetic energies of the
n-butane molecules employed in our experiments are significantly lower than the
binding energy of n-butane in the $\alpha_1$ state.[66]

We suggest that a dynamical effect causes the adsorption probability into the $\alpha_1$
state to lie below unity. Specifically, we assert that low kinetic-energy n-butane
molecules become trapped within the potential field of the PdO(101) surface with
(nearly) unit probability, but that only a fraction of these trapped species convert to $\sigma$-
complexes on the cus-Pd row at temperatures where the trapped species are unable to
accumulate, i.e., above the peak temperature of the $\alpha_2$ TPD feature (Figure 6-3). In this case, one may envision that n-butane molecules adsorbed in relatively weakly-bound states act as precursors for n-butane $\sigma$-complex formation on PdO(101). Such a mechanism seems reasonable because the adsorbed $\sigma$-complexes adopt specific molecular configurations and form only on the cus-Pd sites, which constitute only half of the total number of surface Pd atoms. In contrast, physical adsorption is less stERICally demanding than $\sigma$-complex formation, and should thus occur more readily during the initial gas-surface interaction.

The data reveals a significant KIE in the initial dissociation of n-butane on PdO(101). For example, the initial dissociation probabilities of n-butane-$d_0$ and $d_{10}$ are equal to 0.57 and 0.27 at a surface temperature of 350 K, respectively. The KIE, defined as the ratio of $S_0$ to $S_{10}$, is equal to $2.0 \pm 0.2$ for temperatures ranging from 312 to 400 K, and does not exhibit an obvious trend with the surface temperature. The average value of the KIE estimated from the initial dissociation probabilities is close to the value of 1.8 that we determined from the dissociated fractions measured in TPRS experiments with n-butane-$d_0$ and $d_{10}$. The data also reveal that the initial dissociation probabilities of n-butane-$d_6$ on PdO(101) lie well below the values found for n-butane-$d_0$, but lie only slightly above those for n-butane-$d_{10}$ at temperatures between ~300 and 400 K. Above 300 K, the ratios $S_6:S_0$ and $S_6:S_{10}$ have average values of 1.6 and 1.2, respectively. This behavior suggests that deuteration of the methyl groups is primarily responsible for the large KIE observed upon completely deuterating n-butane, and thus that primary C-H bond cleavage is the preferred pathway for the dissociative chemisorption of n-butane-$d_0$ on PdO(101) in the limit of zero coverage. Since the TPRS results indicate a nearly
equal preference for $1^\circ$ vs. $2^\circ$ C-H bond cleavage at moderate to high coverage, the King and Wells data suggest that the $1^\circ$ C-H bond selectivity increases as the n-butane coverage decreases sufficiently on PdO(101).

### 6.3.5 Kinetic Analysis

We analyzed the $S_j$ vs. $T_s$ data within the context of the precursor-mediated model described above to estimate kinetic parameters governing C-H bond selectivity during the initial dissociation of n-butane on PdO(101). For the analysis, we assume that the temperature dependence of the rate coefficients $k_{rj}$ and $k_d$ is accurately described by the Polanyi-Wigner equation which may be written as:

$$k_j = v_j \exp(-\frac{E_j}{RT_s})$$

where $v_j$ and $E_j$ represent the pre-factor and activation energy for reaction $j$, $T_s$ is the surface temperature and $R$ is the gas constant. Recall that $k_{rj}$ is an effective rate coefficient for dissociation and that this quantity does not describe a single elementary reaction step but instead is equal to a sum of rate coefficients for $1^\circ$ and $2^\circ$ C-H or C-D bond cleavage, depending on the isotopologue. The use of individual Polanyi-Wigner equations to describe each $k_{rj}$ is thus an approximate way to represent the measured temperature dependence of the dissociation probabilities within the “resolution” that can be achieved in the experiments.[96] From the definition of the branching ratio for isotopologue $j$ given by Equation (6-5) and using Polanyi-Wigner expressions to describe the rate coefficients, one may express the temperature dependence of $S_j$ in the following Arrhenius form,

$$\ln\left(\frac{\alpha}{S_j} - 1\right) = \ln\left(\frac{k_{rj}}{k_d}\right) = \ln\left(\frac{v_j}{v_d}\right) - \frac{(E_{rj}-E_d)}{RT_s}$$
Figure 6-8 shows plots of \( \ln \left( \frac{\alpha}{s_j} - 1 \right) \) vs. \( 1/T_s \) for each n-butane isotopologue studied for surface temperatures ranging from 300 to 425 K. We set the molecular adsorption probability \( \alpha \) equal to 0.78 in formulating the Arrhenius plots for each isotopologue, and assume that \( \alpha \) is independent of the surface temperature for the conditions studied. Each of the datasets shown in Figure 6-8 is well described by a linear function, indicating that the model accurately captures the kinetics governing the initial dissociation of n-butane on PdO(101). Apparent pre-factors and activation energies for dissociation, defined as \( \frac{v_{rj}}{v_d} \) and \( E_{rj} - E_d \), may be determined from the Arrhenius plots for each isotopologue.

Table 1 lists the apparent pre-factors and activation energies that we determined from the Arrhenius analysis along with the uncertainty in each quantity. To estimate the uncertainties in the pre-factors and activation energies, we calculated the uncertainty in the function;

\[
g(S_j) = \ln \left( \frac{\alpha}{s_j} - 1 \right)
\]

using the formula;

\[
\Delta g(S_j) = \frac{dg}{dS_j} \Delta S_j
\]

where the experimental uncertainty in the initial dissociation probabilities is estimated as \( \Delta S_j = \pm 0.05 \). The uncertainties reported in Table 1 correspond to standard deviations in the pre-factors and activation energies determined from Arrhenius analysis of the three functions \( g \) and \( g \pm \Delta g \) evaluated for each \( S_j \) vs. \( T_s \) dataset. The uncertainty in the function \( g(S_j) \) grows sharply when the value of \( S_j \) approaches the molecular adsorption probability. For this reason, we analyzed the data obtained from n-butane-\( d_0 \) over the
temperature range from 325 to 425 K since the values of \( S_0 \) are high at temperatures below 325 K. We analyzed the n-butane-\( d_6 \) and \( d_{10} \) data over the temperature range from 300 to 375 K, and omitted the small values of \( S_6 \) and \( S_{10} \) obtained at 400 K in our analysis.

The kinetic parameters obtained from the Arrhenius analysis are physically reasonable and compare well with prior data obtained for propane dissociation on PdO(101). For n-butane-\( d_0 \), we find values of \( \frac{v_d}{v_{r0}} = 1212 \pm 135 \) and \( E_d - E_{r0} = 23.2 \pm 0.6 \) kJ/mol for the apparent pre-factor and activation energy, where these quantities are shown as apparent kinetic parameters for desorption. The analysis thus predicts that the activation energy for n-butane-\( d_0 \) dissociation on PdO(101) lies 23.2 kJ/mol below the gas-phase energy level. In prior work, we reported an apparent pre-factor and activation energy of \(~2600\) and \(16.2\) kJ/mol for the initial dissociation of propane on PdO(101).[32] The present results indicate that the apparent activation energy is lower by 7 kJ/mol for n-butane vs. propane dissociation on PdO(101). This difference is consistent with expectations since alkane desorption energies increase linearly with the alkane chain length,[35] whereas the C-H bond energies are very similar for propane and n-butane. As confirmed by the analysis, one also expects that the pre-factor for alkane desorption will be greater than the dissociation pre-factor since molecules should gain more entropy in accessing the transition state for desorption compared with dissociation. According to our analysis, the apparent pre-factors for propane and n-butane dissociation on PdO(101) differ by about a factor of two. We are reluctant to attribute significance to this difference due to experimental uncertainty.
The analysis reveals key differences in the kinetic parameters among the n-butane isotopologues. For example, we find that the apparent activation energy for n-butane-\(d_0\) dissociation is 5.0 kJ/mol lower than that for n-butane-\(d_{10}\) dissociation, whereas the apparent pre-factor for n-butane-\(d_0\) dissociation is about 1.2 times lower than that for n-butane-\(d_{10}\). The difference in activation energies for n-butane-\(d_0\) vs. \(d_{10}\) dissociation agrees well with the zero-point energy difference of 4.8 kJ/mol between an alkane C-H and C-D bond.[116] The apparent activation energy for n-butane-\(d_6\) dissociation on PdO(101) is closer in value to that for n-butane-\(d_{10}\) than \(d_0\) (Table 1), which is consistent with the observation that the \(d_6\) dissociation probabilities are closer to the \(d_{10}\) than \(d_0\) values (Figure 6-7). Compared with the activation energies, the differences in apparent pre-factors are more slight among the isotopologues. Notably, we predict that the differences in the apparent activation energies among the isotopologues lie outside of the estimated uncertainties in these quantities. The pre-factors fall into a closer range of values and lie within the error limits of the analysis.

The kinetic parameters determined from the Arrhenius analysis allow estimation of the branching probability as well as apparent kinetic parameters for 1° C-H bond cleavage. In particular, the branching ratios for each isotopologue may be computed as a function of the surface temperature from the Polanyi-Wigner equation with the apparent kinetic parameters given in Table 1. Using Equation (6-10), we then calculate the branching probability for 1° C-H bond cleavage \(p_1\) as a function of the surface temperature. We find that \(p_1\) varies from 0.89 to 0.84 with increasing surface temperature from 300 to 425 K. For the temperature range considered, error analysis predicts an average uncertainty of \(\Delta p_1 = \pm 0.18\) in the \(p_1\) values computed using Equation
(6-10) based on the uncertainty in the kinetic parameters (Table 1). The analysis thus predicts a preference of about 87% for $1^\circ$ C-H bond cleavage during the dissociation of n-butane on PdO(101) in the limit of zero coverage for the temperature range studied. We have recently reported a selectivity of $\sim$90% for $1^\circ$ C-H bond cleavage during the low-temperature (< 200 K) dissociation of propane on PdO(101). However, the strong preference for $1^\circ$ C-H bond cleavage determined from the King and Wells data differs from the nearly equal preference for $1^\circ$ vs. $2^\circ$ C-H bond cleavage that we determined from the TPRS data for n-butane on PdO(101). We discuss this difference in more detail below.

Given $p_1$ as a function of the surface temperature, it is possible to estimate an apparent pre-factor and activation energy for $1^\circ$ C-H bond cleavage. From the definition of $p_1$ given in terms of rate coefficients for $1^\circ$ vs. $2^\circ$ C-H bond cleavage (Equation (6-7)), one may formulate the following Arrhenius construction,

$$\ln\left(\frac{1}{p_1} - 1\right) = \ln\left(\frac{k_{3H}}{k_{4H}}\right) = \ln\left(\frac{v_{2H}}{v_{1H}}\right) - \frac{(E_{2H} - E_{1H})}{RT_s}$$  (6-15)

where $\frac{v_{2H}}{v_{1H}}$ and $E_{2H} - E_{1H}$ represent the ratio of pre-factors and difference in activation energies for $2^\circ$ vs. $1^\circ$ C-H bond cleavage of the molecular n-butane precursor on PdO(101). Figure 6-9 shows that a plot of $\ln\left(\frac{1}{p_1} - 1\right)$ vs. $1/T_s$ is well-described by a linear function. From the slope and intercept of the Arrhenius plot, we estimate values of $\frac{v_{1H}}{v_{2H}} = 2.0 \pm 4.8$ and $E_{1H} - E_{2H} = -3.5 \pm 1.8$ kJ/mol for the kinetic parameters of $1^\circ$ relative to $2^\circ$ C-H bond cleavage of n-butane on PdO(101) in the limit of zero coverage. The analysis thus reveals that both entropic and energetic factors cause $1^\circ$ C-H bond
cleavage to be favored over 2° C-H bond cleavage in the initial dissociation of n-butane on PdO(101).

6.4 Discussion

We find that n-butane preferentially dissociates by 1° C-H bond cleavage on PdO(101) in the limit of zero n-butane coverage, but that the 1° C-H bond selectivity decreases with increasing n-butane coverage such that 1° and 2° C-H bond cleavage become nearly equally probable when the coverage of n-butane σ-complexes increases to about 40% of the saturation coverage (~0.03 ML). A preference for 1° C-H bond cleavage of alkanes is generally unexpected because 1° C-H bonds are about 12 kJ/mol stronger than 2° C-H bonds when bond cleavage occurs homolytically. We have recently reported dispersion-corrected DFT calculations (DFT-D3) which show that propane C-H bond cleavage occurs heterolytically on PdO(101) via hydrogen transfer to a cus-O atom, and that 1° C-H bond cleavage is intrinsically favored because the 1-propyl transition structure (TS) adopts a more stabilizing charge distribution than the 2-propyl transition structure.[105] The effect that we predict is consistent with stabilization via substituent polarization whereby the ethyl substituent of the 1-propyl TS is able to form a larger group dipole than the individual methyl groups, and thereby better stabilizes the negatively charged C atom that is generated via heterolytic scission of a 1° C-H bond.

We have conducted initial DFT-D3 calculations which predict that n-butane also dissociates preferentially on PdO(101) by 1° C-H bond cleavage. We used the same computational procedures in our calculations with n-butane as in earlier studies[66] and plan to submit more details of these findings in a future publication. As discussed
above, we find that the preferred n-butane σ-complex on PdO(101) is a $\eta^1(2H)$ complex (Figure 6-4), in which the n-butane molecule forms two H-Pd dative bonds along the cus-Pd row.[66] One of the H-Pd dative bonds occurs at a CH$_3$ group, and the other occurs at the next closest CH$_2$ group, i.e., at the C$_1$ and C$_3$ positions. We have identified other adsorbed n-butane complexes on PdO(101) using DFT-D3, but find that the $\eta^1(2H)$ complex is the most stable by at least 10 kJ/mol. We have also shown previously that alkane C-H bond cleavage on PdO(101) is only facile for the C-H bonds that coordinate with the cus-Pd atoms of the surface.[107] The n-butane $\eta^1(2H)$ complex can thus serve as a precursor for either 1° or 2° C-H bond cleavage since each type of C-H bond coordinates with a cus-Pd atom in this complex. Using DFT-D3, we predict zero-point corrected energy barriers of 56.3 and 60.3 kJ/mol for 1° vs. 2° C-H bond cleavage, respectively, of the $\eta^1(2H)$ n-butane complex on PdO(101). The DFT-predicted difference of 4.0 kJ/mol between the 1° and 2° C-H bond cleavage barriers agrees well with our experimental estimate of 3.5 kJ/mol.

Atomic charge analysis of the n-butane initial state and transition states indicates that C-H bond cleavage of n-butane is heterolytic on PdO(101), with a positively-charged H-atom transferring to a cus-O atom. Similar to our recent results with propane,[105] the analysis shows that the 1-butyl transition structure adopts a more stabilizing charge distribution than the 2-butyl transition structure. The greater charge stabilization of the 1- vs. 2-butyl transition structures appears to be the key factor causing the barrier for 1° C-H bond cleavage to be lower than that for 2° C-H bond cleavage. The initial DFT-D3 calculations are consistent with our experimental finding of a strong preference for 1° C-H bond cleavage in the initial dissociation of n-butane on
PdO(101), and also agree with the high selectivity for 1° C-H bond cleavage of propane on PdO(101) reported previously.[85]

Our experimental results provide evidence that the 1° C-H bond selectivity decreases as the coverage of n-butane σ-complexes initially increases to ~0.03 ML, but remains constant at 49% as the coverage increases from 0.03 to 0.073 ML. This conclusion is based primarily on a comparison of the results of our King and Wells measurements (zero coverage limit) and the TPRS data obtained at moderate to high coverage. We note, however, that the branching probabilities for 1° C-H bond cleavage estimated from the TPRS data do exhibit a marked increase as the coverage decreases below ~0.03 ML (Figure 6-6), in agreement with the King and Wells data which reveal that the probability for 1° C-H bond cleavage is ~87% in the limit of zero coverage of n-butane on PdO(101) at temperatures between 300 and 425 K.

A possible interpretation for the change in C-H bond selectivity is that n-butane dissociation occurs on different reaction sites, and that the contributions from these sites change with the n-butane coverage. For example, dissociation at defect sites could be prevalent at low n-butane coverage, but dissociation on the PdO(101) terraces may become dominant at higher coverages. Such an interpretation would imply that defect sites are more active than the PdO(101) terrace sites toward alkane C-H bond scission. However, we have not observed indications that defect sites play a role in alkane C-H bond activation on PdO(101) in any of our prior studies.[32; 35; 66; 85] For example, we have recently found that propane activation on partially oxidized Pd(111) surfaces occurs exclusively on PdO(101) domains and that the presence of coexisting phases, such as PdO(101) + metal or two-dimensional oxides, and their domain boundaries
have a negligible influence on the surface reactivity.\textsuperscript{[117]} Prior experimental and computational results also demonstrate clearly that the prevalent \textit{cus}-Pd and \textit{cus}-O sites of the PdO(101) surface are highly active toward alkane C-H bond cleavage, as evidenced by C-H bond scission barriers that lie well below the gas-phase energy level.\textsuperscript{[105; 107]} Among our prior studies of PdO(101) surface chemistry, we have found evidence that defect sites influence only the dissociation of \textit{H}_2. In that case, our results suggest that \textit{H}_2 initially dissociates on reduced sites of the surface, before activating on the PdO(101) terraces at higher \textit{H}_2 coverages.\textsuperscript{[42]} Evidence for \textit{H}_2 dissociation on metallic defect sites of the surface came, in part, from observations of a recombinative \textit{H}_2 TPD feature at temperatures at which H-atoms recombine on metallic Pd surfaces. In contrast, we do not observe \textit{H}_2 desorption during TPRS experiments with alkanes on PdO(101). This finding suggests that alkane C-H bond activation occurs to a negligible extent on reduced sites that may exist on the PdO(101) surface.

Assuming that n-butane dissociates only the PdO(101) terraces, a logical conclusion is that interactions among n-butane molecules are responsible for the observed change in C-H bond selectivity with increasing n-butane coverage. For example, intermolecular interactions could cause n-butane molecules to adopt new configurations along the \textit{cus}-Pd row as the coverage increases, and the C-H bond selectivity could vary among these species. The presence of neighboring n-butane molecules could also alter the reaction pathways for 1\textdegree{} vs. 2\textdegree{} C-H bond cleavage of an \textit{\eta} \textsuperscript{1} n-butane complex in different ways, thereby causing the C-H bond selectivity to change with coverage. Indeed, the difference between the 1\textdegree{} and 2\textdegree{} C-H bond cleavage
barriers would only need to change by a few kJ/mol to effect a large change in C-H bond selectivity.

The specific nature of the coverage dependence of the n-butane C-H bond selectivity on PdO(101) is difficult to explain from the available data. In particular, it is unclear why the selectivity only changes with coverage at values below 40% of the saturation coverage, but remains constant as the coverage increases from ~40% to 100%. We note that a n-butane coverage equal to 40% of the $\alpha_1$ state saturation coverage is equivalent to ~9% of the $\textit{cus}$-Pd site density or 0.36 C atoms per $\textit{cus}$-Pd atom. A possible reason that the C-H bond selectivity changes with coverage only at low coverages is that the n-butane $\sigma$-complexes form pairs or larger aggregates on PdO(101) due to attractive intermolecular interactions. In this case, the invariance of the C-H bond selectivity at higher coverage may indicate that the concentration of n-butane $\sigma$-complexes with at least one nearest neighbor reaches saturation at a relatively low total coverage, and thus that further increases in the coverage do not alter the local reaction environment. Such behavior would mean that the n-butane molecules are sufficiently mobile to form pairs at low coverage and that the intermolecular interactions are indeed attractive. Overall, because the results of prior investigations provide evidence that defect sites contribute negligibly to alkane C-H bond activation on PdO(101) under UHV conditions, we assert that intermolecular interactions among the n-butane complexes are responsible for the variation in C-H bond selectivity that occurs as the n-butane coverage decreases below 0.03 ML. Determining the exact cause of this coverage dependence requires a more detailed understanding of the structure of the n-butane adlayer on PdO(101) and must await future investigations.
6.5 Summary

We used TPRS and King and Wells measurements to investigate the initial C-H(D) bond cleavage of n-butane isotopologues on PdO(101). We observe significant kinetic isotope effects in the initial C-H(D) bond cleavage of n-butane on PdO(101) such that the dissociated fraction of n-butane-\(d_0\) obtained during TPRS is 1.8 times larger than that of n-butane-\(d_{10}\) over a range of initial n-butane coverages. Similarly, King and Wells measurements show that the initial dissociation probability of n-butane-\(d_0\) on PdO(101) is about twice that of n-butane-\(d_{10}\) at surface temperatures between 300 and 400 K. We also observe differences between the reactivity of the partially-deuterated n-butane-\(d_6\) compound and both n-butane-\(d_0\) and \(d_{10}\) which allow quantification of the initial C-H bond selectivity using kinetic modeling. The model that we employed considers that a molecularly-adsorbed n-butane species acts as a precursor to either 1° or 2° C-H bond cleavage on PdO(101), and that the net dissociation probability is determined by a kinetic branching between C-H bond cleavage and desorption of the molecular precursor. Based on the dissociation yields measured using TPRS, the model predicts that the initial C-H bond selectivity is equal to 49% at low temperature and remains constant at this value for initial coverages of the n-butane precursor between ~40% and 100% of the saturation value.

We also measured the initial dissociation probabilities of the n-butane isotopologues on PdO(101) as a function of the surface temperature using the King and Wells method. We find that the initial dissociation probabilities decrease with increasing surface temperature from ~300 to 400 K, and observe differences in the reactivity among the n-butane isotopologues studied. The precursor-mediated kinetic model
accurately describes the temperature dependence of the initial dissociation probability of each n-butane isotopologue on PdO(101). From the kinetic model we estimate that, in the limit of zero coverage, the apparent activation energy for initial C-H bond cleavage of n-butane-\(d_0\) on PdO(101) lies 23.2 kJ/mol below the gas-zero energy level, and that the activation energy for the initial C-D bond cleavage of n-butane-\(d_{10}\) is about 5.0 kJ/mol higher than that of n-butane-\(d_0\). Analysis of the initial dissociation probabilities also predicts that the branching probability for \(^1\)C-H bond cleavage of n-butane on PdO(101) is equal to \(~87\%\) in the limit of zero coverage, and varies only weakly with the surface temperature between 300 and 400 K. The analysis further predicts that the \(^1\)C-H bond cleavage of n-butane is favored both entropically and energetically on PdO(101); we estimate that the pre-factor and activation energy for \(^1\) relative to \(^2\)C-H bond cleavage are equal to 2.0 and -3.5 kJ/mol, respectively. Finally, our results provide evidence that the selectivity for \(^1\)C-H bond cleavage decreases from \(87\%\) to \(49\%\) as the n-butane coverage increases to 40% of the saturation coverage of the molecular precursor state on PdO(101), and remains constant at \(49\%\) with further increases in coverage. We speculate that intermolecular interactions among the adsorbed n-butane \(\sigma\)-complexes are responsible for the variation in C-H bond selectivity with the n-butane coverage.
Figure 6-1. Partial pressure of n-butane vs. time obtained during separate King and Wells measurements in which a n-butane molecular beam was scattered from PdO(101) or Pd(111). Traces are shown for beam reflection from PdO(101) at 325 K (black) and also from Pd(111) at 90 K (blue) and 400 K (red). Pressures needed to compute the initial adsorption probability are indicated for the trace obtained from PdO(101).
Figure 6-2. Model representation of PdO(101) surface. (a) Top and (b) side view of the PdO(101) thin film structure. The orange and blue atoms represent O and Pd atoms, respectively. Rows of 3-fold coordinated (cus) Pd and O atoms are indicated. The a and b directions correspond to the [010] and [101] crystallographic directions of PdO.
Figure 6-3. TPRS spectra of n-butane and CO\textsubscript{2} obtained after saturating the n-butane monolayer on PdO(101) at a substrate temperature of 90 K. The spectra are obtained in separate experiments using n-butane-d\textsubscript{0}, d\textsubscript{6} and d\textsubscript{10}. The TPRS spectra are obtained using a constant heating rate of 1K/s.
Figure 6-4. Representations of the preferred n-butane $\eta_1(2H)$ complex on PdO(101) predicted by DFT-D3 (top and side view).[107] A H-Pd dative bond forms at a CH$_3$ group and at a CH$_2$ group in this configuration.
Figure 6-5. CO$_2$ yield (ML) versus the initial coverage of n-butane $\sigma$-complexes ($\alpha_1$ state) on PdO(101) as determined from TPRS experiments at an initial surface temperature of 90 K. Data is shown for butane-$d_0$, butane-$d_6$ and butane-$d_{10}$ and the solid lines represent linear fits to each dataset.
Figure 6-6. Conditional probability for \(1^\circ\) C-H bond cleavage of n-butane on PdO(101), given that n-butane reacts, as a function of the initial n-butane coverage in the \(\alpha_1\) state calculated from TPRS experiments.
Figure 6-7. Initial adsorption probability as a function of the surface temperature for n-butane isotopologues on PdO(101) as determined from beam reflectivity measurements. Data is shown for n-butane-d0, d6, and d10 and the dotted curve represents a fit to the n-butane-d0 data using the kinetic model discussed in the text.
Figure 6-8. Arrhenius plots of $\ln\left(\frac{\alpha}{S_j} - 1\right)$ vs. $1/T_s$ for the dissociative chemisorption of n-butane-d0, d6 and d10 on PdO(101) at surface temperatures from ~300 to 425 K. The Arrhenius construction is obtained from the precursor-mediated model discussed in the text. The abscissa is calculated using initial dissociation probabilities $S_j$ obtained from King and Wells measurements, and assuming a value of $\alpha = 0.78$ for the molecular adsorption probability of each isotopologue. Linear fits for each data set are shown. The kinetic parameters determined from the fits are given in Table 6-1.
Figure 6-9. Arrhenius plot of $\ln\left(\frac{1}{P_1} - 1\right)$ vs. $1/T_s$ where $p_1$ represents the conditional probability for $1^\circ$ C-H bond cleavage of n-butane on PdO(101) in the limit of zero coverage. The values of $p_1$ are computed (open circles) using Equation (6-10) with kinetic parameters taken from analysis of the initial dissociation probabilities obtained from n-butane isotopologues as a function of the surface temperature. The dashed line represents a linear fit of the computed $p_1$ values.
Table 6-1. Apparent kinetic parameters for the initial dissociation of n-butane isotopologues on PdO(101) determined from initial dissociation probabilities measured as a function of the surface temperature from ~300 to 400 K.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>$\nu_d/\nu_{rj}$</th>
<th>$E_d - E_{rj}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C$<em>4$H$</em>{10}$ ($d_0$)</td>
<td>1212 ± 135</td>
<td>23.2 ± 0.6</td>
</tr>
<tr>
<td>CD$_3$CH$_2$CH$_2$CD$_3$ ($d_6$)</td>
<td>973 ± 189</td>
<td>19.3 ± 0.2</td>
</tr>
<tr>
<td>n-C$<em>4$D$</em>{10}$ ($d_{10}$)</td>
<td>982 ± 514</td>
<td>18.2 ± 0.6</td>
</tr>
</tbody>
</table>
7.1 Motivation of the Reactivity of Oxide Phases Study

The oxidation of late transition metals plays a central role in several applications of oxidation catalysis, including the catalytic combustion of natural gas, exhaust gas remediation in automobiles and fuel cell catalysis. A key issue for describing such catalytic processes is identification of the catalytically active surface phase(s) and developing a more detailed understanding of the coupling between the surface chemical activity and the surface phase distribution. The catalytic combustion of methane over supported Pd catalysts is a particularly relevant example in this context as many prior studies provide evidence that PdO is highly active toward methane oxidation and that the formation of a bulk-like PdO layer is responsible for the exceptionally high activity of supported Pd catalysts for the catalytic combustion of natural gas [2-9]. Consistent with these findings, we have recently reported that the activation and oxidation of \( n \)-alkanes (> \( C_2 \)) is facile on a PdO(101) thin film under ultrahigh vacuum (UHV) conditions [35; 66; 107]. In contrast, we find that ordered two-dimensional (2D) oxides are unreactive toward alkanes in UHV. In the present study, we report the results of an experimental investigation of the reactivity of partially oxidized Pd(111) surfaces toward the oxidation of propane and find that only PdO(101) domains are active in promoting this reaction under the conditions investigated.

Motivation for the present study comes largely from observations that the activity of Pd surfaces toward the catalytic combustion of methane depends not only on the total surface oxygen coverage but also on the manner in which the oxygen coverage is generated. The reason for this dependence is that the surface phase distribution
obtained at a given oxygen coverage can depend on whether the partially-oxidized surface is generated by oxidizing the metal or reducing the oxide. Prior studies indeed show that changes in the surface-oxygen phase distribution produce a kinetic hysteresis in the oxidation rate of methane on Pd catalysts during cycles of heating vs. cooling [3; 5; 8; 22]. The methane oxidation rate is higher when a given oxygen coverage is obtained by oxidizing the metal rather than reducing PdO in the hysteresis regime. Based on measurements using ambient-pressure XPS, Gabasch et al. [8] have presented evidence that a precursor oxide phase, so-called PdO seeds, is highly reactive toward CH$_4$ oxidation on Pd(111), and that the formation of PdO seeds causes the reactivity of oxidized Pd(111) to be higher during surface oxidation than reduction. These workers report that bulk PdO is also highly active toward methane oxidation, in agreement with a recent *in situ* investigation of methane oxidation on Pd(100) [118]. These findings provide substantial motivation for pursuing a more detailed understanding of the reactivity of various oxide phases generated on Pd surfaces during surface oxidation vs. reduction.

Previous studies provide detailed information about the oxidation mechanism of Pd(111) and the nature of oxygen phases that develop during the course of oxidation [11-13; 39; 119-129]. These studies show that oxygen atoms initially chemisorb on Pd(111) up to 0.25 ML and organize into a p(2×2) structure, where we define 1 ML as equal to the surface atom density of Pd(111) of 1.5 × 10$^{15}$ cm$^{-2}$. Above 0.25 ML, two-dimensional (2D) oxide phases develop on Pd(111) and saturate at an oxygen atom density of ~0.70 ML [13; 124; 126]. Klikovits et al. report that a variety of similar 2D oxides grow on Pd(111) below 600 K, but that these phases transform into a more
stable Pd$_5$O$_4$ 2D oxide above 600 K [126]. After the surface oxide phase saturates, further increases in the oxygen coverage produce a PdO precursor phase that transforms into a bulk PdO(101) thin film [12; 39]. TPD measurements show that the precursor phase decomposes to yield an O$_2$ desorption feature centered at 600 K, whereas decomposition of the 2D oxide phase(s) as well as multilayer PdO(101) domains on Pd(111) produce sharp O$_2$ TPD peaks at ~750 K. Prior work provides evidence that the precursor phase corresponds to small oxide domains of about two layers in thickness, which is consistent with the PdO seeds identified by Gabasch et al. using AP-XPS [8].

The thermal stability of the PdO seeds has a significant influence on the kinetics of oxide growth on Pd(111) as well as the morphological evolution of the oxide phases. Kan and Weaver have recently identified two kinetic regimes for the oxidation of Pd(111), with the distinction between these regimes determined by whether PdO formation and growth occurs below or above a surface temperature at which PdO seeds are stable [12]. For the O-atom incident fluxes employed in that work, the so-called stable oxidation regime occurs at temperatures below about 600 K while meta-stable oxidation occurs at temperatures above 600 K. A key difference between these regimes is the dominance of nucleation over growth in the stable regime and a reversal of this competition in the meta-stable regime. For example, oxidation at 500 K produces stable PdO seeds which reach a maximum concentration at ~1.3 ML, and coexist with bulk PdO(101) domains up to a total oxygen coverage of ~2 ML [12]. The PdO(101) film on Pd(111) reaches an effective saturation coverage of ~3 to 4 ML during oxidation at 500 K, and is characterized by large, flat crystalline domains.
The oxidation of Pd(111) at 650 K occurs in the meta-stable regime in which growth dominates PdO seed formation. In this case, PdO domains thicken considerably before they agglomerate to produce a closed PdO(101) film. As a result, PdO(101) domains coexist with 2D oxide domains over a wide range of oxygen coverage and the PdO(101) film saturates at a greater thickness compared with oxidation in the stable regime. At 650 K, the PdO(101) film saturates at an oxygen coverage of ~14 ML, which corresponds to about 21 oxide layers, and PdO(101) domains co-exist with 2D oxide domains up to a total oxygen coverage of at least 12 ML [12]. Oxidation at 650 K (meta-stable regime) thus produces a relatively rough and heterogeneous surface that is comprised of thick PdO(101) domains as well as 2D oxide domains before the oxide saturates. In contrast, oxidation at 500 K (stable regime) produces a more uniform PdO(101) thin film and also allows the generation of surfaces containing stable PdO seeds in coexistence with either 2D oxide or bulk PdO(101) domains. These differences in the morphological evolution of oxide phases are significant and could influence the chemical reactivity of partially oxidized Pd(111).

The reduction of PdO thin films can also produce surface phase distributions and morphologies that differ from those obtained during Pd oxidation. As mentioned above, prior studies provide evidence that PdO seeds form during the initial oxidation of Pd(111) but that the seeds do not evolve during PdO reduction. A recent STM investigation also reveals that the thermal decomposition of PdO(101) thin films produces surface structures that have not been observed during PdO growth [130]. For example, STM shows that reduction of the PdO(101) surface produces long chains of reduced sites within the PdO(101) terraces as well as large domains of reduced sites,
some of which are disordered while others exhibit local ordering that resembles that of 2D oxide phases on Pd(111). Partially reduced PdO(101) films also exhibit large domains containing PdO(101) islands which result from the re-oxidation of reduced surface domains by oxygen atoms that migrate from the bulk to the surface of the PdO film. An unsettled issue from this recent STM study is whether the reduced phases which form during PdO(101) decomposition are metallic or oxidic layers [130]. We address this issue in the present study. Overall, the wide variety of domain types observed on partially reduced PdO(101) surfaces suggests the possibility of diverse surface chemical properties since each phase and their domain boundaries offer a broad distribution of sites.

In the present study, we generated partially oxidized Pd(111) and partially reduced PdO(101) surfaces under different conditions and investigated the reactivity of these surfaces toward the complete oxidation of propane using temperature programmed reaction spectroscopy (TPRS). Our results show that only PdO(101) domains are reactive toward propane and that the CO\textsubscript{2} product yields scale directly with the PdO(101) areal fraction on the surface, irrespective of the types and distribution of phases which co-exist with PdO(101) domains. We also observe differences in the molecular binding of propane on phases of chemisorbed oxygen atoms, 2D oxide and PdO(101), and show that deconvolution of propane TPD spectra allows an approximate quantification of the areal fractions of different surface phases on partially oxidized Pd(111) and partially reduced PdO(101). This latter analysis clarifies the surface phase evolution that occurs during Pd(111) oxidation and PdO(101) reduction.
7.2 Experimental Details

Previous studies [37; 38] provide details of the three-level UHV chamber utilized for the present experiments. The Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder that is held in thermal contact with a liquid nitrogen cooled reservoir. A type K thermocouple spot-welded to the backside of the crystal allows sample temperature measurements. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports maintaining or linearly ramping the sample temperature from 81 K to 1250 K. Initially, sample cleaning consisted of sputtering with 600 eV Ar\(^+\) ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to 923 K to desorb oxygen and carbon oxides. As discussed previously, we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in preparing the PdO(101) thin films used in this study [39]. We considered the Pd(111) sample to be clean when we could no longer detect contaminants with X-ray photoelectron spectroscopy (XPS), obtained sharp low energy electron diffraction (LEED) patterns consistent with the Pd(111) surface, and did not detect CO or CO\(_2\) production during flash desorption after oxygen adsorption.

A two-stage differentially-pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system [37; 38]. We used O-atom beams to prepare
partially oxidized surfaces and PdO(101) films in this study, conducting the beam exposures at 500 and 650 K to generate different morphologies and coexisting phases during oxide growth, as described in the Introduction and elaborated further in the sections that follow. In the present study, we find that the oxygen uptake at 500 vs. 650 K effectively saturates once the PdO(101) film reaches a thickness equivalent to ~3.2 vs. 13.0 ML of oxygen atoms, respectively, for the beam flux employed. We generated the saturated PdO(101) film at 500 K by exposing the Pd(111) sample to an ~12 ML dose of gaseous oxygen atoms supplied in a beam. This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains ~3.2 ML of oxygen atoms and is about 12 Å thick [11; 12]. For oxidation at 650 K, we find that an ~50 ML dose of gaseous oxygen atoms generates a PdO(101) film that contains ~13.0 ML of oxygen atoms and is about 50 Å thick. The structure of the PdO(101) surface is discussed in detail below. After preparing the thin or thick PdO(101) films, we annealed these surfaces at 680 K and 720 K, respectively, for various durations in order to generate partially-reduced surfaces [130]. Below, we provide details about the conditions used for partially reducing the PdO(101) layers.

We investigated the reactivity of various partially oxidized surfaces toward the complete oxidation of propane using TPRS. We delivered propane (Matheson, 99.993%) to the sample using a calibrated beam doser with the propane incident flux set to approximately $8.7 \times 10^{-4}$ ML s$^{-1}$. We set the sample to doser distance to ~50 mm to ensure uniform impingement of the propane across the sample surface. Due to this large distance, the direct flux of propane at the sample surface was only about 2.5 times higher than the background flux. After the propane exposures, we conducted TPRS
experiments by positioning the sample in front of the QMS and then heating at a constant rate of 1 K s$^{-1}$ until the sample temperature reached 923 K. The PdO thin films completely decompose when heated to 923 K so it was necessary to prepare fresh PdO films for each propane adsorption experiment. We estimate propane coverages by scaling the integrated desorption spectra of 29 amu by an integrated TPD spectrum collected from a monolayer of propane adsorbed on Pd(111) at 110 K, and assuming that the monolayer saturates at 0.205 ML on Pd(111). This value corresponds to the saturation coverage of the propane monolayer on Pt(111) as determined from calibrated molecular beam experiments by Carlsson and Madix [63]. Kao and Madix [131] have shown that the binding energy of propane is similar on Pd(111) and Pt(111) so it is reasonable to assume that the propane monolayer saturates at the same coverage on these surfaces.

We find that propane molecules react with the PdO(101) surface to produce CO$_2$ and H$_2$O which desorb during temperature programmed reaction spectroscopy (TPRS) experiments [32]. To estimate the CO$_2$ desorption yields, we conducted TPRS experiments of CO oxidation on Pd(111) initially covered with adsorbed oxygen atoms. We performed these experiments by adsorbing less than 0.25 ML of oxygen atoms on Pd(111), and then exposing the surface to large doses of CO with the sample held at 100 K. In subsequent TPRS experiments, only CO and CO$_2$ evolve from the surface, indicating that atomic oxygen was the limiting reactant. The measured CO$_2$ TPRS peak areas were then set equal to the initial oxygen coverages, which were determined in separate TPD experiments conducted immediately before the CO oxidation experiments. We estimate atomic oxygen coverages on Pd(111) by scaling integrated
O₂ TPD spectra with those obtained after exposing Pd(111) at 300 K to a saturation
dose of O₂, and assuming that the O₂ exposure generates an atomic oxygen coverage
of 0.25 ML.

7.3 Experimental Results

7.3.1 Structure of PdO(101)

A model representation of the stoichiometric PdO(101) surface that we
investigated in this study is shown in Figure 7-1. Bulk crystalline PdO has a tetragonal
unit cell and consists of square planar units of Pd atoms fourfold coordinated with
oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit
cell, where the a and b lattice vectors coincide with the [010] and [T01] directions of the
PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating
rows of threefold or fourfold coordinated Pd or O atoms that run parallel to the a
direction shown in Figure 7-1. Thus, half of the surface O and Pd atoms are
coordinatively unsaturated (cus). The side view of PdO(101) shows that the coordinative
environment associated with each cus-Pd atom resembles a square planar Pd complex
with a coordination vacancy directed away from the surface and three oxygen ligands,
one of which is a cus-O atom. The areal density of each type of coordinatively-distinct
atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111)
surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML (monolayer), and
each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms, where we
define 1 ML as equal to the surface atom density of Pd(111).

7.3.2 Thermal Reduction of PdO(101) Films

We generated partially-reduced surfaces by isothermally decomposing PdO(101)
films. Figure 7-2 shows O₂ desorption traces obtained during the isothermal
decomposition of the thin vs. thick PdO(101) films prepared at 500 and 650 K, respectively. As noted in the Figure 7-2, the isothermal desorption traces are shown for decomposition of the thin vs. thick films at temperatures of 680 vs. 720 K, respectively. We selected the decomposition temperatures such that the time required to fully decompose each PdO(101) film was approximately 60 minutes. This selection affords a similar level of control and reproducibility in generating partially reduced surfaces. Not surprisingly, the thick PdO(101) film requires a higher temperature to fully decompose in 60 minutes compared with the thin film. We annealed the PdO(101) films for varying durations in order to generate partially reduced surfaces with different oxygen content.

We have recently reported results of an STM investigation of the structural changes that occur during isothermal decomposition of PdO(101) thin films, and discussed the characteristic kinetic regimes for isothermal decomposition [130]. Briefly, the isothermal decomposition traces exhibit four regions, labeled as $\beta_1$, $\beta_2$, $\beta_3$ and $\beta_4$ in Figure 7-2. After the temperature initially stabilizes, the $O_2$ desorption rate decreases ($\beta_1$ region) until reaching a nearly steady value. After a period over which the $O_2$ desorption rate changes slowly with time ($\beta_2$ region), the desorption rate begins to increase more rapidly and reaches a maximum value ($\beta_3$ region). The $\beta_3$ region represents an autocatalytic regime wherein the $O_2$ desorption rate increases as PdO film decomposition progresses. STM measurements reveal that reduced sites promote further PdO(101) reduction, and hence that the decomposition process occurs autocatalytically since the concentration of reduced sites increases as the PdO(101) surface liberates oxygen [130]. Depletion of oxygen from the film causes the $O_2$ desorption rate to decrease toward the zero baseline during the final stages of
isorthermal PdO(101) film decomposition ($\beta_4$ region). Our prior STM results reveal that different types of reduced domains develop during isothermal decomposition and that PdO(101) domains are also regenerated. In the present study, we investigated the surface reactivity as a function of the extent of oxide reduction and find that the presence of different surface phases produces distinct features in the propane TPD spectra. This latter characteristic allows us to estimate how the areal fractions of coexisting surface phases evolve during thermal reduction of the PdO(101) films.

7.3.3 Adsorption and Reactivity of Propane on Oxygen Phases Generated on Pd(111) at 500 K

Figure 7-3a shows propane TPD spectra obtained from representative oxygen phases on Pd(111) after saturating the surfaces with propane at 85 K. For these experiments, we prepared oxygen-covered surfaces by exposing Pd(111) to an oxygen atom beam at a surface temperature of 500 K. The TPD spectra reveal clear differences in the binding of propane on Pd(111), the 2D oxide(s) and PdO(101). The propane TPD spectrum obtained from clean Pd(111) exhibits a predominant peak at 153 K arising from propane physisorbed in a monolayer as well as a small feature at ~125 K which likely originates from a small quantity of second layer molecules. Desorption of propane from a p(2×2)-O layer on Pd(111) produces a TPD spectrum that is nearly identical to that obtained from clean Pd(111), demonstrating that chemisorbed oxygen atoms have a negligible effect on the molecular binding of propane on Pd(111), at least up to an oxygen coverage of 0.25 ML. TPD data are also shown for propane adsorbed on two types of 2D oxides. One of the 2D oxides corresponds to a mixture of meta-stable structures [13; 122] that we generate by adsorbing ~0.70 ML of oxygen atoms on Pd(111) at 500 K, while the second is the stable Pd$_5$O$_4$ structure which forms upon
heating the meta-stable 2D oxide to 625 K. LEED clearly shows the formation of the Pd₅O₄ structure during surface heating [124]. The propane TPD spectrum obtained from Pd₅O₄ exhibits a single sharp peak at 138 K, revealing that propane binds more weakly on the 2D oxide than on clean Pd(111). The propane TPD spectrum obtained from the meta-stable 2D oxide also exhibits a peak at 138 K as well as a smaller peak at ~150 K. This latter peak most likely arises from propane desorbing from unoxidized surface domains which are covered by chemisorbed oxygen atoms. The close overlap of the main propane TPD peaks obtained from the meta-stable 2D oxide and Pd₅O₄ suggests that the molecular binding of propane is effectively identical on the various 2D oxides of Pd(111).

The propane TPD spectrum obtained from the ~3.2 ML PdO(101) thin film is broad and exhibits two desorption maxima at 131 and 193 K, labeled as $\alpha_2$ and $\alpha_1$, respectively. We have previously shown that the $\alpha_1$ peak corresponds to a propane $\sigma$-complex which datively bonds with cus-Pd atoms of the surface, and that this molecular species acts as a precursor to propane C-H bond activation on PdO(101) [32; 35; 66; 85]. Taking into account the quantity of $\alpha_1$ propane molecules which react during TPRS, we estimate that the saturation coverages in the $\alpha_2$ and $\alpha_1$ states are nearly the same at ~0.09 ML. Since the concentration of cus-Pd and 4f-Pd sites are also the same on PdO(101), the similar saturation coverages of the $\alpha_2$ and $\alpha_1$ states is consistent with the idea that the $\alpha_2$ peak is associated with propane adsorbed on the 4f-Pd facet. We also find that pre-adsorbing O₂ or H₂O to selectively block the cus-Pd sites hinders the adsorption of propane into the $\alpha_1$ state but has little effect on the coverage attained in the $\alpha_2$ state [66], which further supports our interpretation of the propane TPD peaks.
Lastly, we show a propane TPD spectrum labeled as “precursor” that was obtained from Pd(111) containing 1.3 ML of oxygen atoms that were adsorbed at 500 K. At a total oxygen coverage of 1.3 ML, PdO seeds are present at their maximum concentration and coexist with 2D oxide and newly-formed PdO(101) domains [130]. The corresponding propane TPD spectrum exhibits a predominant peak at 131 K as well as a shoulder at 138 K and a low intensity feature at 193 K. We attribute the shoulder at 138 K to propane desorbing from 2D oxide domains that coexist with the PdO seeds. The peaks at 131 and 193 K overlap with the desorption maxima obtained from propane adsorbed on the PdO(101) film. This overlap suggests that the PdO seeds provide similar binding sites for propane as the ideal PdO(101) surface, which is reasonable considering that the PdO seeds transform to fully developed PdO(101) domains as the oxygen coverage increases. However, the $\alpha_2: \alpha_1$ peak intensity ratio is considerably higher in the propane TPD trace obtained from the seed-covered surface compared with PdO(101), even after subtracting a contribution at 138 K due to propane desorption from 2D oxide domains.

A possible interpretation of the high $\alpha_2: \alpha_1$ ratio is that the PdO seeds are predominantly covered with sites that weakly bind propane ($\alpha_2$ peak), and thus that the seeds differ structurally and/or compositionally from stoichiometric PdO(101). Alternatively, the surface structure of the seeds may be similar to PdO(101) but the close proximity of their surfaces to the 2D oxide and/or metal substrate might weaken the binding of the propane $\sigma$-complexes. It is worth noting that prior studies provide evidence that the PdO seeds have distinct properties compared with the 2D oxide and PdO(101). For example, ion scattering measurements suggest that the seeds have a
higher surface concentration of oxygen atoms compared with both the 2D oxide and PdO(101) [39]. This difference as well as the relatively low thermal stability of the seeds further supports the idea that the PdO seeds have different surface structural characteristics than PdO(101), though the exact structure of the PdO seeds remains unresolved. Overall, the propane TPD data shows that propane binds more weakly on the PdO seeds than on PdO(101).

As a final point, we note that the propane saturation coverage is \(\sim 0.175 \pm 0.02\) ML for all of the oxygen phases on Pd(111) that we investigated. This coverage estimate accounts for the amount of propane which reacts during the TPRS measurements. We thus conclude that each oxygen phase as well as clean Pd(111) can accommodate approximately the same amount of propane, even though the propane binding energies vary among these surfaces. This similarity may indicate that intermolecular interactions determine the saturation coverages of the propane monolayer on the surfaces investigated here. Based on the reported structure, [132] we estimate that the most densely-packed plane of a bulk propane crystal contains 0.23 ML of propane molecules, and that the average planar density is 0.13 ML. These values are within about 25% of the 0.175 ML saturation coverage estimated in the present study, and thus lend support to the idea that intermolecular interactions play a dominant role in determining the maximum packing density within the propane monolayers studied here.

Figure 7-3b shows CO\(_2\) TPRS spectra obtained after adsorbing propane on the surface oxygen phases discussed above. The CO\(_2\) desorption yields are representative of the quantity of propane that reacts during the TPRS experiment since water is the only other reaction product that evolves from any of the surfaces. The oxidation of
propane to CO$_2$ (and H$_2$O) occurs to an immeasurable extent on the 2D oxide and p(2×2)-O phases during TPRS. With increasing oxygen coverage, CO$_2$ desorption first becomes evident when PdO seeds are present on the surface and the CO$_2$ yield increases with further increases in the oxygen coverage as bulk PdO(101) domains develop. We find that the production of CO$_2$, obtained as a function of the initial oxygen coverage, correlates with the yield of propane desorbing in the $\alpha_1$ TPD peak [32]. In fact, the CO$_2$ desorption yield and the desorption yield of propane in the $\alpha_1$ peak maintain a nearly constant ratio above an $\alpha_1$ propane coverage of ~0.01 ML, which suggests that propane only reacts when PdO(101)-like domains are present.

We define the fractional dissociation yield of propane adsorbed in the $\alpha_1$ state as the quantity of propane which reacts divided by the quantity of propane which reacts plus the amount which desorbs in the $\alpha_1$ peak. Assuming that the $\alpha_1$ propane state is the only adsorbed propane species which dissociates, then the $\alpha_1$ dissociation yield is equal to one third of the total CO$_2$ desorption yield. With this assumption, we find that the dissociation fraction of the $\alpha_1$ propane remains constant at ~40% for initial oxygen coverages above about 1.5 ML and generated at 500 K, in excellent agreement with the dissociation fraction reported previously for propane on a fully-developed PdO(101) film [32]. We find that the $\alpha_1$ dissociation fraction also remains invariant with the initial oxygen coverage for oxygen phases generated by oxidizing Pd(111) at 650 K as well as by partially reducing thin vs. thick PdO(101) films. In each of those cases, we estimate that the $\alpha_1$ dissociation fraction is ~48%, which is 20% higher than the value determined for surfaces prepared by Pd(111) oxidation at 500 K. This difference appears to be associated with experimental uncertainty in our absolute calibration of the propane
coverages. The error does not affect the major conclusions of this study, as elaborated below.

### 7.3.4 Reactivity of Partially Oxidized vs. Reduced Surfaces

We used TPRS to quantify and compare the oxidation of propane on surface oxygen phases generated during Pd(111) oxidation vs. PdO(101) reduction. In each experiment, we generated a given oxygen coverage and subsequently saturated the surface with propane at 85 K prior to performing a TPRS measurement in which we monitored the propane, CO$_2$ and H$_2$O desorption rates. Figure 7-4a shows the CO$_2$ yield obtained during propane oxidation as a function of the total oxygen coverage prepared by adsorbing atomic oxygen on Pd(111) at 500 K (“oxidation”) vs. partially reducing a thin PdO(101) film grown at 500 K (“reduction”), for which the initial oxygen coverage was ~3.2 ML. We reduced the thin PdO(101) film by annealing at 680 K for varying durations (Figure 7-2).

On the “oxidation” branch, the CO$_2$ yield remains negligible as the oxygen coverage increases to 0.70 ML, at which point the 2D oxide phase becomes saturated. The CO$_2$ yield begins to increase with increasing coverage above ~0.70 ML which coincides with the initial formation of PdO seeds, followed by the development of bulk-like PdO(101) domains above ~1.3 ML. The CO$_2$ yield reaches a maximum value of 0.12 ML when the PdO(101) film saturates at 3.2 ML. The CO$_2$ yield also decreases steadily with decreasing oxygen coverage for the partially reduced PdO(101) film. Interestingly, the plot shown in Figure 7-4a exhibits a pronounced hysteresis at oxygen coverages between about 1.75 and 3.0 ML. Specifically, the CO$_2$ yield is higher when a particular oxygen coverage, between 1.75 and 3.0 ML, is generated by oxidizing Pd(111) compared with reducing the PdO(101) thin film. For example, at a total oxygen
coverage of ~2.5 ML, the CO$_2$ yield is about 0.085 ML vs. 0.06 ML for the oxidation vs. reduction branches. Below, we show that the higher reactivity arises from a greater fraction of the surface being covered by bulk-like PdO(101) domains when the oxygen coverage is produced during Pd(111) oxidation vs. PdO(101) reduction. We note that PdO seeds have been nearly completely consumed once the oxygen coverage reaches ~2.0 ML during oxidation at 500 K, and thus that the PdO seeds are not responsible for the pronounced hysteresis observed in the present experiments.

Figure 7-4b shows the CO$_2$ yields obtained during propane oxidation as a function of the total oxygen coverage produced by adsorbing oxygen on Pd(111) at 650 K vs. partially reducing a thick PdO(101) film grown at 650 K. Recall that the thick PdO(101) film has an oxygen content of ~13 ML, which corresponds to about 20 oxide layers, and that oxidation at 650 K produces a more heterogeneous surface compared with oxidation at 500 K in that PdO(101) domains thicken significantly before agglomerating to generate a closed PdO(101) film and thus co-exist with 2D oxide domains over wide range of oxygen coverage. Also, PdO seeds rapidly decompose at 650 K after the atomic oxygen exposure is terminated, and thus are not present during propane adsorption on the surfaces oxidized at 650 K.

For the oxidation branch, the CO$_2$ yield remains initially low and begins steadily increasing as the oxygen coverage increases above about 2 ML. The CO$_2$ yield rises to a maximum value of ~0.11 ML when the thick PdO(101) film becomes effectively saturated at an oxygen coverage of 13 ML. The maximum CO$_2$ yield obtained from the thick PdO(101) film is close to that obtained from the thin PdO(101) film generated at 500 K, demonstrating that film thickness has little effect on the reactivity of the
PdO(101) surface toward propane oxidation. The slightly lower value of the CO$_2$ yield obtained from the thick PdO(101) film, compared with the thin film, may indicate that the thick film did not completely cover the surface and thus was not fully saturated in our experiments. The CO$_2$ yields decrease steadily with decreasing oxygen coverage for surfaces prepared by partially reducing the thick PdO(101) film. In contrast to the data obtained for oxidation at 500 K vs. reduction of the thin film grown at 500 K, the CO$_2$ yield curves for the 650 K oxidation vs. thick film reduction data overlap relatively closely and a hysteresis region is lacking. This difference between data sets suggests a similar morphological evolution for oxidation at 650 K compared with reduction of the thick PdO film grown at 650 K, at least with respect to the quantity of surface domains that are active toward propane oxidation at a given oxygen coverage.

### 7.3.5 Deconvolution of Propane TPD spectra

Figure 7-5 shows propane TPD spectra obtained following propane saturation of a fully-developed PdO(101) thin film (~3.2 ML) and a thin film that was thermally decomposed until the oxygen coverage reached 30% of its initial value (~0.9 ML). The propane TPD spectrum obtained from the partially-reduced film exhibits pronounced peaks at 140 and 153 K as well as a small feature at ~120 K. The peaks at 140 and 153 K are consistent with propane desorption from coexisting Pd(111) and 2D oxide domains, respectively. The desorption feature at ~120 K overlaps the leading edge of the $\alpha_2$ peak seen in the propane TPD spectrum obtained from a fully-developed PdO(101) thin film. Below, we discuss the possible origin of the peak at 120 K. Lastly, the $\alpha_1$ TPD feature is nearly unobservable in the propane TPD spectrum obtained from the partially-reduced surface, and accordingly CO$_2$ production is very low (Figure 7-4a).
The propane TPD spectrum shown in Figure 7-5 differs from that obtained if a similar oxygen coverage is generated by adsorbing oxygen on Pd(111). Based on a deconvolution of the TPD spectrum (dashed curve), we estimate that 2D oxide and metallic domains cover 57% and 37% of the partially-reduced surface, respectively. In contrast, after the adsorption of 0.9 ML of oxygen atoms on Pd(111), 2D oxide completely covers the metal surface and coexists with either a small quantity of PdO seeds or PdO(101) domains, depending on the surface temperature during oxidation [12]. This example illustrates that the surface phase distribution can depend sensitively on the manner in which a given oxygen coverage is generated on Pd(111).

To estimate how the surface phase distribution evolves as a function of the oxygen coverage, we fit propane TPD spectra obtained from partially oxidized and reduced surfaces by superposing TPD spectra obtained from reference surfaces, including clean Pd(111), pure 2D oxide and a fully-developed PdO(101) thin film. The analysis assumes that the total propane coverage $[RH]$ on a mixture of surface phases can be expressed as a sum of the contributions from each phase, as given by the equation;

$$[RH] = \sum f_i[RH]_i,$$

where $f_i$ and $[RH]_i$ represent the fractional area of the surface covered by phase $i$ and the saturation propane coverage on phase $i$, respectively. This approximation should be reasonable when the surface is saturated with propane. At lower coverages, however, propane may diffuse among coexisting surface oxide phases prior to desorbing or reacting. Future studies directed toward investigating such diffusion effects may be interesting to pursue. In our fitting procedure, we superposed the propane TPD spectra
obtained from the reference surfaces after multiplying by fractions that were varied until we obtained the best fit between the computed and measured TPD spectra. For each spectrum, we determined the weighting fraction for the propane/PdO(101) reference spectrum by optimizing the agreement between the $\alpha_1$ peaks of the measured and computed TPD spectra. This approach should ensure an accurate estimate of the PdO(101) surface fraction since the $\alpha_1$ peak lies at higher temperature than the desorption peaks associated with all of the other surface oxygen phases. We adjusted the weighting fractions for the reference propane TPD spectra obtained from the Pd$_5$O$_4$ 2D oxide and clean Pd(111) to optimize the fit between the computed and measured peaks at $\sim$140 and 153 K, respectively. Finally, since the propane saturation coverages are nearly the same on each of the oxygen phases investigated, the weighting fractions used in the spectral convolution are approximately equal to the fractional coverages of the different oxygen phases.

We find that the computed TPD spectra accurately reproduce the TPD features at temperatures above $\sim$130 K, but tend to underestimate the desorption feature(s) below $\sim$130 K. As a result, the difference spectra generally exhibit positive, residual area below 130 K and the weighting fractions determined for the Pd(111), 2D oxide and PdO(101) reference spectra sum to a value less than one. This behavior suggests that the low temperature feature observed in the measured TPD spectra is associated with a previously-unidentified oxide phase. We estimate the fractional coverage of this “weakly-binding” phase as the normalized difference between the total area of the measured propane TPD trace and the sum of the best-fit TPD areas, which represent propane desorption contributions from the Pd(111), 2D oxide and PdO(101) phases.
which co-exist on the partially-reduced or oxidized surface. As an example, the computed spectrum shown in Figure 7-5 reproduces the TPD peaks at ~140 and 153 K but underestimates the spectral intensity near 120 K. For this case, we find that the weighting fractions for the 2D oxide and metallic phases sum to only 0.94, and thus estimate that the weakly binding oxide has a fractional coverage of 6%. Interestingly, propane desorption from PdO seeds gives rise to behavior which is similar to that observed on the partially reduced surfaces in that the ratio of $\alpha_2$ to $\alpha_1$ peaks is higher than that observed in propane desorption from the fully-developed PdO(101) film (Figure 7-3a). This similarity suggests that the weakly-binding oxide and the PdO seeds provide similar binding sites for propane.

7.3.6 Surface Phase Evolution During Pd(111) Oxidation vs. PdO(101) Reduction

Figure 7-6a shows the estimated surface fractions of various phases as a function of the oxygen coverage generated by reducing thin and thick PdO(101) films at temperatures of 680 and 720 K, respectively, where the thin and thick films have initial oxygen coverages of 3.2 and 13 ML. The PdO(101) fraction on both surfaces decreases monotonically toward zero as the oxygen coverage decreases during reduction. Initially, the PdO surface fraction decreases sharply with decreasing oxygen coverage, while the 2D oxide surface fraction increases. The metallic surface fraction also increases slightly during the initial reduction, but remains small compared with the 2D oxide fraction. For both oxide films, the 2D oxide surface fraction reaches a maximum once the oxygen coverage decreases to 45-55% of its initial value. Further decreases in the oxygen coverage during reduction cause the 2D oxide fraction to decrease while the metallic surface fraction starts to increase more rapidly as the metal becomes the dominant
surface phase. Lastly, the surface fraction of the so-called weakly-binding oxide remains below 10% as the surfaces are reduced to about 30% of the initial oxygen coverage, and rises to ~18% after more extensive reduction.

Although qualitatively similar, we find significant quantitative differences in the surface phase evolution during reduction of the thin vs. thick PdO(101) films. In particular, compared with reduction of the thick film at 720 K, the PdO surface fraction decreases more abruptly and the 2D oxide surface fraction increases more sharply during reduction of the thin film at 680 K. For example, the 2D oxide fraction reaches a maximum of ~75% during reduction of the thin PdO(101) film, whereas the maximum 2D oxide fraction is only ~30% during reduction of the thick PdO(101) film (Figures 7-6a and b). At the maximum 2D oxide fractions, the PdO surface fractions are 8% and 52% for the initially thin vs. thick PdO(101) films. Notably, the 2D oxide surface fractions reach maximum values near the end of the $\beta_2$ kinetic regions of the isothermal decomposition curves (Figure 7-2) where the $O_2$ desorption rate is slowly-changing and beginning to enter the autocatalytic decomposition regime ($\beta_3$ region). As mentioned above, previous STM results reveal the presence of large fractions of reduced surface domains after a PdO(101) film is annealed to the start of the autocatalytic decomposition regime, as well as PdO(101) islands which result from re-oxidation of the reduced surface domains by O-atoms which migrate from underlying layers of the PdO film [130]. Our current results suggest that the reduced domains observed previously with STM [130] are predominantly 2D oxide in character up to the onset of the autocatalytic decomposition regime, though metallic domains also seem to be present in small quantities on the partially reduced surfaces.
The more abrupt decrease in the PdO(101) surface fraction suggests that re-oxidation of the 2D oxide surface domains is slower during reduction of the thin vs. thick PdO(101) films under the conditions studied. A possibility is that PdO(101) domains are regenerated more rapidly during decomposition of the thick film because we decomposed the thick film at a higher temperature than the thin film (720 vs. 680 K). However, we cannot rule out the possibility that differences in film thickness and morphology also influence the phase evolution, and perhaps have a more dominant effect than the temperature. Further study is needed to determine why the PdO and 2D oxide surface fractions evolve at different rates during thermal decomposition of the thin vs. thick PdO(101) films under the conditions investigated.

Figures 7-7a and b show the estimated PdO(101) surface fractions as a function of the total oxygen coverage for the growth and reduction of the thin vs. thick PdO(101) films that we investigated. For the thin PdO(101) film, our analysis estimates that the PdO(101) surface fraction is significantly higher during oxide growth than reduction at oxygen coverages between ~1.5 to 3 ML. For example, at an oxygen coverage of 2.5 ML, we estimate that the PdO(101) surface fractions are 45% and 88% after reduction of the thin film at 680 K and during PdO(101) growth at 500 K, respectively (Fig. 7-7a). In contrast, the PdO(101) surface fractions have similar values when a given oxygen coverage is generated by reduction vs. growth of the thick PdO(101) film (Fig. 7-7b). The PdO(101) surface fractions and the CO$_2$ yields exhibit similar behavior as a function of the total oxygen coverage for given surface preparation conditions. In fact, we find that the CO$_2$ yield scales linearly with the estimated PdO(101) surface fraction, and that plotting the CO$_2$ yields vs. the PdO(101) surface fractions collapses all of the data into a
narrow band (Figure 7-8). The correlation between CO$_2$ yield and PdO(101) surface fraction suggests that propane oxidation occurs exclusively on PdO(101) surface domains, and that the surface morphology and nature of the co-existing phases have only a secondary influence on the reactivity. We thus conclude that PdO seeds are largely inactive toward propane oxidation, and that the formation of PdO seeds is not responsible for the higher surface reactivity observed for surfaces generated by Pd(111) oxidation at 500 K vs. partial reduction of the resulting PdO(101) film. Instead, our results show that the higher reactivity occurs because the surface is covered by a larger fraction of bulk-like PdO(101) domains when a given oxygen coverage is generated by oxidizing the metal at 500 K vs. reducing the resulting oxide film at higher temperature.

7.4 Summary

We used TPRS to investigate the adsorption and complete oxidation of propane on partially-oxidized Pd(111) and partially-reduced PdO(101) surfaces. The propane TPD spectra reveal clear differences in the molecular binding of propane on the surface oxygen phases investigated, with the main desorption peaks appearing at temperatures of 153 K for propane adsorbed on clean Pd(111) and the p(2\times2)-O phase, 138 K for propane on the 2D oxide(s) and 120 and 190 K for propane on PdO(101). The TPRS results also show that propane oxidation occurs to a negligible extent on the p(2\times2)-O and 2D oxide phases, whereas reaction is facile on fully-developed PdO(101) films. For partially oxidized and reduced surfaces, we find that the CO$_2$ yield increases continuously with increasing oxygen coverage above about 1 ML and observe a hysteresis in the surface reactivity such that the CO$_2$ yield is higher when a given
oxygen coverage, between ~1.5 and 3 ML, is generated during the growth vs. the reduction of a thin PdO(101) film prepared at 500 K.

We show that the fractional surface areas of co-existing oxygen phases can be estimated by fitting propane TPD spectra obtained from partially oxidized surfaces using TPD spectra obtained from reference surfaces. This analysis shows that the CO$_2$ yield scales linearly with the PdO(101) surface fraction, irrespective of the types and amounts of other phases that are present on the surface, and reveals that the observed hysteresis in reactivity is associated with differences in the amount of PdO(101) surface domains that are available. Our data shows that the PdO seeds which form during low temperature Pd(111) oxidation are relatively inactive toward propane oxidation. Quantitative estimates of the areal fractions also provide insights for understanding how the surface phases evolve during the thermal reduction of PdO(101) films. The analysis reveals that 2D oxide domains grow on the surface during the first ~50% of PdO(101) film reduction, while metallic surface domains become prevalent only during the latter half of oxide reduction as the 2D oxide coverage diminishes. A key finding of this study is that the activation of propane on partially oxidized Pd(111) surfaces is relatively insensitive to the complexity of the surface phase distribution, and depends almost entirely on the availability of PdO(101) surface domains.
Figure 7-1. Model representation of PdO(101) surface. (a) Top and (b) side view of the PdO(101) thin film structure. The orange and blue atoms represent O and Pd atoms, respectively. Rows of 3-fold coordinated (cus) Pd and O atoms are indicated. The a and b directions correspond to the [010] and [101] crystallographic directions of PdO.
Figure 7-2. Isothermal O\textsubscript{2} desorption rate as a function of time obtained at 680 K and 720 K from PdO(101) films with initial coverages of ~3.2 and ~13.0 ML, respectively.
Figure 7-3. TPD spectra of propane and CO$_2$. a: Propane TPD spectra obtained from clean Pd(111) and different surface oxygen phases generated on Pd(111) after saturating the surfaces with propane at a sample temperature of 85 K. b: CO$_2$ TPRS spectra obtained from surface oxygen phases on Pd(111) after saturating the surfaces with propane at a sample temperature of 85 K.
Figure 7-4. CO$_2$ desorption yield (ML) as a function of the total oxygen coverage (ML) obtained after saturating partially oxidized and reduced surfaces with propane at 85 K. (A) shows data obtained from Pd(111) that was oxidized at 500 K and a thin PdO(101) film, initially with 3.2 ML of oxygen, that was partially reduced at 680 K, while (B) shows data obtained from Pd(111) that was oxidized at 650 K and a thick PdO(101) film, initially with 13 ML of oxygen, that was partially reduced at 720 K.
Figure 7-5. Propane TPD spectra obtained from a fully-developed PdO(101) thin film containing 3.2 ML of oxygen atoms and after reducing the PdO(101) thin film to an oxygen coverage equal to 30% of its initial value (0.9 ML). In each measurement, propane was adsorbed to saturation at a sample temperature of 85 K. The dashed curve is a fit of the measured TPD spectrum obtained from the partially reduced surface, using the method described in the text.
Figure 7-6. The areal fractions of Pd(111), 2D oxide, PdO(101) and a weakly-binding oxide as a function of the total remaining oxygen coverage obtained during the thermal reduction of the (a) thin PdO(101) film (3.2 ML) at 680 K and (b) the thick PdO(101) film (13 ML) at 720 K. The trend lines are polynomial fits of the data.
Figure 7-7. PdO(101) surface fraction versus total oxygen coverage during the growth and reduction of the (a) thin and (b) thick PdO(101) films. The thin PdO(101) film was grown at 500 K and reduced at 680 K, while the thick PdO(101) film was grown at 650 K and reduced at 720 K. The PdO(101) surface fraction was estimated by deconvoluting propane TPD spectra as described in the text.
Figure 7-8. CO\textsubscript{2} yield vs. estimated PdO(101) surface fraction during the growth and reduction of the thin and thick PdO(101) films.
CHAPTER 8
CONCLUSION

We have investigated the interactions between various molecules and oxidized Pd(111) surface. In most of our studies, we have focused on the reactivity of the PdO(101) surface. The reason why we have investigated the (101) surface thoroughly is that the bulk termination of the fully oxidized Pd(111) surface is PdO(101) as well as the surface termination of the higher coverages of the oxidized Pd(100) is also PdO(101). Furthermore, it has been found that[118] the surface oxide on Pd(100) does not have the reactive properties of the bulk PdO(101) although it possesses the same (101) structure. In our studies we have found numerous evidences of both geometric and electronic configurations of the different types of sites occurring on the oxide surfaces are responsible for their extra-ordinary interactions with various molecules. PdO(101) surface has kinks as opposed to Pd(111) surface which is flat, and therefore PdO surface offers more distinct sites for promoting reactivity. Furthermore, localization or delocalization of electrons on these sites further strengthens their interactions with adsorbates. The cus-Pd site on the PdO(101) surface has been the main site that promotes reactivity with the molecules tested; hydrogen, methanol, propane, butane and pentane. Additionally, it is the adsorption site for methane and ethane although it does not promote a reaction with these adsorbates under the conditions studied. In addition to the cus-Pd site, the neighboring cus-O site also plays a significant role in these reactions. All of the molecules studied undergo heterogeneous bond cleavage (except for H₂) with one of the hydrogen creating O-H on top of cus-O leaving rest of the molecule on top of cus-Pd. We can conclude that the local geometric and electronic configurations of the adsorption sites are one of the most important features of the
catalyst surface for heterogeneous catalysis. Furthermore, we have also checked the effects of partial oxidation or reduction to the reactivity of the PdO surface. We have concluded that although different oxide phases coexist on the surface during reduction or growth of the oxide surface, the PdO(101) is the only reactive phase towards the reactant studied (propane) under the conditions examined.

In addition to reactivity, we have also observed kinetic isotope effects among all of the isotope systems we have studied. We have compared hydrogen reactivity to deuterium reactivity as well as alkanes with their partial and fully deuterated isotopologues. Deuterium reactivity has been found to be significantly less than hydrogen and therefore the deuterated alkane molecule reactivity also decreases significantly. As it was mentioned in second chapter, the difference between the hydrogen and deuterium molecular reactivity on the PdO(101) surface is due to tunneling effects occurring during the activation of the molecule on PdO surface.

The oxidation of palladium and the reactivity of the palladium oxide surface towards alkanes and other adsorbates have been extensively studied by our group. However, there is always more information to be discovered in scientific research. In order to learn more, we have built a new chamber capable of FTIR measurements in our new lab and we are planning to further investigate the reactivity of PdO(101) surface. By utilizing the IR spectroscopy, we will be able to investigate vibrational mode softening during the temperature programmed reaction experiments and therefore it will be possible to investigate experimentally each step of a reaction on the catalysts surface in their entirety. Another method that can be utilized, with the collaboration of Dr. Edvin Lundgren’s group, is high resolution XPS. With this method, it is possible to
have all the information that XPS can give with the advantage of depth sensitivity. This would allow us to further investigate the interaction of the adsorbates on the PdO(101) surface previously examined as well as other future samples and oxide surfaces.

One such additional oxide surface that we think is promising is IrO$_2$(110). Our studies will begin with the oxidation of Ir (111) single crystal and investigation of various possible oxides on this transition metal. Another future direction our lab could follow is to investigate the oxidation characteristics of Rh and reactivity of rhodium oxide. Rhodium is already a widely used catalyst in automobile catalytic converters as well as other catalytic processes. However, the level of detail in the understanding of these catalytic reactions can benefit greatly from the extensive surface science studies.

As a result of these studies, we can say that the PdO(101) has proven to be a very good catalyst for the oxidation of the molecules studied under UHV conditions. Furthermore, numerous findings in literature show that the UHV experimental findings are not only relevant but also accurate in predicting the behavior of many catalyst surfaces under normal process conditions including palladium. It is possible to assume that all of the transition metal catalysts used under atmospheric conditions or under oxygen rich conditions will have an oxide layer as the outer most layer and this is the surface molecules are interacting with. Therefore, UHV experimental studies accurately predict the physics and kinetics behind the observed phenomenon and it is a powerful tool in design of improved and new catalysts.
APPENDIX A
INTERACTIONS OF CO WITH PALLADIUM OXIDE SURFACES

We have investigated the interactions of CO with PdO(101) as well as different states of oxidation of the Pd(111) surface. The experimental setup that was used in these experiments is the same with the system used in studies detailed in chapter 2 through chapter 7. To examine the adsorption behavior of the CO molecule on PdO(101) surface, we exposed the surface to different CO doses and collected TPDs.

Figure A-1 shows the TPD spectra collected after exposing the PdO(101) surface to CO molecules at a surface temperature of 85K. CO desorbs from the PdO(101) surface with four main peaks evolving independently from coverage. The weakly bound CO state desorbs around 110K. However, the more strongly bound CO state actually consists of two distinct states with peak temperatures at about 320 K and 380 K. The peak with the highest desorption temperature desorbs at around 550 K. The total coverage calculated for the CO desorbing from the PdO(101) surface is 0.05 ML. Furthermore, most of the CO on the PdO(101) surface reacts and produces CO\textsubscript{2}, which is evidenced by the TPRS spectra of CO\textsubscript{2} in the Figure A-2. The saturation exposure of CO on this surface produces 0.21 ML of CO\textsubscript{2}, after including the CO desorption, it is found that 0.26 ML of CO will saturate the PdO(101) surface. Interestingly, since PdO(101) surface has 0.35 ML of cus-Pd and 0.35 ML of cus-O sites that should, in theory, accommodate more CO molecules than 0.26 ML. Furthermore, the coverage results are more curious since the CO\textsubscript{2} desorption features also point out to four distinct states on the surface which further indicates that the adsorption and reaction of CO on PdO(101) is affected significantly by molecule to molecule interactions. The evolution of the two higher temperature state CO\textsubscript{2} features (320 K and 380 K) supports this idea.
The peak that desorbs at 320 K is higher than the peak at 380 K at the lowest coverage examined in this study, 0.1 ML of initial CO, however, as the initial CO exposure increases, the state desorbing at 350 K is populated more. As a result, we can say that the preference for the pathway that produces CO\(_2\) desorbing at 380 K is preferred after about 0.1 ML of sites are occupied. Additionally, we have plotted the CO\(_2\) yields with respect to initial CO coverage, and the separate states examined as well as the total CO\(_2\) yield scales linearly with the CO coverage which shows although the coverage effects the relative abundance of two higher temperature CO\(_2\) states, it does not affect the overall reactivity of the PdO(101) surface.

Furthermore, we investigated the adsorption and reaction characteristics of CO on different phases of oxidation in addition to PdO(101). Figure A-4 and A-5 shows the TPD and TPRS results of these experiments. It can be seen that CO is being oxidized on the surface producing CO\(_2\) in all the phases of oxidation we have identified. On PdO(101) surface, CO is almost fully oxidized with the least amount of CO desorbing from this surface with respect to other oxygen phases. Interestingly the chemisorbed oxygen (p(2x2)) phase, generally inactive with almost all of the species we have examined, has one of the highest CO\(_2\) desorption peak area. Although it also has one of the higher CO desorption peak so it does not create better yield of CO\(_2\) production than PdO(101). CO and CO\(_2\) desorption peaks are completely different and consists of many different peaks on every surface we tested, making the analysis of this study very difficult. We will revisit CO oxidation with the help of FTIR measurements in the future.
Figure A-1. The TPD spectra of CO adsorbed on PdO(101) surface. The surface temperature during the exposure is 85K. The coverages reported on the graph represent the desorbed CO molecules.
Figure A-2. The TPRS spectra of CO$_2$ produced after the PdO(101) surface is exposed to CO at the sample temperature of 85K. The coverages reported on the graph represent the total desorbed CO$_2$ molecules.
Figure A-3. CO2 yield with respect to total initial CO coverage.
Figure A-4. The TPD spectra of CO adsorbed on reference oxidation states. Different oxidation states were created by variance of the atomic oxygen exposure prior to saturation CO exposure.
Figure A-5. The TPRS spectra of CO$_2$ produced following CO adsorption on reference oxidation states. Different oxidation states were created by variance of the atomic oxygen exposure prior to saturation CO exposure.
APPENDIX B
PROPANE INTERACTIONS WITH PdO(101) SURFACE; HIGH RESOLUTION XPS STUDY

We have investigated the interactions of propane with PdO(101) surface at low temperatures using high resolution XPS spectroscopy. These experiments were made possible with the collaboration of Dr. Edvin Lundgren’s group in Lund University, Sweden and utilizing the i311 beamline in the Maxlab synchrotron. Prior to these experiments, we have investigated the interactions between the propane molecule and the PdO(101) surface using TPRS experiments, and some of the results can be seen in our previous publications [citation] as well as chapter 5 of this dissertation. In the studies mentioned, we have discovered that the propane molecule adsorbed at low temperatures on the PdO(101) surface will react and produce CO$_2$ and H$_2$O as the temperature increases during the TPRS measurements. From DFT calculations, we predicted that the propane molecule adsorbed on the cus-Pd site is the precursor to this reactivity and with further experiments, we also showed that 90% of the reacted propane, does so with the primary C-H bond cleavage.

In these current experiments, we utilized HR-XPS measurements to better understand the reactivity of propane on PdO(101) surface. The results that are shown in the Figures B-1, B-2 and B-3 are from the same set of experiments and starts with a clean PdO(101) surface created by exposing the Pd(111) surface to an atomic oxygen beam created with thermal oxygen cracker. After the PdO(101) surface is created, the propane is dosed to the surface with incremental exposures shown on the right side of the plots. When the surface is saturated with propane at 100 K, the sample temperature is increased with steps and the HR-XPS spectra are collected after every increment of the exposure and the step of the temperature ramp.
In the figure B-1, the clean PdO(101) XPS spectra shows clear PdO shift in the Pd 3d peak centered about 336.6 eV. As the propane coverage on the surface increases, the Pd 3d peak intensity decreases and it shifts slightly to the left due to propane adsorption on the cus-Pd sites. This Pd 3d spectrum of PdO(101) has been analyzed by Lundgren et. al. [133] and according to their calculations there are two components in the peak centered about 336.6 eV, and these components are separated by 0.5 eV. The lower energy component is associated with the 3 fold (cus) Pd sites and therefore the adsorption of the propane molecules on this site affects the signal and reduces this peak intensity. However, no significant change in Pd 3d peak is observed until the sample is flashed to 403 K. At this temperature, the desorption limited water has desorbed from the surface and therefore the surface has started to have oxygen vacancies. As the temperature increases to 473 K, the total oxidation of propane initialized on the surface and both CO₂ and H₂O are desorbing and surface is losing more oxygen giving rise to the metallic Pd shoulder in the Pd 3d plot. As all of the reactants and products desorbed from the surface at 673 K, the surface loose more oxygen and the XPS spectrum resembles an XPS spectrum of the surface oxide on Pd surface.

As we examine the O 1s XPS spectra during the same experiment in Figure B-2, there are further supporting evidence of the findings we established with the Pd 3d spectra and additional information. The new peak that appears even at 0.1 L propane exposure at 100K around 531.6 eV is associated with O-H bonding and this shows that the activation of propane occurs even at 100 K. As the exposure is increased, the O-H peak intensity increases and after flashing to the temperatures where the products
desorb from the surface, the effects of oxygen loss from the surface can be seen since the peaks at the low energy side of the spectrum starts to diminish.

When the C 1s spectra are investigated, it can be seen that as the propane exposure increases, the carbon peak at 284 eV also increases. As the sample temperature is increased to 403 K, additional peaks at higher binding energies appear. According to our TPRS experiments, the fully oxidized products have started to desorb from the surface but the desorption of these peaks have not been completed at 403 K. The new peak that is centered about 287.2 eV may be associated with CO or CO$_2$ like species on a cus-Pd site since the CO on Pt metal binding energy has been found to be 286.9 eV[133].
Figure B-1. Pd 3d HR-XPS spectra collected before and during propane adsorption as well as during and after propane desorption.
Figure B-2. O 1s HR-XPS spectra collected before and during propane adsorption as well as during and after propane desorption.
Figure B-3. C 1s HR-XPS spectra collected before and during propane adsorption as well as during and after propane desorption.
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BIOGRAPHICAL SKETCH

Can Hakanoglu was born in Adana, Turkey to Teslime and Izzettin Hakanoglu. He graduated from Adana Anatolian High School in 2002 and continued his education in Istanbul Technical University. He received his Bachelor of Science degree in chemical engineering June 2006. He worked as a product engineer in Mavi Kimya Chemicals until he joined the chemical engineering master's program at the University of Florida in August 2007. He began working with Dr. Jason Weaver in May 2008, and transferred into the PhD program at the chemical engineering department in August 2009. He received his PhD degree in May 2013.