GROWTH, CHARACTERIZATION AND REACTIVITY OF RUTILE IrO$_2$(100) AND RuO$_2$(110) THIN FILMS

By

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To my parents and my sister
ACKNOWLEDGMENTS

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<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DFT-D3</td>
<td>dispersion corrected density functional theory</td>
</tr>
<tr>
<td>ISS</td>
<td>ion scattering spectroscopy</td>
</tr>
<tr>
<td>LEED</td>
<td>low energy electron spectroscopy</td>
</tr>
<tr>
<td>LEISS</td>
<td>low energy ion scattering spectroscopy</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer, where 1 ML is defined as one adsorbate per substrate atom</td>
</tr>
<tr>
<td>QMS</td>
<td>quadrupole mass spectrometer</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature programmed desorption</td>
</tr>
<tr>
<td>TPRS</td>
<td>temperature programmed reaction spectroscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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GROWTH, CHARACTERIZATION AND REACTIVITY OF RUTILE IrO$_2$(100) AND RuO$_2$(110) THIN FILMS

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Chair: Jason F. Weaver
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Oxidation of Ir(100) and Ir(111) surfaces using gas-phase atomic oxygen beam was investigated by employing temperature programmed desorption (TPD), low energy electron microscopy (LEED). TPD results provide evidence of decomposition of high concentration oxygen phases (up to 3.4 ML oxygen coverage) on Ir(100) at ~725 K that is consistent with formation of multilayer oxide, although the Ir oxide structure lacks long-range domains unique to any known Ir oxide in LEED. Temperature programmed reaction spectroscopy (TPRS) experiments reveal that these Ir oxide on Ir(100) surface are chemically inactive toward CO and propane indicating lack of Ir$_{\text{cus}}$ on the oxidized surface.

A rutile IrO$_2$(100) layer develops on Ir(111) after formation of a well-ordered surface oxide with ($\sqrt{3} \times \sqrt{3}$)R30° periodicity. The IrO$_2$(100) layer effectively saturates at a thickness of about four layers and decomposes at ~770 K during TPD in a single sharp O$_2$ desorption peak. Low energy ion scattering spectroscopy (LEISS) and density functional theory (DFT) combined with TPRS experiments after adsorbing CO and H$_2$O reveal that the IrO$_2$(100) layer grown in our experiments is oxygen-terminated, and hence lacks Ir$_{\text{cus}}$ and O$_{\text{br}}$ atoms that can strongly adsorb and oxidize molecular species.
TPRS was employed to investigate adsorption and oxidation of methanol on stoichiometric (s-), O-rich and chlorinated RuO$_2$(110) surfaces. Complete oxidation of CH$_3$OH dominates on s-RuO$_2$(110) during TPRS for initial CH$_3$OH coverages below ~0.33 ML, and involves formation of CH$_2$O$_2$ species as a key reaction intermediate. CH$_2$O$_2$ formation is facile on s-RuO$_2$(110) but is strongly dependent on availability of free O$_{br}$ atoms. Partial oxidation of CH$_3$OH to primarily CH$_2$O becomes increasingly favored above 0.33 ML CH$_3$OH coverages. Coupled dehydrogenation and hydrogenation reaction among adsorbed CH$_3$O groups facilitates concurrent evolution of CH$_2$O and CH$_3$OH at 385 K. O-rich RuO$_2$(110) surface strongly promotes complete oxidation of CH$_3$OH by facilitating low temperature H$_2$O desorption. RuO$_{2-x}$Cl$_x$(110) surface, on the other hand, extraordinarily suppresses complete oxidation of methanol without severely affecting partial oxidation to CH$_2$O. We present evident that surface chlorination suppresses the formation of the intermediate CH$_2$O$_2$ essential for complete oxidation by reducing the number of available O$_{br}$ atoms, thereby leading to a sharp decrease in CO$_2$ yield.
CHAPTER 1
INTRODUCTION

1.1 Motivation

A vast majority of industrially produced chemicals include at least one step that involves catalysis. Late transition metals serve as catalyst in many applications of heterogeneous catalysis including fuel cells, fuel-processing applications, gas sensors, selective oxidation of organic compounds, and catalytic converters for pollution control in automobiles. It has been well established that active surface of a catalyst can be in an oxidized state under industrially relevant operating (oxidizing) conditions, and the extent of oxidation can considerably alter the efficiency and performance of the catalyst due to differences in physical and chemical properties of the oxide and its parent metal. Oxidation of a transition metal may lead to formation of multiple oxygen phases, which are fundamentally different from ‘dilute’ chemisorbed layer and bulk oxides. In general, oxygen concentrations above a certain threshold can cause surface reconstruction that may lead to formation of thin epitaxial surface oxide phases. The surface oxide may act as a precursor phases to multilayer oxide formation upon further oxidation.\textsuperscript{1,2} The prospect that these different oxygen phases may have unique chemical properties strongly motivate numerous theoretical and experimental investigations in catalysis and surface science to develop atomic-level understanding of the oxidation of late transition metal surfaces. Surface science investigations under a controlled environment such as ultra-high vacuum (UHV) enable us to understand the underlying chemistry of these surfaces at the fundamental level. Growing oxide films on the metal surface in UHV is a complex process because very often the oxidation process is kinetically limited by oxidant flux under UHV conditions. For example, oxidation of low index Pd(111) surface by prolonged exposure of a molecular oxygen beam under UHV conditions can only produce 0.25 monolayer (ML) of chemisorbed O-atoms.\textsuperscript{3} Researchers have
used other oxidants like NO\textsubscript{2} and atomic oxygen beam to study oxidation of different surfaces in order to increase the net oxidant flux at the substrate. Our lab utilizes RF plasma generated atomic oxygen beam for oxidation in order to increase the oxidant flux at substrate surfaces.

Motivation of my work stems from a theoretical study reported by Antony using density functional theory (DFT) that compares energy for initial C-H bond activation in CH\textsubscript{4} on different late transition metal oxide surfaces.\textsuperscript{4} The author estimates the binding energy of adsorbed CH\textsubscript{4} molecule on PdO(101), RuO\textsubscript{2}(110), IrO\textsubscript{2}(110) and IrO\textsubscript{2}(100) surfaces and energy required to break C-H bond of adsorbed CH\textsubscript{4} molecule using dispersion corrected DFT (DFT-D3), and predicts that CH\textsubscript{4} activation is particularly facile on IrO\textsubscript{2}(110) surface. In these predictions, CH\textsubscript{4} binds strongly on all these surfaces forming σ-complex by binding datively with cus-metal site on the oxide. The favored methane σ-complex on PdO(101) resembles a η\textsuperscript{2} complex in which an H-C-H bond straddles Pd\textsubscript{cus} atom. The predicted binding energy for this structure agrees well with experimental results.\textsuperscript{5} Similar to PdO(101), methane also forms a σ-complex on RuO\textsubscript{2}(110), IrO\textsubscript{2}(110) and IrO\textsubscript{2}(100) resembling an η\textsuperscript{2} complex, although and nature of interactions between the adsorbate and surface alter the orientation of the σ-complex on the rutile oxide surfaces. Figure 1-1 shows the DFT-D3 predicted energy diagram for initial C-H bond cleavage of methane on PdO(101), RuO\textsubscript{2}(110), IrO\textsubscript{2}(110) and IrO\textsubscript{2}(100) surfaces.\textsuperscript{4} The zero reference energy is set as the sum of the total energies of an isolated methane molecule and an isolated bare oxide surface, therefore negative value of energy suggests a more stable structure with respect to the reference. The energy diagram shows that the σ-complex of methane on IrO\textsubscript{2}(110) surface is not only most stable, but also has the lowest activation barrier for initial C-H bond cleavage on this surface. In fact, the predicted negative apparent barrier indicates that CH\textsubscript{4} activation should be facile at very low temperature. Furthermore, DFT predicts that IrO\textsubscript{2}(110) surface can also oxidize several other molecules such as NO, NH\textsubscript{3} and CO,\textsuperscript{6} which presents an interesting
opportunity to develop IrO$_2$(110) as a new oxidation catalyst. My research work is eventually targeted toward experimental investigation of the CH$_4$ activation process on a well-defined IrO$_2$(110) surface under UHV conditions.

The first step of this experimental investigation is to prepare and characterize a well-defined IrO$_2$(110) surface in UHV environment. Bulk IrO$_2$ has rutile structure and is isostructural with RuO$_2$ that has been extensively investigated. Over et al. demonstrated that a multilayer RuO$_2$ phase predominantly grows in [110] direction on Ru(0001) under sufficiently oxidizing conditions and that the RuO$_2$ phase is highly active in promoting CO oxidation. Studies show that the RuO$_2$(110) surface can also effectively oxidize several other compounds such as CO, H$_2$, NH$_3$, C$_2$H$_4$ and HCl. In contrast to RuO$_2$, fundamental understanding of surface chemistry of IrO$_2$ surface is still sparse because the growth of a well-defined IrO$_2$ film under UHV conditions is a challenging task. Under typical UHV conditions, O$_2$ adsorption on Ir(111) effectively saturates at 0.50 ML O-atom coverage due to kinetic limitations. Recent studies of oxidation of Ir surfaces show that the formation of rutile IrO$_2$ on Ir(111) requires high oxygen chemical potential and elevated temperatures to overcome the kinetic limitations. We investigated oxidation of Ir(100) and Ir(111) surfaces in UHV using RF plasma generated atomic oxygen beam. Chapter 2 in this document discusses the results of oxidation of Ir(100) surface in UHV environment, while Chapter 3 discusses results of the detailed investigation of oxidation of Ir(111) surface.

It is well-known that exposed pairs of coordinatively-unsaturated (cus) metal and oxygen atoms on late transition-metal oxide (TMO) surfaces tend to exhibit strong reactivity toward activating and oxidizing adsorbed molecules, although in most cases reactive TMO completely oxidizes adsorbed molecules to CO$_2$ and H$_2$O. The next part of my research intends to explore
the possibility of controlling the product selectivity of oxidation reaction on rutile oxide surfaces, more specifically, the RuO$_2$(110) surface. As mentioned earlier, RuO$_2$(110) surface is highly reactive in oxidizing a variety of molecules. I investigated chemical activity of RuO$_2$(110) surface toward methanol and found that RuO$_2$(110) effectively oxidizes methanol to CH$_2$O, CO$_2$ and H$_2$O. Methanol is simplest alcohol with C-H, C-O and O-H bonds, which makes it an excellent probe molecule to study selective activation of chemical bonds and oxidation pathways of more complex molecules.$^{12-15}$ I investigated the effect of surface chlorination on oxidation of methanol on RuO$_2$(110) surface. Crihan and coworkers presented evidence that during oxidation of HCl on RuO$_2$(110), Cl atoms selectively replace the bridging surface oxygen (O$_{br}$), transforming active Brønsted base sites into inactive (Cl$_{br}$) sites.$^{16}$ The site blocking via Cl-atoms essentially reduces the number of active sites for oxidation leading to a loss of catalytic activity of the surface. The underlying hypothesis behind investigating the effect of surface chlorination was to explore the possibility of limiting the yield of complete oxidation products in favor of more valuable partial oxidation products. Limiting the active oxygen (O$_{br}$) supply via surface chlorination may avoid complete oxidation of methanol, however it is also possible that chlorination of the RuO$_2$(110) surface may lead to completely new reaction pathways resulting in formation of new products. I investigated the effect of selective and self-limited replacement of O$_{br}$ sites with Cl$_{br}$ on oxidation of methanol. In Chapters 4 and 5, I report the results of my investigation of reactivity of RuO$_2$(110) surface toward methanol and the effect of chlorination of RuO$_2$(110) surface on methanol oxidation, respectively.

1.2 Experimental Apparatus

Figure 1-2 shows a rough schematic of upper and lower levels of the three-level UHV chamber employed for my experimental work. The figure shows schematic arrangement of the equipment utilized during surface preparation and experimental measurement. Previous studies
provide a detailed description of the UHV chamber.\textsuperscript{2,17} The chamber is equipped with a
turbomolecular pump (245 L/s), an ion pump (400 L/s) and a titanium sublimation pump that is
inserted into a liquid nitrogen cooled cryoshield, which allow us to reach a base pressure as low
as $2 \times 10^{-10}$ Torr. The single crystal sample is attached to a custom-designed sample manipulator
that is mounted on top of the UHV chamber. The manipulator allows the sample to translate in
all three Cartesian directions and rotate 360° along the vertical axis. The top end of the
manipulator is attached to a reservoir that can be filled with liquid nitrogen to cool the crystal to
temperatures as low as 80 K. We employ resistive heating, controlled using a PID controller that
varies the output of a programmable DC power supply, to maintain or linearly ramp the sample
from 85 K to 1500 K. Prior to any experiment in UHV, we must first ensure the cleanliness of
the surface. Ar\textsuperscript+ sputtering is one of the commonly employed methods in a UHV system to clean
a crystal surface. The upper level of the chamber is equipped with a Specs PU-IQE 11/35 model
ion source that is connect to ultra-high purity Argon gas. The ion source ionizes the Ar gas
entering the UHV system and forms a beam of high energy ionized gas directed onto the sample.
These high energy Ar\textsuperscript+ ions collide and knock off contaminant atoms from the sample surface;
however the process can also damage the lattice arrangement. We anneal the surface at high
temperatures (1400 K for Ir and 1500 K for Ru) after each sputtering process in order to heal the
damage caused by sputtering. We oxidize the surface using gas-phase atomic oxygen beam that
is generated in the beam chamber using a RF plasma source (Oxford Scientific) coupled with
Advanced Energy RFX-600 RF. The plasma source involves plasma generation using the
principles of electromagnetic induction. When a radio frequency electric current is passed
through a coil surrounding a quartz tube that confines rarefied oxygen, it creates a magnetic field
around the coil that in turn induces azimuthal electric field in gas phase, leading to formation of
plasma. The quartz tube has 0.5 mm diameter aperture at the front to form an atomic oxygen beam from the plasma volume. Electrons and charged oxygen particles are filtered from the atomic oxygen beam using ion traps. After flowing through a conical skimmer, the gaseous O-atom beam travels down a quartz tube (60 mm long, 6 mm ID) to enter main chamber and impinge on the sample. A calibrated doser on the upper level of the chamber allows us to conduct controlled and efficient molecular adsorption experiments on the sample without excessively increasing the background pressure of the whole system. After sample preparation, oxidation and/or adsorption comes the step of measurement and analysis. The lower level of the UHV system is equipped with Specs LEED 1000-A and Hiden quadruple mass spectrometer. LEED allows us to look at the surface and adsorbate structures in reciprocal space, while the mass spectrometer allows quantitative measurement of desorbing species. Furthermore, the upper level of the system is also equipped with Specs EA 10 hemispherical analyzer, high intensity twin anode Specs XR-50 X-Ray source and Specs PU-EQ 22 electron source, which combined together allow us to perform XPS, EELS and AES experiments on the sample surface. One can also conduct ion scattering spectroscopy experiments using the ion source and the hemispherical analyzer. The hemispherical analyzer can be operated in two modes - Constant Analyzer Energy (CAE) and Constant Retard Ratio (CRR). In CAE mode, the pass energy of the analyzer is held at a constant value, while the transfer lens system retard the given kinetic energy channel to a range accepted by the analyzer. XPS experiments are typically performed by operating the detector in CAE mode. The CRR mode, on the other hand, scans the lens system and adjusts the pass energy (PE) to maintain a constant value for the ratio of initial electron energy and analyzer PE. This mode is generally used to collect Auger and ion scattering spectra to avoid damage to the detector from the intense low energy background without sacrificing weak peaks at high kinetic energies.
1.3 Analytical methods

1.3.1 Low Energy Electron Diffraction (LEED)

LEED is the most commonly used surface science technique to probe long-range periodic domains on the surface. It can provide valuable information on partially disordered systems without involving elaborate structural analysis. LEED utilizes the wave nature of low energy electrons in accordance with de Broglie hypothesis. When a wave (slow moving electron) scatters from a periodic array, constructive interference occurs if the scattered waves are in phase. In general, LEED optics consists of an electron gun, three or four concentric grid filters and a concentric fluorescent screen. Electron gun emits a monochromatic beam of electrons with desired energy (eV) that hits the grounded sample at normal incidence. Back scattered electrons from the sample are passed thru a series of concentric grids to filter inelastically scattered electrons and accelerated onto a concentric fluorescent screen. Diffraction pattern can be observed on the screen at the positions of interference maxima.

LEED can be also used to obtain qualitative information about the symmetry of the surface structure by recording the diffraction pattern. In presence of adsorbates, basic analysis and comparison of LEED patterns can also provide information about size and rotational arrangement of overlayer unit cell with respect to the substrate unit cell. One can also generate the so-called I-V curves by measuring intensity of diffracted spots as a function of incident electron beam energy. By comparing these I-V curves with theoretical curves, valuable information about the actual structure of the sub-surface atomic layers can be obtained.

1.3.2 Temperature Programmed Desorption and Reaction Spectroscopy

Temperature programmed desorption (TPD) and temperature programmed reaction spectroscopy (TPRS) are one of the most commonly used technique in our lab to measure the concentration of adsorbed species on the sample surface. The procedure to conduct these
experiments is simple: expose the surface to a known amount of adsorbate molecules at desired surface temperature, heat the exposed surface at a controlled rate, while monitoring the species that desorb from the surface using a mass spectrometer. TPD or TPRS spectrum is a plot of desorption rate of an observed species as a function of temperature. When one or more of the monitored species are products of reaction(s) on the surface, the spectrum is referred as TPRS. If the simple desorption without any surface reaction is observed, the spectra is called TPD. There are a series of desorption spectra corresponding to each of the reaction product in case of TPRS.

TPD provides quantitative information about amount of adsorbate on the surface because desorption rate is directly proportional to coverage of the adsorbate. One can correlate an observed spectrum with a reference spectrum with known adsorbate coverage. A commonly implemented method to estimate surface coverages is to collect TPD spectra under conditions (surface temperature and adsorbate partial pressure) that limit the type of adsorption sites available for the adsorbate to a known value, therefore allowing calculating coverage as the fraction of the site. TPD (or TPRS) can also be used to quantify the influence of adsorbate phase behavior on the kinetic of the surface. The rate of desorption initially increases with temperature reaching a maximum and then begins to drop as surface run out of the species in that “state”. The shape of the TPD spectra and corresponding desorption temperature provide valuable insights into the adsorbate phase and binding energy. For example, Figure 1-3 shows a series of TPD spectra obtained after preparing different oxygen atom coverages (Θ₀) on Ir(111) surface using a gas-phase atomic oxygen beam. The oxygen desorption feature rapidly intensifies and shifts toward higher temperature with increasing oxygen coverage. Such sharp and explosive oxygen desorption is indicative of autocatalytic decomposition of a multilayer oxide – IrO₂(100) in this case. I’ll discuss oxidation of Ir(111) in more detail in chapter 3.
Researchers often observe multiple desorption peaks in TPD from same adsorbate. This is indicative of presence of multiple kinetic processes (“states”) on the surface during desorption of the adsorbate. The process with lowest activation barrier will have lowest peak temperature in TPD spectrum, and so on. One can also utilize the TPD data to estimate the binding energy of the adsorbate by employing various analytical methods such as Complete Analysis, Leading Edge Analysis, Redhead Analysis and Variable Heating Rate Analysis. We commonly utilize Redhead Analysis in our lab to calculate energy of desorption.

Rate of desorption for a typical TPD process with linear heating rate of $\beta$ can be expressed as Polanyi-Wigner equation assuming that the desorption process follows Arrhenius equation –

$$\frac{d\theta}{dT} = \frac{A}{\beta} \theta^m \exp\left(\frac{-E_d}{RT}\right)$$  \hspace{1cm} (1-1)

where $\theta$ is adsorbate coverage, $T$ is surface temperature, $E_d$ is activation energy of desorption, $R$ is ideal gas constant and $A$ is pre-exponential factor.

Redhead analysis assumes that TPD set-up directly measures the rate of desorption as is the case in all our experiments. The desorption rate attains maximum when

$$\left.\frac{dr_d}{dT}\right|_{T_p} = 0 \text{ or } \left.\frac{d\theta^2}{dT^2}\right|_{T_p} = 0$$  \hspace{1cm} (1-2)

Using Eq. 1-1 and 1-2, we can relate the surface temperature corresponding to maximum rate of desorption ($T_p$) with ramp rate and activation energy

$$\frac{E_d}{RT_p^2} = \frac{A}{\beta} m \theta^{m-1} \exp\left(\frac{-E_d}{RT_p}\right)$$  \hspace{1cm} (1-3)

For non-zero order desorption processes, we can rewrite above equation

$$\frac{E_d}{RT_p} = \ln\left(\frac{AT_pm\theta^{m-1}_p}{\beta}\right) - \ln\left(\frac{E_d}{RT_p}\right)$$  \hspace{1cm} (1-4)
One can solve Eq. 1-4 iteratively to compute the activation energy corresponding to TPD peak temperature or vice versa. In Chapter 3, we use this method to calculate the theoretical temperature for on-top oxygen desorption via recombination using the activation energy predicted by DFT.

1.3.3 Low Energy Ion Scattering Spectroscopy (LEISS)

LEISS (also referred as ISS) is a unique and unusually high surface specific technique that can yield structural and compositional information about the outermost atomic layer of a well-ordered surface. A LEISS experiment is performed by impinging monochromatic, inert-gas ions on the surface and analyzing the energy of ions scattered at a preset angle. The ions collide with surface atoms and leave the surface before lattice atoms can interact with them. Due to short collision time compared with characteristic lattice vibrations, the collision process can be modeled as elastic binary collision. For a given incident energy and inert gas type, kinetic energy (KE) of scattered ions can be calculated by writing conservation of energy and momentum for both gas ion and surface atoms. Different elements on the surface will yield different KEs for a given ion beam. The duration of ISS experiments is usually kept short to minimize sputtering damage to the surface due to impinging ion beam. In our lab, we typically perform LEISS experiment using He\(^+\) ions with incident energy of 1 keV and a scattering angle of 90° and employ the Specs EA 10 hemispherical analyzer in the CRR mode to detect the scattered He\(^+\) ions.

1.3.4 X-ray Photoelectron Spectroscopy (XPS)

XPS is a widely used photoemission technique in surface science to measure elemental composition and chemical state distribution of elements at solid surfaces. A typical XPS spectrum is plot of electron counts as a function of binding energy of photoelectrons. Experimental setup for XPS requires a UHV system, an X-ray source and controller, sample
mount and a remotely controlled electrostatic electron detector and energy analyzer.\textsuperscript{18, 21} The underlying principle of XPS is based upon measuring the kinetic energy of photoelectrons. When irradiated with mono-energetic x-rays, the surface directly ejects electrons by absorbing discrete quanta of energy. An electrostatic charged-particle analyzer is employed to measure kinetic energies of the emitted electrons producing spectral peaks in XPS. Each element produces a characteristic set of spectral peaks at characteristic BE values. Binding energies of emitted electron can be calculated from following equation,

$$\text{BE} = \hbar \nu - \text{KE} - \Delta \phi$$

Where BE is binding energy of electron in solid, $\hbar \nu$ is energy of the incident photon, KE is kinetic energy of the electron and $\Delta \phi$ is the difference in work functions of sample and spectrometer assuming zero charge accumulation at the sample. The analyzer measures the kinetic energy of emitted electrons and the detector measures the signal intensity (counts or counts/s) corresponding to each KE. By applying equation 1-1, binding energies can be calculated to generate the XPS spectrum. Elemental composition of the sample can be deduced by analyzing the XPS spectrum to identify characteristic peaks corresponding to respective elements. Note that all electrons in an atom with binding energy less than the incident photon energy will be excited during XPS, although probability for each type of excitation is different. Valance band structure, shallow core levels, deeper core level and Auger processes occurring in near surface region can typically produce spectral peaks in an XPS spectrum. The exact binding energy of an electron depends on both the oxidation state of the atom and local bonding environment. Any change in either the oxidation state or local bonding environment will affect the binding energy and may cause shall shift in the peak position in the spectra. This phenomenon is called ‘chemical shift’. For example, palladium signal shifts to higher binding energy when the metal is oxidized.\textsuperscript{1} Figure 1-4 provides an example of XPS spectrum collected from clean Ir(100) using
incident Mg Kα x-rays (\(h\nu = 1253.6\) eV). We observe multiple peaks in the XPS spectrum arising from various electronic orbitals of iridium. Ir 4f peak is the strongest in the spectrum as electrons in outer most Ir 4f orbital are most weakly bound.
Figure 1-1. Energy Diagram for initial C-H bond activation of methane on PdO(101), RuO$_2$(110), IrO$_2$(110) and IrO$_2$(100) surfaces. The zero reference energy is set as the sum of the total energies of an isolated methane molecule and an isolated bare oxide surface. Reprinted with permission from ref 4. Copyright 2013 Abbin Antony.
Figure 1-2. Top view of upper and bottom levels of the UHV chamber.
Figure 1-3. Example of TPD spectra. O$_2$ TPD spectra obtained after preparing different oxygen coverages on Ir(111) by gas-phase atomic oxygen beam exposure.

Figure 1-4. XPS spectrum obtained from a clean Ir(100) surface.
CHAPTER 2
OXIDATION OF Ir(100) BY GAS-PHASE ATOMIC OXYGEN BEAM

2.1 Motivation

The importance of developing fundamental understanding of the interaction of oxygen with late transition metal surfaces is crucial in many applications such as catalysis and fuel cells. Over past few decades, researchers have shown through rigorous investigations that high catalytic activity of many late transition metals such as Pd\textsuperscript{1,22}, and Ru\textsuperscript{7,23,24} is a result of formation of oxide layer on these TM surfaces. Oxygen atoms start to occupy subsurface sites above threshold coverage causing significant lattice distortions, which may lead to oxide formation at transition metal surface.\textsuperscript{25} Iridium oxide is well-known as an efficient catalyst for oxygen evolution reaction in water electrolysis and is a promising material to promote other chemical processes such as methane activation.\textsuperscript{26,27} Ir is known to have a metastable oxide – corundum Ir\textsubscript{2}O\textsubscript{3} and a stable oxide – rutile IrO\textsubscript{2}. (110) and (100) facets are thermodynamically most stable facets of rutile IrO\textsubscript{2}. Rutile IrO\textsubscript{2} is isostructural with RuO\textsubscript{2} that makes it an interesting system to explore and draw comparisons with RuO\textsubscript{2} about growth and properties. UHV studies combined with DFT have already provided excellent atomic-level insights into physical and chemical properties of RuO\textsubscript{2}.\textsuperscript{7,28,29} On the other hand, preparation of well-defined IrO\textsubscript{2} surfaces under UHV conditions is more difficult impairing the efforts to experimentally explore oxidation of Ir surfaces.

He and coworkers reported a detailed investigation of oxidation of Ir(111) surface at elevated temperatures using DFT and \textit{in situ} SXRD measurements over a wide range of O\textsubscript{2} partial pressures.\textsuperscript{11} These investigators report that only a corundum Ir\textsubscript{2}O\textsubscript{3} develops as a multilayer oxide on Ir(111) at 575 K and O\textsubscript{2} pressures between 1 and 100 mbar that acts as a metastable precursor to the bulk rutile IrO\textsubscript{2}. The rutile IrO\textsubscript{2} forms on Ir(111) at 775 K and O\textsubscript{2}
pressures near or above 100 mbar and consists of mixed domains of \( \text{IrO}_2(110) \) and \( \text{IrO}_2(100) \). In a recent study, Liang et al report that \( \text{IrO}_2(110) \) layer can be grown by oxidizing \( \text{Ir}(100) \) at 775 K and an \( \text{O}_2 \) partial pressure of 5 torr, and the \( \text{IrO}_2(110) \) surface can facilitate C-H bond cleavage in methane at temperatures as low as 150 K.\(^{26}\)

There is very limited information available in literature about oxidation of \( \text{Ir}(100) \) surface under UHV conditions. The \( \text{Ir}(100) \) surface undergoes reconstruction to produce hexagonal overlayer which is similar to \( \text{Pt}(100) \) and \( \text{Au}(100) \).\(^{30-32}\) The reconstructed \( \text{Ir}(100) \) surface has a smaller unit cell with \((1\times5)\) periodicity compared with \( \text{Pt}(100) \). Küppers and Michel using LEED and ultraviolet photoemission spectroscopy (UPS) show that the \( \text{Ir}(100) \) surface is very unique as the metastable unreconstructed overlayer has \((1\times1)\) periodicity, and is stable up to 800 K due to high activation barrier for self-diffusion of \( \text{Ir} \)-atoms on the surface.\(^{32}\) These authors also report that \((1\times5)\) and \((1\times1)\) surfaces are unique different with respect to oxygen adsorption, and the \((1\times5)\) surface readily activates the adsorbed oxygen. Studies show that adsorption of CO and \( \text{O}_2 \) can locally lift the \((1\times5)\) reconstruction from \( \text{Ir}(100) \) surface.\(^{31,32}\) Both the metastable \( \text{Ir}(100)-(1\times1) \) and stable \( \text{Ir}(100)-(1\times5) \) surfaces can be easily prepared under controlled experimental conditions, although a minimum amount of oxygen and surface temperature of at least 650 K are required to completely lift the reconstruction on \( \text{Ir}(100) \) surface.\(^{31}\) Ali et al. report using \( \text{O}_2 \) molecular beam studies on \( \text{Ir}(100) \) that adsorbate-induced lifting of reconstruction governs the kinetics of oxygen adsorption on \( \text{Ir}(100)-(1\times5) \) surface.\(^{33}\) Oxygen adsorption on \( \text{Ir}(100) \) surface at 500 K saturates at 0.5 ML, and the chemisorbed oxygen desorbs from the surface in two broad features – between 820 K and 1100 K and 1100 K and 1300 K. These researchers further report that oxygen induced lifting of \((1\times5)\) reconstruction stems at defect sites via nucleation and subsequent growth of \((1\times1)\) islands at temperatures above 650 K. Low mobility of adsorbed O-
atoms below 650 K causes random adsorption of additional oxygen on the (1 × 1) islands hindering their growth. Oxygen forms a (1 × 2) overlayer on the Ir(100)-(1 × 1) surface at saturation coverage with preferred adsorption on bridge sites due to significant row pairing of Ir atoms in the surface layer that essentially stabilizes the structure.34

In this chapter, I present the results of my investigation into oxidation of Ir(100) in ultra-high vacuum (UHV) environment using gas-phase atomic oxygen beam at temperatures below 625 K for varying durations. Phase evolution and properties of generated oxygen phases were investigated using temperature programmed desorption (TPD), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). We find that gas-phase O-atoms adsorb efficiently on the Ir(100) leading formation of multilayer oxide film on the Ir surface. The multilayer oxide grown in our experiments is chemically inactive toward CO and propane.

2.2 Experimental Details

Previous studies35,36 provide details of the three-level UHV chamber utilized for the present experiments. The Ir(100) single crystal used in this study is a circular disk (9 mm diameter, 1 mm thickness) with grooves provided to attach W wires. The Ir(100) crystal is fastened to a copper sample holder through 0.015” W wires. The sample holder is held in thermal contact with a liquid nitrogen cooled reservoir. Sample temperature is measured through a type K thermocouple spot-welded to the backside of the crystal. A programmable DC power supply, connected with a PID controller to vary its electrical output, allows resistive heating to maintain or linearly ramp the sample temperature from ∼80 to 1400 K. We initially cleaned the Ir(100) sample by repeated cycles of sputtering with 1 keV Ar+ ions at 900 K followed by annealing to 1400 K for 5 min. O2 treatment (5 × 10^-7 Torr O2 for 20 min at 900 K) followed by annealing to 1400 K for 5 min was employed to remove carbon contamination from the surface. Routine cleaning involved 20 min treatment in 5 × 10^-7 Torr O2 at 900 K followed by 5 min annealing
1400 K. We considered the surface to be clean when the sample exhibited no C 1s and O 1s peaks in XPS as well as negligible quantities of CO and CO$_2$ in reproducible TPD experiments following oxygen adsorption. LEED observations after aforementioned cleaning procedure show a sharp reconstructed (1 × 5) pattern.

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.$^{35,36}$ We exposed Ir(100) to the plasma-generated O-atom beams for varying durations and characterized the resulting surfaces using TPD, LEED and XPS. We collected O$_2$ TPD spectra after an exposure by positioning the sample in front of a shielded mass spectrometer at a distance of about 7-8 mm and then heating at a constant rate of 1 K s$^{-1}$ until the sample temperature reached 1400 K. The final temperature during TPD was limited to 1400 K to avoid damage to the thermocouple connection with the sample. We report oxygen coverages in this chapter by integrating the O$_2$ TPD spectra. Area under the O$_2$ TPD trace is then scaled with that obtained from a saturated chemisorbed oxygen layer prepared by exposing Ir(100)- (1 × 1) to O$_2$ at 530 K and assuming that this procedure produces an O-atom coverage of 0.50 ML. We prepared the clean unreconstructed (1 × 1) surface using the method described by Heinz et al.$^{31}$ We first exposed the reconstructed Ir(100) surface to 6 L O$_2$ at 475 K using a tube doser. Oxygen lifts the reconstruction of the Ir(100) surface upon adsorption. The surface was then heated to 750 K to desorb the oxygen without changing the surface structure. The annealed surface is further treated with 3 L hydrogen at 530 K to remove traces of randomly adsorbed oxygen. Hydrogen reacts with the chemisorbed oxygen to produce water, which readily desorbs at 530 K resulting in clean unreconstructed Ir(100)-(1 × 1) surface. The surface is found to be stable upon
heating until 800 K. For O-atom coverage calibration, the \((1 \times 1)\) surface is exposed to different amounts of oxygen ranging from 0.1 L to 5 L using a tube doser at 530 K and \(O_2\) TPD traces were obtained between 530 K and 1400 K for each exposure to obtain the saturation coverage after \(O_2\) exposure. Ali et al have shown that oxygen saturates on the \(\text{Ir}(100)-(1 \times 1)\) surface yielding a maximum coverage of 0.50 ML.\(^{33}\) O-atom coverage is described in ML (monolayer) units where 1 ML is corresponds to a surface Ir atom density of \(1.32 \times 10^{15}\) atoms/cm\(^2\) of unreconstructed \(\text{Ir}(100)-(1 \times 1)\) surface. On the basis of the uptake of O-atoms on \(\text{Ir}(100)\), as determined from \(O_2\) TPD, we estimate that the O-atom flux at the sample surface was \(~2.90 \times 10^{13}\) cm\(^{-2}\) s\(^{-1}\), which is equivalent to 0.02 ML s\(^{-1}\). We performed XPS measurements using Mg K\(_\alpha\) X-rays (\(h\nu = 1253.6\) eV) with the hemispherical analyzer operating in a retarding mode at a pass energy of 27 eV. We analyzed photoelectrons emitted approximately along the surface normal of the sample and averaged 40 scans each for the Ir 4f, Ir 4d and O 1s spectra. We processed the XPS spectra after applying background subtraction using Shirley method. Finally, we performed LEED experiments using four-grid optics with beam energy between 60 eV and 120 eV.

### 2.3 Results

#### 2.3.1 \(O_2\) TPD for Oxidation of \(\text{Ir}(100)\) at 300 K

Figure 2-1 shows a series of \(O_2\) TPD spectra after preparing different oxygen coverages by exposing clean, reconstructed \(\text{Ir}(100)\) surface to gas-phase atomic oxygen beam at 300 K. We find that at the lowest coverage generated using gas-phase atomic oxygen beam, oxygen desorbs from the \(\text{Ir}(100)\) surface between 850 K and 1300 K in two desorption features (\(\beta_3\) and \(\beta_4\)) centered at 1000 K and 1145 K, respectively (Figure 2-1a). Prior work shows that \(\beta_3\) and \(\beta_4\) desorption features are characteristic of recombinative desorption from chemisorbed oxygen layer that saturates at 0.5 ML.\(^{33}\) Our data suggests that as oxygen coverage increases from 0.5
ML to 0.8 ML, oxygen binding environment does not appreciably change on Ir(100) surface at 300 K resulting in a similar desorption behavior as chemisorbed layer. After increasing the oxygen coverage to 1.1 ML, a new feature $\beta_2$ appears in the spectrum with peak centered at 760 K. The $\beta_2$ feature shifts to lower temperature with increasing coverage and saturates at ~1.6 ML with peak centered at 735 K. Appearance of the $\beta_2$ TPD peak is consistent with formation of an ordered 2D surface oxide at coverages above 1 ML. Oxidation studies on other transition metal surface also report formation of well-defined surface oxides structures that yield sharp O$_2$ TPD peaks prior to desorption features from chemisorbed layer.$^{1,2,37}$ As the O-atom coverage on Ir(100) surface increases above 1.6 ML, $\beta_2$ TPD peak grows slightly and a new feature ($\beta_1$) with peak centered at ~590 K begins to appear in the spectrum at the leading edge of the surface oxide peak. The $\beta_1$ TPD peak intensifies and shifts toward higher temperature after increasing the coverage to 2.1 ML. We attribute the evolution of $\beta_1$ TPD feature to formation of iridium oxide “seeds” based on analogous TPD features observed during oxidation of Pt(100) and Pd(111).$^{1,38}$ As the oxygen coverage further increases on Ir(100) surface, these seeds grow on the surface oxide to form a more stable multilayer oxide resulting in shift of $\beta_1$ peak temperature toward higher temperature.

As the oxygen coverage increases above 2.1 ML (Figure 2-1b), the maximum O$_2$ desorption rate begins to increase non-linearly and the corresponding desorption peak temperature shifts toward higher temperature. O$_2$ TPD from 2.9 ML oxygen covered surface shows a symmetric and explosive desorption of O$_2$ centered at 700 K. The sharp and explosive desorption peak is indicative of autocatalytic decomposition of a multilayer oxide, wherein oxygen transfer from the bulk oxide to the surface oxide results in superheating of the surface oxide leading to large desorption rates during TPD. Researchers have demonstrated that
desorption of multilayer oxide layer grown over Pd(111), Pt, and Ir(111) exhibit similar autocatalytic desorption during TPD.\textsuperscript{1, 2, 38, 39} Note that as the $\beta_1$ peak intensifies, $\beta_2$ peak diminishes until we observe a mere shoulder peak at 2.9 ML coverage. The multilayer oxide saturates at 3.3 ML with a major desorption peak centered at 710 K. We also observe a small peak centered at 825 K in O$_2$ TPD traces above 2.6 ML coverages, however this peak does not grow significantly with increasing coverages. This feature may appear in the TPD spectra due to desorption of a new oxide phase that develops on the oxide-1 domains.

2.3.2 O$_2$ TPD for Oxidation of Ir(100) at 500 K

Figure 2-2 shows TPD spectra obtained after generating various oxygen coverages on reconstructed Ir(100) surface at 500 K using gas-phase atomic oxygen beam. The main objective of this investigation was to understand how the kinetics of oxidation evolves with surface temperature. The overall desorption profile after generating various coverages at 500 K is qualitatively similar to that at 300 K, however, we do observe few important differences in evolution of various oxygen phases between two temperatures. Figure 2-2a shows that oxygen chemisorbs on the Ir(100) in (2 $\times$ 1) pattern up to 0.7 ML coverage resulting in $\beta_3$ and $\beta_4$ TPD features centered at 1000 K and 1145 K, respectively. DFT calculations predict that the chemisorbed oxygen prefer the bridging site on Ir(100) surface.\textsuperscript{34, 40, 41} TPD data shows that the surface oxide begins to form above 0.7 ML coverage producing the $\beta_2$ desorption feature centered at 765 K. The $\beta_2$ TPD peak saturates at $\sim$1.2 ML coverage and shifts to lower temperature with the peak centered at 730 K at saturation. As discussed in later in the chapter, we observe a distinct (4 $\times$ 4) LEED structure on the surface after generating 1.2 ML coverages. After increasing the oxygen coverage above 1.2 ML, we observe the $\beta_1$ TPD peak centered at 640 K from desorption of oxide seeds.
As seen from Figure 2-2b, the $\beta_1$ peak rapidly intensifies and shifts toward higher temperature with increasing coverage producing a sharp desorption peak above 715 K that is consistent with formation of a multilayer oxide above 3.0 ML. The multilayer oxide growth on the Ir(100) surface effectively saturates after 3.4 ML with a predominant peak at 725 K. Note that the saturated oxide layer prepared at 500 K decomposes at considerably higher temperature than that prepared at 300 K. The $\text{O}_2$ desorption spectra shows a small peak centered at 830 K at oxygen coverages above 2.6 ML. The desorption feature (“Oxide-2”) modestly increases and corresponding peak shifts to higher temperature (peak temperature of 845 K at saturation) with increasing oxygen coverages. The prominence of the “oxide 2” TPD peak in $\text{O}_2$ TPD obtain from oxidation at 500 K is another key difference observed from oxidation at 300 K. We find that the ‘oxide-2’ feature peak begins to grow above 2.6 ML and grows simultaneously with multilayer oxide ‘oxide-1’. Additional experiments show that oxygen coverages remain almost same between 300 K and 500 K, while saturation coverage decreases by almost a factor of 2 when Ir(100) is oxidized above 550 K because the oxide formation drops below the oxide decomposition rate. We estimate that O-atom flux generated in our experiments is $\sim 0.02$ ML s$^{-1}$ that essentially confines the maximum obtained coverage on the Ir(100) surface below $\sim 3.5$ ML due to kinetics limitations of oxidation under the conditions studied.

2.3.3 Atomic Oxygen Uptake Curves

Figure 2-3 shows the O-atom coverage as a function of the total atomic oxygen exposure on Ir(100) surface at 500 K and 300 K. Uptake curves are a useful tool to study the effect of incident atomic oxygen flux on oxidation kinetics. The plot shows that the oxygen coverage increases rapidly up to $\sim 2.5$ ML at 300 K and slows down considerably above 2.5 ML. Note that the oxygen uptake does not reach a plateau and instead keeps increasing with a rather slow growth rate, when the Ir(100) surface is oxidized at 300 K. The uptake behavior for exposures at
500 K has few evident differences compared with that at 300 K. oxidation kinetics of Ir(100) at 500 K follows that at 300 K almost identically up to 2.5 ML coverage and then begins to plateau until effectively saturating at ~3.4 ML at 500 K. The initial uptake is almost same at both temperatures, but the uptake at 500 K begin to surpass that at 300 K above 2.0 ML coverages. Note that saturation coverage obtained at 500 K is slightly higher that the highest coverage obtained at 300 K, although the exposure is same at both temperatures. It is likely that the energy barrier for oxygen diffusion into the surface is somewhat overcome by increasing the surface temperature to 500 K resulting in increased oxygen uptake. Studies report that oxidation of Pd, Pt and Ir(111) surfaces shows similar uptake behavior. The shape of the oxygen uptake curve at 500 K suggests that Ir(100) oxidation by gas-phase atomic oxygen beam follows Langmuirian adsorption kinetics and is an adsorption limited process, at least up to 500 K under the conditions studied.

2.3.4 Evolution of LEED Patterns for Oxidation of Ir(111) at 500 K

We employed LEED to investigate different structures formed after generating various oxygen coverages in Ir(100) surface. Figure 2-4 shows LEED images obtained after generating different oxygen coverages on reconstructed Ir(100) at 500 K. These LEED images provide evidence of a distinct surface oxide structures that have not been previously reported. A clean unreconstructed Ir(100) surface has (1 × 1) atomic arrangement. It is well known that the clean Ir(100) surface undergoes reconstruction above 800 K to form a quasi-hexagonal structure with a (1 × 5) periodicity relative to the Ir(100) substrate yielding a symmetric (1 × 5) pattern in LEED. After preparing 0.7 ML oxygen coverage, LEED (Figure 2-4a) shows a (1 × 5) arrangement with faint streaks at (2 × 1) positions. TPD results show that desorption behavior at this coverage is consistent with formation of chemisorbed oxygen overlayer, however the surface reconstruction is not lifted due to oxygen adsorption even at this coverage.
As shown in Figure 2-4b, we observe a \((4 \times 4)\) LEED pattern after generating oxygen coverages between 0.8 ML and 1.2 ML on Ir(100) surface at 500 K. Formation of the \((4 \times 4)\) pattern coincides with growth of the \(\beta_2\) TPD peak in the same coverage, which indicates that the \((4 \times 4)\) structure leads to appearance of the \(\beta_2\) desorption feature in the TPD. Comparison with the oxidation behavior of other transition metal surfaces such as Pd(111)\(^1\) and Pt(100)\(^{36}\) surfaces strongly indicates that the \((4 \times 4)\) structure corresponds to a surface oxide phase that develops on Ir(100) at oxygen coverages near and above 1.0 ML coverages. Further investigations such as scanning tunneling microscopy (STM) and density functional theory (DFT) calculations may help identifying the precise structure of the \((4 \times 4)\) surface oxide. The high quality of the LEED pattern does indicate that the \((4 \times 4)\) surface oxide exists in large crystalline domains after growth at 500 K.

\(\text{O}_2\)TPD data shows desorption peaks consistent with formation of multilayer oxide on Ir(100) surface at 500 K above 2.1 ML oxygen coverage, however we were unable to identify a unique LEED pattern corresponding to an iridium oxide structure at these coverages. Instead, we only observe a \((1 \times 1)\) pattern at coverage above 2.1 ML (Figure 2-4c). This behavior suggests that the predominant multilayer oxide which develops on Ir(100) at 500 K does not exhibit sufficient long-range order to produce diffraction in our experiments. It is possible that under the conditions studies, the multilayer oxide forms in small domains of multifaceted crystalline structures. Although TPD data shows that the multilayer oxide stabilizes as the oxygen coverage increases up to 3.2 ML, we do not observe any change in the \((1 \times 1)\) LEED pattern from the oxide (Figure 2-4e). Annealing the atomic oxygen exposed surface with coverages above 2.1 ML to ~673 K transforms the \((1 \times 1)\) pattern into a new structure (Figure 2-4d and 2-4f), which exhibits a \((2 \times 1)\) pattern combined with four faint spots (red circles, Figure 2-4d) almost
symmetrically positioned around each substrate Ir(100) spots. These new spots adopt a square pattern oriented along the diagonals of the substrate unit cell, and their average distance from the main order spots suggests that the new structure has a lattice constant that is about seven times larger than that of Ir(100). These characteristics are consistent with a rectangular (or square) structure with a relatively large unit cell that is rotated ~45° relative to the substrate lattice.

Additional experiments show that the new ‘rotated square’ LEED pattern (Figures 2-4d and 2-4f) corresponds to a surface oxide rather than a multilayer oxide. In these experiments, we first generated coverage of 1.2 ML at 500 K and observed the (4 × 4) LEED pattern. After heating the oxidized surface to 673 K, the (4 × 4) pattern transforms into the ‘rotated square’ pattern, which further transforms into a well-defined (1 × 2) pattern (which arises from chemisorbed oxygen atoms on Ir(100) surface) upon heating to 750 K. These changes in the LEED pattern suggest that the (4 × 4) structure is a kinetically stabilized meta-stable phase that transforms to the stable ‘rotated-square’ structure upon heating.

2.3.5 XPS characterization of oxidized Ir(100)

Figure 2-5 shows Ir 4d_{5/2} XPS spectra of clean Ir(100) and after generating 3.2 ML oxygen coverage on Ir(100) by exposing the Ir(100) gas-phase atomic oxygen beam at 500 K. XPS experiments on prepared surfaces were conducted at 300 K in order to gain better signal to noise ratio without losing the adsorbates from the surface. The clean Ir(100)-(1 × 5) surface shows Ir 4d_{5/2} peak at 296.7 eV in the XPS spectra (black curve). The Ir 4d_{5/2} peak clearly shifts to higher binding energy by 0.4 eV (solid red curve) after generating 3.2 ML oxygen coverage on the Ir(100) surface. We deconvoluted the XPS spectrum of the oxidized layer assuming two Lorentzian type XPS peaks arising from oxidized (Ir^{4+}) and unoxidized Ir (Ir^{0}). We find that Ir^{0} peak intensity drops by ~25% due to oxidation, and the Ir^{4+}/Ir^{0} ratio for the oxidized surface is
Our XPS data suggest that the oxide layer generated on metal substrate is either very thin or the multilayer oxide grows more favorably in the [100] direction than laterally on the surface resulting in formation of 3D islands of IrOₓ on the surface oxide.

2.3.6 Adsorption of CO and Propane on oxidized Ir(100)

We explored the chemical activity of the high concentration oxygen phases developed on Ir(100) surface in our experiments. Studies show that presence of coordinatively unsaturated (cus) metal and oxygen atoms on stoichiometrically terminated transition metal oxide surface typically lead to high chemical activity. The cus-metal atoms can form strong σ-complexes and the anti-bonding orbital interactions between metal atom and the adsorbate can reduce the intramolecular bond strength of the adsorbate leading to bond activations. The cus-O sites, on the other hand, act as strong Brønsted base and hydrogen acceptor, and can readily leave the lattice in form of oxidized products. We investigated the chemical activity of the oxidized Ir(100) surface using CO and propane.

Figure 2-6 shows TPRS traces of CO and CO₂ after dosing CO on different oxygen covered Ir(100) surfaces at 80 K. Figure 2-6a shows that CO adsorbs strongly on the clean Ir(100) surface and desorbs in two distinct peaks centered at 547 K and 465 K, respectively. Our TPD results agree well with previously reported data. The small CO₂ desorption feature corresponding to the clean Ir(100) surface seen in Figure 2-6b is most likely due to interaction of desorbed CO molecules with the residual oxygen in the background. The 0.7 ML oxygen pre-covered Ir(100) surface shows strong activity toward CO, and almost all the oxygen available on the surface is consumed by CO during TPRS. CO₂ TPRS trace shows multiple desorption features centered at 190 K, 286 K, 322 K, 415 K and 545 K after CO adsorption on the 0.7 ML oxygen pre-covered Ir(100) surface at 80 K. CO oxidation seems to decrease severely as the oxygen coverage further increases on the surface. CO₂ TPRS data reveals that intensities of the
CO₂ desorption features reduce severely on the surface oxide (1.2 ML coverage) compared with 0.7 ML oxygen pre-covered Ir(100) surface. Our data show that the CO₂ desorption peaks after CO oxidation on (4 × 4)-O surface are qualitatively similar to that from 0.7 ML O-atom pre-covered Ir(100) surface suggesting a similar local CO binding and oxidation environment on both surfaces. Although the surface oxide is active toward CO oxidation, the number of active sites for CO adsorptions reduces significantly on the surface oxide compared with chemisorbed layer. CO TPRS data further reveals that high temperature CO desorption features completely disappear on the multilayer oxide (> 2.1 ML coverage) and no significant CO₂ desorption features are observed above 190 K in the corresponding CO₂ TPRS traces.

Figure 2-7 shows C₃H₈ desorption spectra obtained after adsorbing C₃H₈ on clean, reconstructed Ir(100) vs. multilayer oxide layer grown over Ir(100) consisting of 3.2 ML oxygen. C₃H₈ desorbs in a single desorption feature centered at 150 K from the clean, reconstructed Ir(100) surface. C₃H₈ trace obtained from the multilayer oxide shows that C₃H₈ TPD peak shifts to a lower temperature (137 K) on the multilayer oxide. These results contradict our expectations based upon previously reported results about other oxide surfaces like PdO(101) and RuO₂(110). For example, CO adsorbs on RuO₂(110) surface by binding at Ruₕₘ sites, and the RuO₂(110) surface oxidizes ~80% of the adsorbed CO to produce CO₂.⁴³ CO molecules initially adsorb in an atop configuration on Pdₕₘ sites of PdO(101) surface and the surface can oxidize at least 71% of the adsorbed CO molecules into CO₂ producing CO₂ desorption features centered at 330 and 520 K during TPRS.⁴⁴ The weak binding and inactivity of the multilayer oxide grown over Ir(100) toward CO and C₃H₈ strongly indicates that the oxide layer grown in our experiments lacks Irₕₘ sites that can promote strong binding with these molecules.
2.4 Discussion

TPD results presented in section 2.3 show that formation of chemisorbed oxygen layer up to 0.7 ML is the initial step during oxidation of Ir(100) surface by gas-phase-oxygen atoms at temperature up to 500 K. LEED pattern obtained from this chemisorbed oxygen layer (0.7 ML coverage) shows a streaked \((2 \times 1)\) overlayer over \((1 \times 5)\) substrate suggesting that the chemisorbed layer is either largely disordered or forms ordered domains that are too small to produce significant diffraction. These results are in agreement with prior investigations that the \((1 \times 5)\) LEED pattern from the reconstructed Ir(100) surface does not appreciably change due to \(O_2\) exposures below 700 K.\(^{33,45}\) Since the surface was not heated post-exposure before collecting LEED, it is likely that highly reactive oxygen atoms were randomly adsorbed on the surface or incorporated into the near surface region under the experimental conditions, and lack the energy required to overcome the surface diffusion barrier and form large ordered domains of O-atom adlayer. This also explains why we do not observe the oxygen induced lifting of \((1 \times 5)\) reconstruction even at O-atom coverage as high as 0.7 ML.

Above 0.8 ML oxygen coverage, a surface oxide with \((4 \times 4)\) periodicity begins to develop on the Ir(100) surface. The surface oxide saturates at 1.2 ML oxygen coverage after oxidizing Ir(100) at 500 K and produces a distinct \(O_2\) TPD peak at 725 K. As oxygen coverage increases above 1.2 ML, oxide seeds start to grow on the surface, which decompose at \(~640\) K to produce \(\beta_1 O_2\) TPD peak. Prior studies on oxidation of transition metals such as Pd, Pt report similar phase evolution during oxidation, wherein growth of a multilayer oxide generally follows formation of a distinct surface oxide that develops above threshold oxygen coverage.\(^6\) Such behavior also suggests that initial evolution of oxygen phases is relatively insensitive to the oxidant at these coverages.
Above 2.1 ML coverage, we observe O$_2$ TPD peak that is consistent with growth of a multilayer oxide. We find that the multilayer oxide effectively saturates at 3.4 ML under the conditions employed, and decomposes to produce a single sharp peak at 725 K during TPD. Liang et al report IrO$_2$(110) layer grown over Ir(100) at elevated temperature and pressure conditions oxide decomposes in peak at ~900 K during TPD, which is significantly higher than the O$_2$ TPD peak temperatures observed in our experiments. Interestingly, we also observe a second O$_2$ desorption feature during TPD between 830 K and 845 K above 2.6 ML coverages indicating that the oxide layer grown on Ir(100) surface consists of at least two distinct structures. The multilayer oxide in our experiments fails to produce a distinct LEED pattern corresponding to a known ordered Ir oxide surface. We rather observe a (1 × 1) LEED pattern that suggests that Ir(100) oxidation at 500 K produces a rough morphology with co-existing oxide phases that grow in small domains. The lack of an ordered structure points to many possibilities about structures that develop at high oxygen coverages (> 2.1 ML). We further observe that the multilayer oxide (coverages > 2.1 ML) transforms into different structure that exhibits a (2 × 1) pattern combined with the ‘rotated-square’ pattern after annealing to 673 K. Note that the surface oxide layer formed in our experiments is a metastable phase that transforms into the same (2 × 1) pattern combined with the ‘rotated-square’ pattern when annealed to 673 K. We observe the same LEED pattern at all coverages above 1 ML, when the oxygen covered surface is annealed to 673 K. Based on the evolution of O$_2$ TPD and corresponding LEED patterns, a likely possibility is that the epitaxial growth of the IrO$_x$ layer on the Ir(100) surface follows the Stranski–Krastanow growth mechanism. As the surface oxides saturates on the Ir(100) surface, oxide seeds begin to grow upon increasing oxygen coverage. If the growth rate of these seeds in the [100] direction is much higher than that in the lateral directions ([010] and
small domains of IrO$_x$ islands would form on surface oxide layer preventing the development of a conformal oxide layer even at oxygen coverage as high as 3.4 ML. When the surface is heated above 673 K, these oxide domains may rearrange to form new a structure.

The evolution various oxygen phases on Ir(100) is strikingly similar to that observed from Pt(111) oxidation using gaseous O-atom beam.$^{35,37,47}$ Investigation of Pt(111) oxidation by Weaver et al. shows that long-range ordering of chemisorbed O-adlayer diminishes above 0.50 ML and TPD spectra above 0.75 ML displays oxygen peaks consistent with formation of multilayer oxide that saturates at ~2.9 ML.$^{37}$ EELS results provide evidence of formation of oxide structure at coverages above 0.75 ML, however, LEED images obtained from these Pt oxide structures grown on Pt(111) show only a diffused pattern suggesting that the surface is covered with high density of small oxide particles. Further STM investigations confirm that Pt oxide chains begin to grow between close-packed p(2 × 1)-O rows on Pt(111) at oxygen coverages above 0.40 ML and form an interconnected network of Y-shaped branched structures to reduce stress in the oxide overlayer and achieve commensurability.$^{47}$ CO TPRS experiments on oxygen pre-covered Pt(111) show that Pt oxide with oxygen coverages above 1.5 ML is completely inactive toward CO oxidation. These similarities in oxidation of Pt(111) and Ir(100) indicate that oxygen coverages above 2.0 ML on Ir(100) surface lead to formation of small oxide domains.

Recent STM investigations of Rh(111) oxidation by Farber et al. show that oxygen atoms in excess of 0.65 ML dissolve into the subsurface and can lead to formation of RhO$_2$ above threshold concentrations depending on substrate temperature.$^{48}$ LEED images predominantly show (2 × 1) pattern after generating ~6.4 ML oxygen coverage by oxidizing Rh(111) surface at 700 K. These authors conclude that up to 6 ML oxygen atoms can dissolve into the Rh(111)
subsurface at 700 K and create a localized oxygen rich environment. Surface oxide (RhO$_2$) is observed only when the oxidized sample was prepared at or annealed at 700 K at these high coverages. Similarly, Kim et al also report that oxygen coverages as high as 5 ML can be obtained on Ru(0001) by NO$_2$ exposure without forming oxide (RuO$_2$) layer.$^{49}$ These oxygen phases on Ru(0001) yield a single sharp O$_2$ TPD peak at 1050 K and produce a (1 × 1) LEED pattern corresponding to chemisorbed oxygen adlayer despite such high oxygen uptake. Note that peak desorption temperature for these high concentration oxygen phases is similar to that from the decomposition of stoichiometric RuO$_2$(110) layers prepared on Ru(0001). These authors claim that oxygen atoms on the Ru(0001) surface in excess of 1 ML dissolve into the Ru bulk, although no evidence is provided for the claim. A possible implication is that formation of oxide or oxygen adlayers with dissolved oxygen delicately depend upon preparation methods and oxidation conditions. The observed (1 × 1) LEED pattern at high oxygen coverages in our experiments may be a result of oxygen diffusion into the Ir subsurface above 1 ML. Further investigation is required to precisely determine the structures of the (4 × 4) surface oxide and (1×1)-O phases formed above 2 ML.

2.5 Summary

We employed TPD, LEED, XPS and TPRS to investigate oxidation of Ir(100) at 300 K and 600 K temperatures. Our results demonstrate that Ir(100) surface can be oxidized under UHV environment to generate oxygen coverages up to ~3.4 ML using gas-phase atomic oxygen beam. Oxygen phase evolution and saturation coverages on Ir(100) remain almost unchanged at oxidation temperatures between 300 K and 500 K, and the process is governed by kinetics of oxidation. Our results provide evidence of formation of a 2D surface oxide with (4 × 4) periodicity on Ir(100) surface, which saturates above 1 ML oxygen coverages. The (4 × 4) surface oxide is a kinetically stabilized transient phase that transforms into a (2 × 1) pattern
overlapping with a unique “rotated square” LEED pattern after annealing to 675 K.
Decomposition of oxidized Ir(100) surface with coverages above 2.1 ML produces a sharp O₂ TPD peak centered at ~725 K that is consistent with formation of a multilayer oxide. Our TPD data shows that the oxide structures prepared at higher surface temperature are more stable compared with those prepared at low temperature. Oxidized Ir(100) surfaces with coverages above 2.1 ML exhibit a (1 × 1) LEED pattern that transforms into a (2 × 1) pattern overlapping with a unique “rotated square” pattern after annealing to 675 K, which suggests that as grown high concentration phases on Ir(100) in our experiments lack sufficient long-range order to produce distinct diffraction in our experiments. Further investigation is required to determine the exact structure of these oxygen phases. TPD and TPRS experiments after adsorbing CO and C₃H₈ on the oxidized Ir(100) surfaces suggest that reactivity of Ir(100) surface decreases with increasing oxygen coverage and the Ir oxide with oxygen coverage above 2 ML is chemically inactive toward these molecules due to lack of coordinatively unsaturated metal and oxygen atoms.
Figure 2-1. O₂ TPD spectra obtained after exposing a clean, reconstructed Ir(100) surface at 300 K. A) Low O-atom coverages (up to 2.1 ML) and B) high coverages from 2.1 ML to 3.3 ML. The ordinate scale in (B) is expanded by a factor of 10 relative to (A).
Figure 2-2. O$_2$ TPD spectra obtained after exposing a clean, reconstructed Ir(100) surface at 500 K. A) Low O-atom coverages (up to 2.0 ML) and B) high coverages from 2.0 ML to 3.4 ML. Note that the ordinate scale in (B) is expanded by a factor of 10 relative to (A).
Figure 2-3. O-atom uptake as a function of atomic oxygen exposure on Ir(100) surface after O-atom exposure at 500 and 300 K.
Figure 2-4. LEED images obtained after generating various oxygen coverages on Ir(100) surface at 500 K using gas-phase O-atom beam. Oxygen coverages: (a) 0.7 ML, (b) 1.2 ML, (c) 2.1 ML (d) 2.1 ML after annealing to 673 K (e) 3.2 ML and (f) 3.2 ML after annealing to 673 K. All LEED images are taken at 80 K surface temperature using 70 eV incident electron beam energy.
Figure 2-5. Normalized XPS Ir 4d\textsubscript{5/2} spectra obtained from clean and oxidized Ir(100) surfaces.
Figure 2-6. CO CO₂ TPRS spectra obtained after CO adsorption on oxidized Ir(100) surfaces at 80 K. A) CO and B) CO₂ TPRS spectra obtained from clean and oxidized Ir(100) surfaces with various oxygen coverages after adsorbing CO at 80 K. The TPRS spectra were obtained using a constant heating rate of 1 K s⁻¹.
Figure 2-7. \( \text{C}_3\text{H}_8 \) TPD spectra obtained after adsorbing \( \text{C}_3\text{H}_8 \) on clean Ir(100) and 3.2 ML \( \text{IrO}_x \) on Ir(100). The TPD spectra were obtained using a constant heating rate of 1 K s\(^{-1}\).
CHAPTER 3
GROWTH AND TERMINATION OF A RUTILE IrO$_2$(100) LAYER ON Ir(111)

3.1 Motivation

Late transition-metal (TM) oxides can play an important role in applications of oxidation catalysis. Iridium oxide in particular is well known as an effective catalyst for promoting electrochemical H$_2$O splitting and is also a promising material for effecting other chemical transformations. Recent density functional theory (DFT) studies predict that the rutile IrO$_2$(110) surface strongly binds a variety of molecules such as NH$_3$, N$_2$ and CH$_4$, and is active in promoting dehydrogenation reactions. These predictions motivate efforts to generate well-defined IrO$_2$ surfaces and explore the physical and chemical properties of IrO$_2$ surfaces under well-controlled ultrahigh vacuum (UHV) conditions. Such efforts have potential to advance our understanding of the surface chemistry of late TM oxides, beyond the knowledge derived from prior investigations with RuO$_2$(110) and PdO(101). Furthermore, the fact that rutile IrO$_2$ and RuO$_2$ are isostructural can provide insightful comparisons about the growth and surface chemistry of these oxides. In general, however, the growth and surface chemistry of IrO$_2$ has not been widely explored due to difficulties in oxidizing metallic Ir surfaces under UHV conditions.

The dissociative chemisorption of O$_2$ and the properties of chemisorbed oxygen atoms on Ir(111) have been studied in detail and are well understood. Work by Chan and Weinberg shows that O$_2$ dissociation on clean Ir(111) at room temperature produces a sharp (2 × 2) low energy electron diffraction (LEED) pattern. Subsequent DFT calculations predict that the (2 × 2) LEED pattern appears initially at coverages up to 0.25 ML due to the formation of a p(2 × 2) layer and that the (2 × 2) pattern persists up to an O-atom coverage of 0.50 ML due to the

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formation of three equivalent rotational domains of a p(1 × 2) structure. Due to kinetic limitations, the dissociative chemisorption of O$_2$ on Ir(111) effectively saturates at a coverage of 0.50 ML of O-atoms at the low O$_2$ partial pressures utilized in UHV experiments. Early studies have reported the formation of IrO$_2$ on Ir surfaces at elevated temperatures and O$_2$ pressure. Of particular relevance to the present study is a report by Conrad et al. demonstrating that thin oxide layers develop on Ir(111) during exposure to O$_2$ at elevated pressure and surface temperatures above 800 K. Those authors present evidence that the oxide layers are crystalline, but did not make structural assignments. More recently, He et al. have studied the oxidation of Ir(111) using in situ surface X-ray diffraction (SXRD) and find that a rutile IrO$_2$ layer, exposing predominantly IrO$_2$(110) facets, forms only at sufficiently high O$_2$ pressure (up to 100 mbar) and an elevated temperature of 775 K. Those authors find that oxidation at lower pressure and temperature generates other oxide phases, including a monolayer surface oxide as well as a multilayer of corundum Ir$_2$O$_3$(0001). These results provide evidence that the formation of rutile IrO$_2$ on Ir(111) is kinetically limited, occurring only at sufficiently high oxygen chemical potential. Lastly, Chung et al. have recently shown that Ir(111) can be oxidized in UHV using plasma-activated oxygen, with oxide formation initially producing a rutile IrO$_2$(100) multilayer, followed by transformation to Ir$_2$O$_3$(0001) as the oxide layer thickens. These recent studies suggest that the oxide phase evolution on Ir(111) depends sensitively on the oxidation conditions.

In the present study, we investigated the oxidation of Ir(111) by gas-phase O-atoms at temperatures between 500 and 625 K. We find that the formation of a crystalline √3 surface oxide precedes the growth of a rutile IrO$_2$(100) multilayer structure, with saturation of the IrO$_2$(100) layer occurring at a thickness of four oxide layers for the conditions studied. We
present evidence that the IrO$_2$(100) layer grown in our experiments is completely oxygen-terminated, and thus inactive toward binding many molecular adsorbates.

### 3.2 Experimental Details

Previous studies$^{17, 36}$ provide details of the three-level UHV chamber utilized for the present experiments. The Ir(111) single crystal used in this study is a circular disc (9 mm diameter, 1 mm thickness) attached to a copper sample holder through 0.015” W wires. A type K thermocouple spot-welded to the backside of the crystal allows sample temperature measurements. The sample holder 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 up the sample temperature from $\sim$80 to 1400 K. We initially cleaned the Ir(111) sample by repeated cycles of sputtering with 1 keV Ar$^+$ ions at 900 K with annealing to 1400 K and also by O$_2$ treatment at 900 K. Routine cleaning involved Ar$^+$ sputtering at 900 K followed by annealing at 1400 K, treatment in $5 \times 10^{-7}$ Torr O$_2$ at 900 K and finally annealing at 1400 K. We considered the surface to be clean when X-ray photoelectron spectra (XPS) exhibited no C 1s and O 1s peaks and negligible quantities of CO and CO$_2$ were observed in temperature programmed desorption (TPD) experiments following oxygen adsorption. LEED observations after the aforementioned cleaning procedure show a sharp (1 $\times$ 1) pattern with low background intensity.

A two-stage differentially pumped chamber attached to the UHV chamber accommodates an inductively coupled RF plasma source (Oxford Scientific Instruments) employed to generate oxygen atom beams used in this study. We refer the reader to prior work for details of the beam system.$^{17, 36}$ We exposed the Ir(111) sample to the plasma-generated O-atom beams for varying durations to generate different oxygen coverages on the surface, and employed TPD, LEED and low energy ion scattering spectroscopy (LEISS) to characterize the oxidized surfaces. After an
exposure to the plasma-activated oxygen beam, we collected O$_2$ TPD spectra by positioning the sample in front of a shielded mass spectrometer at a distance of about 7-8 mm and then heating at a constant rate of 1 K s$^{-1}$ until the sample temperature reached 1400 K. We estimate O-atom coverages in this work by integrating the O$_2$ TPD spectra. To convert the O$_2$ TPD areas to units of absolute O-atom coverage, we scale the TPD areas with that obtained from a saturated O-atom layer prepared by exposing Ir(111) to O$_2$ at 300 K and assuming that this procedure produces an O-atom coverage of 0.50 ML. We routinely repeat the calibration TPD experiment to ensure accuracy in our analysis. Prior studies have convincingly shown that the O-atom layer on Ir(111) saturates at a coverage 0.50 ML when generated using O$_2$ exposures in UHV at temperatures near 300 K.$^{55,60,61}$ On the basis of the uptake of O-atoms on Ir(111), as determined from O$_2$ TPD, we estimate that the O-atom flux at the sample surface was 0.038 ML s$^{-1}$ in our experiments. For structural characterization, we performed LEED experiments using a four-grid optics with beam energies between 60 eV and 140 eV. Finally, we carried out low energy ion scattering spectroscopy (LEISS) using He$^+$ ions with incident energy of 1 keV and a scattering angle of approximately 90°. We measured the energy distributions of the scattered He$^+$ ions using a hemispherical analyzer operating in constant retarding mode with the retard ratio set equal to three.

3.3 Computational Methods

All plane wave DFT calculations were performed using the projector augmented wave pseudopotentials$^{62}$ provided in the Vienna ab initio simulation package (VASP).$^{63,64}$ The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional$^{65}$ was used with a plane wave expansion cutoff of 400 eV. We employed four layers to model the IrO$_2$(100), IrO$_2$(110), RuO$_2$(100) and RuO$_2$(110) films, resulting in ~ 18, 12, 18 and 12 Å thick slabs, respectively. The bottom layer is fixed, but all other lattice atoms were allowed to relax during the calculations
until the forces are less than 0.03 eV/Å. A vacuum spacing of 20 Å was included, which is sufficient to reduce the periodic interaction in the surface normal direction. In terms of system size, a 1×4 unit cell with a corresponding 4×2×1 Monkhorst-Pack k-point mesh is used.

In the present study, we are primarily interested in determining the variation in energetics to remove individual on-top (ot) and bridging (br) oxygen atoms from both the O-rich and stoichiometric IrO₂ and RuO₂ surfaces. Therefore, we define the binding energy, \( E_b \), of an O atom that is removed from the surface using the expression,

\[
E_b = \left( \frac{E_{O2}}{2} + E_{\text{surf}} \right) - E_{O/\text{surf}},
\]

where \( E_{O/\text{surf}} \) is the energy of the initial state containing the \( O_{ot}/O_{br} \) atoms that will be removed, \( E_{\text{surf}} \) is the energy of the surface with the selected O atom removed, and \( E_{O2} \) is the energy of an isolated \( O_2 \) molecule in the gas phase. From Eq. 3-1, a large positive value for the binding energy indicates a high stability of the O-atom under consideration.

### 3.4 Results

#### 3.4.1 \( O_2 \) TPD for Ir(111) Oxidation at 500 K

Figure 3-1 shows \( O_2 \) TPD spectra obtained as a function of the O-atom coverage prepared by exposing Ir(111) to an O-atom beam at 500 K. The figure also shows an \( O_2 \) TPD trace obtained from a saturated oxygen layer (0.50 ML) that was generated by exposing Ir(111) to \( O_2 \) under vacuum conditions. Prior work demonstrates that the dissociative chemisorption of \( O_2 \) on Ir(111) produces a saturation coverage of 0.50 ML under UHV conditions, and that the adsorbed O-atoms arrange into a \( p(1 \times 2) \) structure.\(^{54, 55}\) Recombinative desorption from the chemisorbed layer gives rise to a broad desorption feature (\( \beta_3 \)) centered at about 1000 K. Our data reveals that the broad TPD peak at \( \sim 1000 \) K undergoes a nearly uniform increase in intensity as the oxygen coverage increases from \( \sim 0.50 \) to 0.94 ML. This characteristic suggests that the oxygen binding
environment during desorption is similar at coverages between about 0.50 and 1 ML, at least when the oxygen layer is generated at 500 K. An implication is that oxide phases do not form appreciably on Ir(111) for oxygen coverages up to 1 ML prepared at 500 K as well as during subsequent heating.

After increasing the oxygen coverage to 1.25 ML, the O$_2$ TPD trace exhibits a sharp peak ($\beta_2$) at 680 K as well as the broad feature centered at 1000 K. The sharp peak intensifies as the coverage increases to ~1.6 ML, but diminishes with further increases in coverage to ~1.8 ML. As discussed below, we attribute the $\beta_2$ TPD peak to the decomposition of an ordered 2D surface oxide that develops on the Ir(111) surface at coverages above 1 ML. Indeed, prior studies show that the formation of ordered surface oxides is common in the oxidation of late transition metal surfaces, and that surface oxide decomposition gives rise to sharp O$_2$ TPD peaks, similar to that seen in Figure 3-1a.$^{1,66,67}$ The slight decrease in the $\beta_2$ peak intensity for coverages just above 1.6 ML coincides with the appearance of a small TPD peak ($\beta_1$) on the leading edge of the $\beta_2$ peak that intensifies and upshifts to 540 K as the coverage increases to 1.8 ML. We have previously reported a similar evolution of O$_2$ TPD features during the oxidation of Pt(100) and Pd(111) and shown that peaks analogous to the $\beta_1$ TPD peak result from the decomposition of small “seeds” of the multilayer oxide.$^{1,38}$ These small seeds develop into larger and more stable domains of multilayer oxide as the oxygen coverage increases.

At high coverage, the O$_2$ TPD spectra exhibit characteristics that are indicative of the decomposition of a multilayer oxide film. Specifically, at coverages above about 2 ML, a sharp peak develops in the O$_2$ TPD spectra that shifts toward higher temperature and intensifies dramatically with increasing coverage. At saturation of the oxide layer (~3.6 ML), the O$_2$ TPD peak is centered at ~770 K and has a maximum desorption rate that is nearly thirty times greater
than that observed in TPD spectra obtained from the chemisorbed layer. Previous studies report that multilayer oxide films grown on Pt and Pd surfaces decompose explosively during TPD, producing analogous behavior to that observed in the present study.\textsuperscript{1, 23, 24, 37, 38, 67, 68} In those cases, explosive desorption results from an autocatalytic mechanism wherein reduced sites promote further decomposition of the oxide. As such, the rate of oxide decomposition increases dramatically during TPD because the total concentration of reduced sites increases as the oxide thermally decomposes. Overall, the $O_2$ TPD data suggests an oxygen phase evolution on Ir(111) that is similar to that reported for other systems, wherein a 2D oxide structure develops prior to a multilayer oxide.

From the $O_2$ TPD spectra, we find that the oxygen uptake on Ir(111) saturates at a coverage of $\sim$3.6 ML for oxidation at a surface temperature of 500 K and the O-atom flux employed. We obtain similar saturation coverages by oxidizing at temperatures between 300 and 625 K. The maximum coverage that we could generate decreases sharply with increasing temperature above 650 K because the oxide decomposition rate begins to surpass the oxide formation rate. Our results thus demonstrate that the kinetics of oxidation limits the IrO$_x$ film thickness to coverages below $\sim$4 ML when Ir(111) is oxidized using an O-atom flux less than about 0.1 ML/s. The formation of thicker IrO$_x$ layers likely requires higher temperatures and thus higher oxidant flux so that the rate of oxygen supplied to the surface overcomes the rate of oxide decomposition, and thereby results in net oxide growth.

### 3.4.2 Evolution of LEED patterns for Ir(111) oxidation at 500 K

Figure 3-2 shows LEED patterns obtained after generating different oxygen coverages on Ir(111) at 500 K. We observe the (1 × 1) LEED pattern from the substrate for coverages up to $\sim$1 ML generated at 500 K. Heating to above 650 K but prior to substantial $O_2$ desorption causes a sharp (2 × 2) LEED pattern to emerge (not shown). The observation of a (2 × 2) LEED pattern
after heating suggests the possibility that chemisorbed O-atoms rearrange to form high density (2 × 2)-3O structures at coverages just below 1 ML, similar to that observed on Ru(0001) at oxygen coverages in the range of 0.5 ML to 1 ML. A fraction of the oxygen atoms might also occupy subsurface sites of Ir(111) at coverages near 1 ML. As mentioned above, the lack of new O$_2$ TPD features developing with increasing coverage between 0.50 and 1.0 ML suggests that the surface binding environment is similar for the O-atoms that desorb at these coverages. The occupation of subsurface sites at oxygen coverages above 0.50 ML as well as structural rearrangements within the adlayer during TPD could explain similarities in the O$_2$ TPD traces obtained at 0.50 and 0.94 ML (Figure 3-1a) as well as the observation of a (2 × 2) LEED pattern for an O-atom coverage of nearly 1 ML. Additional investigations are needed to clarify the types of oxygen phases that develop between 0.50 and 1 ML. In the present study, we omit a detailed evaluation of the low-coverage oxygen phases, focusing instead on characterizing the formation of Ir oxides.

We observe a clear (√3 × √3)R30° LEED pattern after generating an oxygen coverage of 1.37 ML (Figure 3-2b) and attribute the √3 structure to a surface oxide. The emergence of the √3 LEED pattern coincides with the initial appearance of the sharp β$_2$ TPD peak at coverages above ~1 ML, thus suggesting that decomposition of the √3 structure is responsible for the β$_2$ TPD peak. Consistent with this interpretation, we find that the (2 × 2) LEED pattern replaces the √3 pattern after we heat the surface to 650 K to desorb a large fraction of the β$_2$ state. Our observation of the √3 LEED pattern only at coverages above 1 ML further supports the conclusion that the corresponding structure results from a surface oxide rather than a high-density chemisorbed layer. As elaborated below, the √3 surface oxide may arise from a trilayer structure resembling the hexagonal (0001)-orientation of corundum Ir$_2$O$_3$. The √3 LEED pattern
begins to fade after generating an oxygen coverage of 1.6 ML, and the (1 × 1) spots appear slightly more diffuse (Figure 3-2c). These changes coincide with the initial appearance of the $\beta_1$ TPD peak and thus suggest that the formation of multilayer oxide seeds disrupts the long-range order of the $\sqrt{3}$ structure.

Figure 3-2d shows a representative LEED pattern obtained after preparing an oxygen coverage of 3.0 ML at 500 K. The $\sqrt{3}$ pattern is no longer visible and two diffuse diffraction spots are evident near each of the 1 × 1 spots. Chung et al. have recently shown that the diffuse LEED spots are consistent with three domains of the rutile IrO$_2$(100) structure $^{59}$. The diffuse nature of the diffraction spots is indicative of weak long-range ordering, and may indicate that the IrO$_2$(100) structure forms in small domains during oxidation at 500 K. Heating the oxidized surface only marginally improves the quality of the IrO$_2$(100) LEED pattern before the oxide decomposes. Overall, our LEED observations provide evidence that a well-ordered surface oxide with ($\sqrt{3} \times \sqrt{3}$)R30° periodicity develops on Ir(111) after saturation of the chemisorbed/subsurface layer and that further oxidation under the conditions studied mainly causes a transformation to multilayer IrO$_2$(100).

3.4.3 Structural Characterization of the Rutile IrO$_2$ Layer on Ir(111)

We find that the crystallinity of the rutile IrO$_2$ layer improves significantly when the Ir(111) surface is oxidized at surface temperatures above about 600 K. Figures 3-3a and 3-3b show LEED patterns (70 and 120 eV) obtained after generating an oxygen coverage of ~2.2 ML on Ir(111) at 625 K. The LEED pattern exhibits two, well-resolved diffraction spots (red arrows, Figure 3-3a) near each of the (1 × 1) spots of the substrate that are consistent with diffraction from rutile IrO$_2$(100), as mentioned above. Two additional faint spots are also evident in the LEED pattern obtained at 70 eV (yellow arrow, Figure 3-3a), where these spots lie close to the
well-defined IrO₂(100) spots but are displaced toward the (0, 0) position. The LEED pattern obtained at 120 eV further shows that the two, well-resolved spots are part of a hexagonal arrangement of spots that surrounds each of the substrate spots (Figure 3-3b). This hexagonal arrangement corresponds to the moiré pattern that results from superposition of the IrO₂(100) and Ir(111) lattices. A similar but better-resolved LEED pattern was reported by Conrad et al. after oxidizing the Ir(111) crystal at high O₂ pressure and elevated temperature (1300 K)⁵⁸, though those authors did not provide a structural assignment.

Figure 3-3c shows the LEED pattern simulated for IrO₂(100) as well as the moiré pattern that results from the coincidence structure produced at the IrO₂(100)/Ir(111) interface. The IrO₂(100) unit cell is rectangular with lattice constants of b₁ = 3.16 Å and b₂ = 4.52 Å, and is favorably lattice-matched with Ir(111) because the b₂ lattice constant is close to twice the row-spacing (√3a = 4.69 Å) of the Ir(111) substrate. The optimal matching between the IrO₂(100) and Ir(111) lattices is obtained when the b₁ direction aligns along a close-packed direction of Ir(111) and the b₂ lattice constant is equal to √3a, thus resulting in a coincident unit cell with dimensions of (6b₁ × b₂) (Figure 3-3d). In terms of the Ir(111) lattice vectors, the IrO₂(100) structure and the coincidence structure are given by the matrices \[
\begin{pmatrix}
\frac{7}{6} & 0 \\
1 & 2
\end{pmatrix}
\] and \[
\begin{pmatrix}
7 & 0 \\
1 & 2
\end{pmatrix}
\], respectively. Hereafter, we refer to the IrO₂(100)/Ir(111) coincidence structure as a “(6 × 1)”, referencing the superstructure to the IrO₂(100) unit cell. For comparison, the rectangular unit cell of IrO₂(110) (b₁ = 3.16 Å, b₂ = 6.39 Å) is matched less favorably with Ir(111) because the b₂ lattice constant is considerably larger than that of IrO₂(100). The simulated LEED pattern shown in Figure 3-3c assumes that IrO₂(100) adopts the structure shown in Figure 3-3d, and forms three equivalent rotational domains on the Ir(111) substrate. After correcting the experimentally-measured LEED pattern for geometrical distortion, we find that the positions of the (1, 1) spots, referenced to the
(b₁, b₂) basis (Figure 3-3c), agree to within 2.6% of those simulated for the IrO₂(100) structure on Ir(111). In addition, our simulation of the moiré pattern, resulting from the IrO₂(100)/Ir(111) coincidence structure, reproduces the hexagonal arrangement of spots that are centered on the main spots obtained from the Ir(111) substrate (blue spots, Figure 3-3c), in excellent agreement with our experimental observations.

The positions of the more faint spots (yellow arrow, Figure 3-3a) agree to within about 10% of the reciprocal space points simulated for IrO₂(110) with lattice constants of b₁ = 1.17a and b₂ = 2.31a, where these lattice constants are strained by +0.4% and -1.6% from the bulk values to produce a (6b₁ × 3b₂) coincident unit cell at the IrO₂(110)/Ir(111) interface. While the agreement between the simulated and measured positions of the faint diffraction spots is reasonable, it is important to note that the identification of the IrO₂(110) structure is more uncertain than that of IrO₂(100) because the positions of the faint spots are more difficult to identify and fewer spots are resolved. Overall, our analysis demonstrates that rutile IrO₂ preferentially adopts the (100) orientation on Ir(111) during the early stages of IrO₂ formation, in agreement with recent findings¹¹,⁵⁹, and provides evidence that IrO₂(110) also forms in small quantities as the oxide layer approaches saturation at the oxidation conditions studied.

3.4.4 Atomic termination of the IrO₂ layer: Adsorption of probe molecules and LEISS measurements

Determining the atomic termination of the IrO₂(100) layer on Ir(111) is important for understanding the surface chemical properties of this oxide. Prior studies demonstrate that stoichiometrically-terminated surfaces of late transition-metal oxides, including rutile IrO₂ surfaces, tend to exhibit high chemical activity because these surfaces expose pairs of coordinatively unsaturated (cus) metal and oxygen atoms⁸,⁵³. The cus-metal atoms bind molecules strongly and activate intramolecular bonds, while the cus-O atoms are efficient
hydrogen acceptors and can be readily released from the oxide lattice and incorporated into oxidized products. Figure 3-3e shows model representations of the rutile IrO$_2$(100) surface with stoichiometric vs. O-rich terminations. Along the <100> direction, the IrO$_2$ structure consists of layers of O-atoms separated by layers of Ir atoms where each layer consists of about 0.90 ML and 0.45 ML of O-atoms and Ir-atoms, respectively. We thus estimate that the 3.6 ML IrO$_2$(100) film grown in our experiments consists of about four oxide layers and is about 9 Å thick. In the stoichiometric termination, the IrO$_2$(100) surface features rows of Ir$_{\text{cus}}$ atoms and adjacent rows of bridging O-atoms (O$_{\text{br}}$) where each of these atom types is missing a bonding partner relative to the bulk and thus exposes a single coordination vacancy toward the vacuum. In the O-rich termination, an O-atom bonds “on-top” of each Ir$_{\text{cus}}$ atom, and produces a surface in which equal quantities of O$_{\text{ot}}$ and O$_{\text{br}}$ atoms are exposed and the surface Ir atoms are coordinatively saturated and unavailable for binding molecules from the gas-phase.

We find that the thin IrO$_2$(100) layer grown on Ir(111) is inactive toward the binding and oxidation of various probe molecules. For example, TPD experiments show that CO adsorbs in negligible quantities on the oxide layer at surface temperatures as low as 90 K, suggesting that Ir$_{\text{cus}}$ sites are unavailable for binding CO molecules. TPD also shows that water binds relatively weakly on the IrO$_2$ layer, rather than populating a strongly-bound state that would be expected for H$_2$O molecules that coordinate with Ir$_{\text{cus}}$ atoms. Figure 3-4a shows H$_2$O TPD spectra obtained after adsorbing H$_2$O on clean Ir(111) vs. a rutile IrO$_2$(100) layer on Ir(111) at 85 K. The TPD trace obtained from water-covered Ir(111) exhibits two sharp peaks at 162 and 173 K that originate from H$_2$O desorbing from multilayer and monolayer states, respectively. The H$_2$O TPD trace obtained from the water-exposed IrO$_2$ layer also exhibits a multilayer peak at 162 K as well as a shoulder at 173 K and a slightly broader trailing edge compared with the water TPD trace.
from Ir(111). These characteristics are indicative of relatively weak bonding of water to the IrO$_2$ layer, and are inconsistent with water adsorbed on Ir$_{\text{cus}}$ sites. For comparison, previous studies show that H$_2$O molecules bound to cus-metal sites on the stoichiometric PdO(101) and RuO$_2$(110) surfaces desorb in distinct TPD features at temperatures between 300 and 400 K $^{73, 74}$. We assert that the weak binding of H$_2$O and CO on the IrO$_2$ layer occurs because the IrO$_2$ facets that form in our experiments are oxygen terminated and thus lack Ir$_{\text{cus}}$ sites that can strongly bind these molecules.

We also conducted He$^+$ LEISS measurements to further characterize the surface oxygen phases that develop during Ir(111) oxidation and assess the possibility that the IrO$_2$ layer exposes oxygen-terminated facets. Figure 3-4b shows representative LEISS spectra obtained after oxidizing Ir(111) to varying extents at 625 K using an O-atom beam, where each spectrum is scaled by the height of the Ir peak obtained from the clean Ir(111) surface. The LEISS spectra obtained from the oxygen-exposed surfaces exhibit two main peaks centered at ~632 and 927 eV caused by inelastic He$^+$ scattering from surface O and Ir atoms, respectively. The LEISS data shows that the intensity of the Ir peak decreases significantly with increasing oxygen coverage while the O peak intensity concurrently increases. For the saturated p(1 × 2)-O layer (0.50 ML) on Ir(111), the Ir peak intensity is 62% of the value obtained from clean Ir(111), and the oxygen peak has a height of 0.07. Further increasing the oxygen coverage to 1.1 ML causes the Ir peak height to decrease to 0.53 and the O peak height to increase to 0.11, corresponding to a factor of 1.8 decrease in the Ir:O peak height ratio relative to the (1 × 2)-O layer. This decrease suggests that the surface O-atom density of the $\sqrt{3}$ oxide is higher than that of the (1 × 2)-O chemisorbed layer, which is consistent with viable structural models of the $\sqrt{3}$ surface oxide. For example,
assuming a trilayer structure, one estimates that the $\sqrt{3}$ surface oxide would terminate with a surface O-atom density in the range of 0.67 to 1.0 ML.

The Ir:O peak height ratio decreases significantly after generating an IrO$_2$(100) layer on Ir(111), which is indicative of an oxygen-terminated oxide surface. The Ir and O peak heights are both equal to 0.26 in the LEISS spectrum obtained from a 2.2 ML IrO$_2$(100) layer, and the Ir:O LEISS peak ratio obtained from the IrO$_2$(100) layer is 4.8 times smaller than that obtained from the $\sqrt{3}$ surface oxide. The tail on the low-energy side of the Ir peak originates from He$^+$ ions that neutralize and scatter from subsurface layers, and are reionized near the surface during the outbound trajectory. The more pronounced tail observed in the LEISS spectra obtained from the IrO$_2$(100) layer is consistent with ion scattering from a multilayer oxide with an electronic structure that is distinct from metallic Ir. The very low value of the Ir:O peak ratio obtained from the IrO$_2$ layer relative to the $\sqrt{3}$ surface oxide, together with the low chemical activity of the IrO$_2$ layer, strongly suggest that the IrO$_2$(100) structure on Ir(111) forms an oxygen-terminated surface under the oxidation conditions studied.

3.4.5 DFT Calculations

We performed DFT calculations to investigate the stability of O$_{ot}$ atoms on the IrO$_2$(100) surface, and make comparisons with O$_{ot}$ atom binding on the well-characterized RuO$_2$(110) surface. We predict that O$_{ot}$ atoms achieve stronger bonding on IrO$_2$(100) compared with RuO$_2$(110), and that O$_{ot}$ atoms should be stable on IrO$_2$(100) at the oxidation temperatures employed in the present study ($\sim$625 K). According to our calculations, the O$_{ot}$ binding energy decreases from 0.99 to 0.78 eV per O$_{ot}$ atom as the O$_{ot}$ coverage increases from 25% to 100% on IrO$_2$(100). The O$_{ot}$ binding energies also decrease with increasing coverage on RuO$_2$(110), and are 0.11 to 0.21 eV lower than the values obtained for IrO$_2$(100) (Table 3-1). Averaging the
binding energies computed as a function of the O\textsubscript{ot} coverage gives values of 0.93 and 0.71 eV for O\textsubscript{ot} atoms on IrO\textsubscript{2}(100) and RuO\textsubscript{2}(110), respectively, corresponding to average activation energies of 1.86 and 1.42 eV for the recombinative desorption of O\textsubscript{ot} atoms from these surfaces. For these activation energies and assuming a desorption pre-factor of $10^{14}$ s\textsuperscript{-1}, the Redhead equation gives values of 637 K and 490 K for the TPD peak temperatures resulting from O\textsubscript{ot} desorption from IrO\textsubscript{2}(100) and RuO\textsubscript{2}(110), respectively. The predicted TPD peak temperature for O\textsubscript{ot} desorption from RuO\textsubscript{2}(110) lies within the range (400 to 500 K) of previously reported values\textsuperscript{8, 76}, thus suggesting that our approximate analysis and assumed value of the desorption pre-factor provide reasonably accurate estimates of the O\textsubscript{ot} TPD peak temperatures.

Significantly, the predicted TPD peak temperature for O\textsubscript{ot} desorption from IrO\textsubscript{2}(100) is slightly higher than the surface temperatures ($\sim$625 K) at which we grew the IrO\textsubscript{2} layer on Ir(111) in the present study. This prediction suggests that O\textsubscript{ot} atoms are stable and should thus form on the IrO\textsubscript{2}(100) layer under the growth conditions employed, in agreement with the LEISS results and chemical inactivity that we observe experimentally (Figure 3-4).

The present study also reveals a significant difference in the thermal stability of the O-rich IrO\textsubscript{2}(100) and RuO\textsubscript{2}(110) surfaces. Prior studies show that the recombinative desorption of O\textsubscript{ot} atoms on RuO\textsubscript{2}(110) and thermal decomposition of the RuO\textsubscript{2}(110) film on Ru(0001) yield distinct O\textsubscript{2} TPD peaks at $\sim$450 K and 1040 K, respectively\textsuperscript{8, 76}, indicating that O\textsubscript{ot} atoms are more weakly-bound than O\textsubscript{br} atoms on RuO\textsubscript{2}(110). This characteristic allows preparation of both stoichiometric as well as O\textsubscript{ot}-covered RuO\textsubscript{2}(110) surfaces for model studies. In contrast, we observe only a single O\textsubscript{2} TPD peak at $\sim$750 K as the IrO\textsubscript{2}(100) layer decomposes during heating (Figure 3-1), even though both our experimental and computational results provide strong evidence that the IrO\textsubscript{2}(100) films are completely terminated by O\textsubscript{ot} atoms. Taken together, these
results suggest that the $O_{ot}$ and $O_{br}$ atoms of O-rich IrO$_2$(100) desorb over the same temperature range during TPD, and thus that these oxygen atoms have similar thermal stabilities, in sharp contrast with the well-established behavior of O-rich RuO$_2$(110). While an extensive study of the thermal decomposition mechanisms of these O-rich oxide surfaces is ultimately needed, initial DFT calculations reveal a significant difference in the thermal stability of O-atoms on the (100) and (110) surfaces of IrO$_2$ and RuO$_2$ that may explain, at least in part, the differences that the present study reveals.

According to our DFT calculations, $O_{ot}$ atoms destabilize $O_{br}$ atoms to a significantly greater extent on the (100) surfaces of IrO$_2$ and RuO$_2$ compared with the (110) surfaces. This destabilization could be largely responsible for our observation that $O_{ot}$ atom desorption and IrO$_2$(100) decomposition occur over a similar range of temperature during TPD. Table 3-2 shows the binding energies of $O_{br}$ atoms computed for stoichiometric/ partially-reduced and O-rich (100) and (110) surfaces of IrO$_2$ and RuO$_2$, where the binding energies are given as a function of the initial coverage of $O_{br}$ atoms. In these calculations, we considered oxide surfaces with varying coverages of $O_{br}$ atoms coexisting with either 100% $O_{ot}$ atoms (“O-rich”) or 0% $O_{ot}$ atoms. In the absence of $O_{ot}$ atoms, a surface with an $O_{br}$ coverage of 100% corresponds to the stoichiometric termination while the surfaces with $O_{br}$ coverages less than 100% are partially-reduced. The columns labeled as $\Delta E$ list the corresponding difference in $O_{br}$ binding energy for each stoichiometric/partially-reduced and O-rich surface with a given initial $O_{br}$ atom coverage.

Firstly, we find that the $O_{br}$ atoms exhibit a similar range of binding energies on the stoichiometric/partially-reduced IrO$_2$(100) and RuO$_2$(110) surfaces, with the computed values ranging from 2.2 to 2.75 eV for IrO$_2$(100) vs. 2.3 to 2.43 eV for RuO$_2$(110), depending on the initial coverage of $O_{br}$ atoms. The $O_{br}$ binding energies on the stoichiometric/partially-reduced
surfaces (Table 3-2) are significantly higher than the binding energies of \( \text{O}_{\text{ot}} \) atoms (Table 3-1). For this reason, one might speculate that \( \text{O}_{\text{ot}} \) atoms would desorb at lower temperature than \( \text{O}_{\text{br}} \) atoms during TPD, as observed in prior studies with RuO\(_2\)(110).

We also predict, however, that the binding energies of the \( \text{O}_{\text{br}} \) atoms are lower on the O-rich surfaces compared with the stoichiometric/partially-reduced surfaces for each oxide surface considered, demonstrating that destabilization of \( \text{O}_{\text{br}} \) atoms by \( \text{O}_{\text{ot}} \) atoms is a common effect on these surfaces. In general, our calculations predict that this destabilization is significantly more pronounced on the (100) surfaces compared with the (110) surfaces, and is thus largely attributable to the structural differences between the (100) and (110) surfaces rather than to electronic differences between IrO\(_2\) and RuO\(_2\). For example, we predict that the \( \text{O}_{\text{ot}} \) binding energies are lower by between 0.31 and 1.47 eV on the O-rich vs. stoichiometric/partially-reduced IrO\(_2\)(100) surfaces, whereas the addition of \( \text{O}_{\text{ot}} \) atoms destabilizes the \( \text{O}_{\text{br}} \) atoms on IrO\(_2\)(110) by between only 0.18 and 0.26 eV. Similarly, \( \text{O}_{\text{ot}} \) atoms lower the \( \text{O}_{\text{br}} \) binding energies by between 1.1 and 2.18 eV on RuO\(_2\)(100) and by 0.32 to 0.52 eV on RuO\(_2\)(110). If the destabilization is sufficiently large, then \( \text{O}_{\text{br}} \) and \( \text{O}_{\text{ot}} \) atoms could start to release from the oxide surfaces at similar temperatures during TPD.

We emphasize that our DFT results do not prove that the destabilization phenomenon is responsible for our observation that \( \text{O}_{\text{br}} \) and \( \text{O}_{\text{ot}} \) atoms seem to desorb from O-rich IrO\(_2\)(100) at similar temperatures. Indeed, the computed binding energies of the \( \text{O}_{\text{br}} \) atoms on O-rich IrO\(_2\)(100) (Table 3-2) remain considerably larger than the binding energies of the \( \text{O}_{\text{ot}} \) atoms (Table 3-1). Notably, an investigation by Chung et al. provides evidence that decomposition of the O-rich IrO\(_2\)(110) surface does not involve the direct recombination of \( \text{O}_{\text{br}} \) atoms, but instead occurs by multiple step pathways, one of which involves the conversion of \( \text{O}_{\text{br}} \) atoms to \( \text{O}_{\text{ot}} \)
atoms followed by recombinative desorption. This latter pathway provides a relatively facile route for the desorption of \( \text{O}_{\text{br}} \) atoms from \( \text{IrO}_2(110) \) in that the energetic requirement for \( \text{O}_{\text{br}} \) to \( \text{O}_{\text{ot}} \) atom conversion is much less than the \( \text{O}_{\text{br}} \) binding energy. This prior finding supports the idea that the destabilization of \( \text{O}_{\text{br}} \) atoms by \( \text{O}_{\text{ot}} \) atoms could allow these species to desorb at similar rates, even though the intrinsic binding energies of the \( \text{O}_{\text{br}} \) atoms are higher than those of the \( \text{O}_{\text{ot}} \) atoms. Thus, while a more thorough computational study of the oxide decomposition mechanism is clearly needed, the much more pronounced destabilization of \( \text{O}_{\text{br}} \) atoms by \( \text{O}_{\text{ot}} \) atoms on \( \text{IrO}_2(100) \) compared with \( \text{RuO}_2(110) \) is consistent with observations that these species desorb at similar rates from O-rich \( \text{IrO}_2(100) \) but vastly different rates from O-rich \( \text{RuO}_2(110) \).

### 3.5 Discussion

The results of the present study reveal that the oxidation of \( \text{Ir}(111) \) by gas-phase oxygen atoms at temperatures up to 625 K occurs initially by the development of a chemisorbed layer of \( \text{O} \)-atoms and possibly through the formation of subsurface oxygen as the coverage increases to \( \sim 1 \) ML. Continued oxygen uptake induces the formation of a crystalline \( \sqrt{3} \) surface oxide that persists to \( \sim 1.4 \) ML, after which a rutile \( \text{IrO}_2 \) layer dominated by the \( \text{IrO}_2(100) \) facet develops with saturation occurring at \( \sim 3.6 \) ML for the oxidation conditions studied. The phase evolution that we observe is indeed similar to that reported for the oxidation of other metal surfaces, including \( \text{Ir}(111) \), wherein the formation of a distinct surface oxide precedes the growth of a multilayer oxide. Interestingly, comparison with prior studies of \( \text{Ir}(111) \) oxidation reveals differences that warrant discussion.

Previous studies demonstrate that the (0001) orientation of corundum \( \text{Ir}_2\text{O}_3 \) can develop during the oxidation of \( \text{Ir}(111) \) and that this structure is likely responsible for the \( (\sqrt{3} \times \sqrt{3})\text{R}30^\circ \) LEED pattern that we observe. The bulk-terminated \( \text{Ir}_2\text{O}_3(0001) \) surface exhibits hexagonal
symmetry with a lattice constant of 5.23 Å, and would experience compressive strain of 10.3% to adopt a \((\sqrt{3} \times \sqrt{3})R30^\circ\) lattice relative to the Ir(111) substrate. Similar to the present study, Chung et al. have observed a \((\sqrt{3} \times \sqrt{3})R30^\circ\) LEED pattern after oxidizing Ir(111) with plasma-generated atomic oxygen, but report that this pattern is generated by a multilayer \(\text{Ir}_2\text{O}_3(0001)\) structure rather than a surface oxide.\(^{59}\) He et al. also report that a multilayer \(\text{Ir}_2\text{O}_3(0001)\) structure can develop on Ir(111) prior to the formation of rutile \(\text{IrO}_2.\(^{11}\)

Interestingly, He et al. show that a hexagonal O-Ir-O trilayer oxide forms on Ir(111)\(^{11}\), where the structure of this trilayer oxide is distinct from the \(\sqrt{3}\) surface oxide that we observe. The hexagonal trilayer oxide has \(\text{IrO}_2\) stoichiometry and forms a coincidence lattice that can be described as a \((6 \times 6)\) trilayer oxide on a \((7 \times 7)\) Ir(111) surface, corresponding to an oxygen coverage of 1.47 ML. The structure of the trilayer oxide is close to that of a hexagonal \((\sqrt{3} \times \sqrt{3})R30^\circ\) oxide on a \((2 \times 2)\) Ir(111) surface, containing 1.5 ML of O-atoms, that has been predicted by DFT to be a favorable structure on Ir(111).\(^{10}\) The study by He et al.\(^{11}\) demonstrates that formation of the trilayer oxide precedes the growth of multilayer oxides on Ir(111) over a wide range of conditions.\(^{11}\) Our LEED results do not provide evidence of the \((6 \times 6)\) or \((\sqrt{3} \times \sqrt{3})R30^\circ/(2 \times 2)\) structures under the conditions studied, and instead show that a \(\sqrt{3}\) surface oxide forms prior to the multilayer \(\text{IrO}_2(100)\) structure. The \(\sqrt{3}\) surface oxide saturates at a coverage near 1.4 ML in our experiments, and could thus be accommodated in a structure resembling a single trilayer of \(\text{Ir}_2\text{O}_3(0001)\). Further work is needed to determine the exact structure of the \(\sqrt{3}\) surface oxide that we observe, and is beyond the scope of the present study. It is worth noting that surface oxides typically form because the direct formation of the bulk-like, multilayer oxide (e.g., rutile \(\text{IrO}_2\)) is kinetically hindered under typical oxidation conditions.\(^{66}\) Observations of different types of surface oxide structures on Ir(111) (e.g., \(\sqrt{3}\) vs. \(7 \times 7\)) among the studies.
reported thus suggest that the formation of a specific surface oxide can depend sensitively on the oxidation mechanism and hence reaction conditions.

We find that a rutile IrO\(_2\) layer begins to develop on Ir(111) at coverages above about 1.4 ML and reaches a saturation coverage near 3.6 ML for the oxidation conditions studied. In agreement with prior work\(^59\), we find that the rutile IrO\(_2\) layer grows predominantly in the (100) orientation on Ir(111) up to a thickness of about four oxide layers. Favorable lattice matching appears to drive the growth of rutile IrO\(_2\)(100) during the early stages of Ir(111) oxidation. Indeed, the predicted (6 \(\times\) 1) superstructure of IrO\(_2\)(100) on Ir(111) gives rise to a clear moiré pattern in the LEED images that we obtained after growing the oxide above 600 K (Figure 3-3). The apparent saturation thickness of four oxide layers is likely caused by kinetic limitations in the diffusion of Ir and O atoms at the moderate temperatures (< 650 K) at which we oxidized Ir(111). Consistent with this assertion, He et al. report that thicker IrO\(_2\) layers develop during the oxidation of Ir(111) at elevated O\(_2\) pressure and temperature (775 K)\(^11\). These authors also find that the thick, rutile IrO\(_2\) layers grown on Ir(111) mainly expose the IrO\(_2\)(110) facet, with IrO\(_2\)(100) present in smaller quantities. Because IrO\(_2\)(110) is the thermodynamically-preferred facet of bulk IrO\(_2\), it is reasonable to expect that the IrO\(_2\)(100) film structure will transform to IrO\(_2\)(110) as the oxide layer thickens beyond four layers. The dim spots seen in our LEED images are consistent with IrO\(_2\)(110) (Figure 3-3), and may indicate that small quantities of IrO\(_2\)(110) are already present in the four-layer oxide grown in the present study.

It is instructive to briefly contrast the oxidation behavior of Ir(111) with that of Ru(0001) since both metal surfaces are hexagonally close-packed and rutile dioxides develop in both cases. The oxidation of Ru(0001) at temperatures between about 650 and 750 K produces a flat RuO\(_2\)(110) layer that terminates at a thickness of about 10 to 20 Å due to diffusion limitations.\(^7\).
Thicker but also rougher RuO$_2$(110) layers form during the oxidation of Ru(0001) at higher temperatures. The dominance of the RuO$_2$(110) structure on Ru(0001) is consistent with the high stability of this facet in bulk crystallites of rutile RuO$_2$. Similar to the present case of IrO$_2$/Ir(111), RuO$_2$(100) can achieve better lattice matching with Ru(0001) than does RuO$_2$(110) but yet does not develop as the dominant facet of ultrathin RuO$_2$ films grown on Ru(0001).

A RuO$_2$(100) film does grow preferentially on the Ru(10$ar{1}$0) surface during oxidation at elevated temperatures (600 to 770 K), reaching thicknesses up to ~20 layers. The large corrugation of Ru(10$ar{1}$0) as well as good lattice matching at the oxide-metal interface is thought to govern the preferential growth of RuO$_2$(100) on Ru(10$ar{1}$0). STM experiments reveal that the RuO$_2$(100) film on Ru(10$ar{1}$0) is atomically flat and comprised of separate domains with either (1 × 1) or c(2 × 2) periodicity relative to the oxide lattice. The c(2 × 2) domains result from a surface reconstruction of bulk-terminated RuO$_2$(100) and are chemically inactive toward CO. In contrast, the RuO$_2$(100)-(1 × 1) domains are reactive toward CO, consistent with the presence of reactive Ru$_{cus}$ sites and thus the stoichiometric termination of RuO$_2$(100). It is worth noting that the large destabilization of O$_{br}$ atoms by O$_{ot}$ atoms predicted for the rutile (100) surfaces (Table 3-2) could conceivably promote surface reconstructions, such as that observed for RuO$_2$(100) on Ru(10$ar{1}$0). These prior studies indeed demonstrate that the preferred facet of RuO$_2$ can depend sensitively on the structure of the metal surface.

Recently, Flege et al. have shown using low energy electron microscopy (LEEM) that small domains of RuO$_2$(100) form during the early stages of Ru(0001) oxidation. Those authors find that the RuO$_2$(100) domains remain small and act as nucleation centers for the growth of RuO$_2$(101) and RuO$_2$(110) during the early stages of oxidation. Interestingly, the relative amounts of RuO$_2$(100) vs. RuO$_2$(110) which develop during the initial oxidation of
Ru(0001) appear to depend upon the oxidant employed. In particular, oxidation with O$_2$ favors the formation of large RuO$_2$(110) crystallites while only small quantities of RuO$_2$(100) clusters initially develop.$^{84}$ Compared with oxidation using O$_2$, larger quantities of RuO$_2$(100) clusters co-exist with RuO$_2$(110) crystallites during the initial oxidation of Ru(0001) with NO$_2$ at elevated temperature.$^{81,85,86}$ These differences provide evidence that the mechanism by which the gaseous oxidant adsorbs can influence the distribution of RuO$_2$ structures that form on Ru(0001) during the early stages of oxidation. A possible implication is that strong oxidants such as NO$_2$ and gaseous oxygen atoms promote the formation of (100) facets of RuO$_2$ and IrO$_2$ on the closed-packed metal surfaces. However, the present results show that IrO$_2$(100) forms in larger domains and to a significantly greater extent on Ir(111) compared with RuO$_2$(100) on Ru(0001). The reasons that the (100) facets of rutile RuO$_2$ and IrO$_2$ develop to quite different extents during Ru(0001) vs. Ir(111) oxidation are not yet known. Strong bonding at the IrO$_2$-Ir(111) interface may play an important role in causing the preferential growth of IrO$_2$(100) during initial oxidation of Ir(111).

3.6 Summary

We have investigated the oxidation of Ir(111) by gas-phase oxygen atoms at temperatures between 500 and 625 K using TPD, LEED, LEISS and DFT calculations. We find that a well-ordered surface oxide with (\sqrt{3} \times \sqrt{3})R30° periodicity relative to Ir(111) develops prior to the formation of a rutile IrO$_2$(100) layer. Under the conditions studied, oxidation of the Ir(111) surface effectively saturates once the IrO$_2$(100) layer reaches a thickness of about four layers and decomposition of the IrO$_2$ layer yields a single, sharp O$_2$ desorption peak at ~750 K during TPD. LEED demonstrates that the rutile IrO$_2$ layer grows predominantly in the (100) orientation on Ir(111) for oxide thicknesses up to four layers, and reveals a moiré pattern resulting from the (6
1) coincidence structure formed at the IrO$_2$(100)/Ir(111) interface. LEED also provides evidence that small domains of IrO$_2$(110) coexist with the IrO$_2$(100) structure in the oxide layers grown. The weak binding affinity of CO and H$_2$O on the IrO$_2$(100) layer as well as LEISS measurements showing large O-enrichment at the oxide surface provide strong evidence that the rutile IrO$_2$(100) layer grown in our experiments is oxygen-terminated and thus lacks cus-Ir atoms that can strongly bind molecular adsorbates.

Calculations using DFT predict that on-top O-atoms are stable on both IrO$_2$(100) and IrO$_2$(110) at temperatures up to ~625 K, and thus support the conclusion that the rutile IrO$_2$(100) layer grown in our experiments is oxygen-terminated. In contrast to the O-rich RuO$_2$(110) surface, our results show that the singly coordinate O$_{ot}$ atoms remain stable on the IrO$_2$(100) surface up to temperatures at which the four-layer oxide begins to thermally decompose. Our DFT calculations predict that O$_{ot}$ atoms destabilize O$_{br}$ atoms to a significantly greater extent on the (100) surfaces of rutile IrO$_2$ and RuO$_2$ compared with the (110) surfaces of these oxides. The predicted destabilization of O$_{br}$ atoms by O$_{ot}$ atoms might cause the O$_{ot}$ and O$_{br}$ atoms to desorb from O-rich IrO$_2$(100) over a similar range of temperatures, consistent with our observation of only a single O$_2$ TPD peak during the thermal decomposition of the IrO$_2$(100) film. This behavior makes it challenging to prepare stoichiometrically-terminated IrO$_2$(100) surfaces for model studies.
Figure 3-1. $\text{O}_2$ TPD spectra obtained after generating various oxygen coverages on Ir(111) at 500 K using an O-atom beam. (a) Low coverages (up to 1.8 ML) and (b) high coverage (1.6 to 3.6 ML). Note that the ordinate scale in (b) is expanded by a factor of 10 relative to (a).
Figure 3-2. LEED patterns obtained from Ir(111) after O-atom adsorption at 500 K to generate the oxygen coverages indicated. Each LEED pattern was recorded using primary beam energy of 70 eV.
Figure 3-3. LEED patterns obtained from IrO$_2$(100) layer and ball-and-stick model of s- and O-rich IrO$_2$(100) surfaces. LEED patterns obtained from an ~2.2 ML IrO$_2$(100) layer prepared by oxidizing Ir(111) at 625 K using primary beam energies of (a) 70 eV and (b) 120 eV. (c) Simulated LEED pattern of a rutile IrO$_2$(100) structure (red) on Ir(111) and spots resulting from the coincidence structure at the IrO$_2$(100)/Ir(111) interface (blue). The spots observed in the experimental LEED pattern are shown as solid circles while the spots that are not resolved are shown as open circles, after correcting for geometrical distortion. (d) Real space representation of the IrO$_2$(100) structure (red circles) on Ir(111) (grey circles). The rectangular unit cell of IrO$_2$(100) (1.17a × 1.73a) is shown in red, and the coincidence unit cell (6b$_1$ × b$_2$) is shown in blue. (e) Ball and stick representations of IrO$_2$(100) with stoichiometric vs. oxygen-rich terminations. patterns obtained from Ir(111) after O-atom adsorption at 500 K to generate the oxygen coverages indicated. Each LEED pattern was recorded using a primary beam energy of 70 eV.
Figure 3-4. H₂O TPD spectra and ISS spectra from IrO₂(100) layer. (a) H₂O TPD spectra obtained after adsorbing water on Ir(111) and an ~3 ML IrO₂ layer on Ir(111) at 85 K; (b) He⁺ LEISS spectra obtained from clean and oxygen-exposed Ir(111) surfaces prepared at 625 K. LEISS spectra are shown for the following oxygen coverages and phases: (2 × 1)-O layer (0.50 ML), √3 surface oxide (1.1 ML) and rutile IrO₂ layer (2.2 ML). Each LEISS spectrum was obtained using He⁺ ions incident at the surface with 1.0 keV of kinetic energy.
Table 3-1. Binding energies of O\textsubscript{ot} atoms on Ir\textsubscript{2}O\textsubscript{2}(100) and Ru\textsubscript{2}O\textsubscript{2}(110) as a function of the coverage of O\textsubscript{ot} atoms as determined by DFT.

<table>
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<tr>
<th>O\textsubscript{ot} coverage</th>
<th>E\textsubscript{ad} (eV)</th>
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<tbody>
<tr>
<td></td>
<td>Ir\textsubscript{2}O\textsubscript{2}(100)</td>
</tr>
<tr>
<td>25%</td>
<td>0.99</td>
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<tr>
<td>50%</td>
<td>0.99</td>
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<td>75%</td>
<td>0.96</td>
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<td>100%</td>
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Table 3-2. Binding energies of O\textsubscript{br} atoms on Ir\textsubscript{2}O\textsubscript{2}(100), Ir\textsubscript{2}O\textsubscript{2}(110), Ru\textsubscript{2}O\textsubscript{2}(100) and Ru\textsubscript{2}O\textsubscript{2}(110) as a function of the coverage of O\textsubscript{br} atoms as determined by DFT. The columns labeled with “O\textsubscript{br} w/ O\textsubscript{ot}” show the binding energies of O\textsubscript{br} atoms on O-rich surfaces (100% coverage of O\textsubscript{ot}) and the columns labeled with “O\textsubscript{br} w/o O\textsubscript{ot}” show the binding energies of O\textsubscript{br} atoms computed for stoichiometrically-terminated and partially-reduced oxide surfaces (0% coverage of O\textsubscript{ot}). For each surface, the binding energy per O\textsubscript{br} atom is given as a function of the initial coverage of O\textsubscript{br} atoms (25% to 100%). The columns labeled with “\(\Delta E\)” give the difference in the binding energy of an O\textsubscript{br} atom on each stoichiometric/partially-reduced vs. O-rich surface with a given initial O\textsubscript{br} coverage.

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<th>Initial O\textsubscript{br} coverage</th>
<th>Eb (eV)</th>
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<tr>
<td></td>
<td>Ir\textsubscript{2}O\textsubscript{2}(100)</td>
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<tr>
<td></td>
<td>O\textsubscript{br} w/ O\textsubscript{ot}</td>
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<td>100%</td>
<td>1.28</td>
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<td>50%</td>
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CHAPTER 4
METHANOL OXIDATION ON STOICHIOMETRIC AND OXYGEN-RICH RuO$_2$(110)

4.1 Motivation

Advancing the fundamental understanding of the surface chemistry of late transition metal oxides is crucial to many applications involving catalytic oxidation reactions under oxygen-rich conditions, including fuel cell catalysis, automobile exhaust remediation and chemical sensing. Researchers have shown that metal oxide phases develop on late transition metal surfaces under sufficiently oxidizing conditions and can dramatically alter the surface catalytic properties. Seminal work by Over et al. was the first to demonstrate that formation of the RuO$_2$(110) facet on Ru(0001) in oxygen-rich conditions strongly enhances the surface activity toward CO oxidation. Subsequent investigations have shown that the RuO$_2$(110) surface efficiently promotes oxidative transformations of several other compounds as well, including H$_2$, NH$_3$, C$_2$H$_4$ and HCl, and that the PdO(101) and IrO$_2$(110) surfaces are also highly active for promoting the oxidation of various compounds. This prior work has established that late transition-metal oxide surfaces that expose pairs of coordinatively-unsaturated (cus) metal and oxygen atoms can exhibit exceptional reactivity toward activating and oxidizing adsorbed molecules, particularly when compared with other classes of metal oxides and even oxygen-covered metal surfaces.

The adsorption and oxidation of methanol has been widely employed as a means to characterize the chemical reactivity of metal oxide surfaces. Methanol with its C-H, C-O and O-H bonds, presents itself as an excellent model system to study the selective activation of

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chemical bonds and oxidation pathways of polyatomic molecules on metal oxide surfaces.\textsuperscript{12-15, 87, 88} Methanol oxidation on RuO\textsubscript{2} is particularly relevant for understanding direct methanol fuel cells since Ru-Pt alloys are widely used as the anode catalyst. Data from ultrahigh vacuum (UHV) investigations probing methanol oxidation on RuO\textsubscript{2} surfaces is relatively sparse.\textsuperscript{15, 89} Results from a single UHV study show that methanol oxidizes readily on RuO\textsubscript{2}(110) to produce CO\textsubscript{2}, CO and CH\textsubscript{2}O during temperature-programmed reaction spectroscopy (TPRS) when the methanol monolayer is saturated at 200 K.\textsuperscript{15} Generally, the mechanisms governing methanol oxidation on RuO\textsubscript{2}(110) remain largely unknown since additional studies of this system have not been reported.

Prior work shows that the PdO(101) surface is also highly active toward methanol, with 100\% of the adsorbed methanol molecules undergoing oxidation during TPRS for initial CH\textsubscript{3}OH coverages up one adsorbed CH\textsubscript{3}OH molecule per cus-Pd-O surface pair, i.e., 1 ML (monolayer).\textsuperscript{13} Complete oxidation of methanol to CO\textsubscript{2} and H\textsubscript{2}O is favored on PdO(101) at low methanol coverages, and partial oxidation to CH\textsubscript{2}O and CH\textsubscript{3}OCHO (methyl formate) becomes dominant with increasing methanol coverage toward saturation. Hakanoglu et al. show that CH\textsubscript{3}OH initially deprotonates to form adsorbed CH\textsubscript{3}O and OH groups on PdO(101), and that an adsorbed dioxyethylene (CH\textsubscript{2}O\textsubscript{2}) species serves as the key intermediate to CO\textsubscript{2} formation.\textsuperscript{13} A computational study reports that CH\textsubscript{2}O\textsubscript{2} formation is also favorable on the RuO\textsubscript{2}(110) surface,\textsuperscript{90} suggesting similarities in the mechanisms governing methanol oxidation on PdO(101) and RuO\textsubscript{2}(110). Overall, these prior studies show that the late transition-metal oxide surfaces, RuO\textsubscript{2}(110) and PdO(101), are highly reactive toward methanol, with behavior that contrasts with that obtained from other metal oxides such as rutile TiO\textsubscript{2} surfaces.\textsuperscript{14, 87, 88, 91, 92}
In the present study, we show that stoichiometric and O-rich RuO$_2$(110) surfaces are highly active toward oxidizing methanol. We find that complete oxidation is favored on s-RuO$_2$(110) at low methanol coverage and that partial oxidation to mainly CH$_2$O becomes increasingly preferred as the initial methanol coverage increases above about 0.33 ML. We present evidence that this change in reaction selectivity coincides with the methanol coverage at which surface O-atoms become the limiting reagent for the conversion of adsorbed CH$_3$OH to a CH$_2$O$_2$ intermediate. We also find that on-top oxygen (O$_{ot}$) atoms strongly promote the complete oxidation of methanol due to facile desorption of H$_2$O and a high chemical reactivity of methanol adsorbed within O$_{ot}$-rich surface regions.

4.2 Experimental Details

Previous studies provide details of the three-level UHV chamber utilized in the present study.$^{17,36}$ For the present study, we employed a circular disk (9 mm × 1 mm) Ru(0001) crystal that is attached to a liquid-nitrogen-cooled, copper sample holder by 0.016” W wires that are secured to the edge of crystal. A type K thermocouple was spot welded to the backside of the crystal for temperature measurements. Resistive heating, controlled using a PID controller that varies the output of a programmable DC power supply, supports linearly ramping from 80 to 1500 K or maintaining the sample temperature. Sample cleaning consisted of cycles of Ar$^+$ sputtering (2000 eV, 10 mA) at 1000 K, followed by annealing at 1500 K for several minutes. We considered the Ru(0001) sample to be clean when we obtained sharp low-energy electron diffraction (LEED) patterns consistent with the Ru(0001) surface and did not detect CO production during flash desorption after adsorbing oxygen.

A two-stage differentially pumped chamber attached to the UHV chamber accommodates the inductively coupled RF plasma source (Oxford Scientific Instruments) that was utilized to partially dissociate O$_2$ (BOC gases 99.999%) to generate atomic oxygen beams for this study.
We refer the reader to previous publications for details of the beam system.\textsuperscript{17, 36} We exposed the Ru(0001) sample held at 750 K to \( \sim 76 \text{ ML}_{\text{Ru}(0001)} \) of gaseous O-atoms supplied by the atomic oxygen beam to produce a stoichiometrically terminated RuO\(_2\)(110) film ("s-RuO\(_2\)(110)")\textsuperscript{17}, where we define 1 ML\(_{\text{Ru}(0001)}\) as equal to the Ru(0001) surface atom density of \( 1.57 \times 10^{15} \text{ cm}^{-2} \). We positioned the sample at a distance of about 50 mm from the end of the final collimating aperture and at a 45° angle from the beam axis to ensure uniform impingement of the beam across the sample. We find that this procedure generates a conformal RuO\(_2\)(110) film that has a stoichiometric surface termination, contains \( \sim 18 \text{ ML}_{\text{Ru}(0001)} \) of oxygen atoms, and is about 4.5 nm thick.\textsuperscript{29, 93} We provide details of the oxidation of Ru(0001) and characterization of the s-RuO\(_2\)(110) film elsewhere, including LEED patterns which exhibit sharp spots from RuO\(_2\)(110) and also demonstrate that the film is conformal.\textsuperscript{16}

Figure 4-1 shows model representations of stoichiometric and oxygen-rich RuO\(_2\)(110) surfaces. The stoichiometric termination of RuO\(_2\)(110) consists of rows of cus-Ru (Ru\(_{\text{cus}}\)) atoms separated by rows of bridging-O atoms (O\(_{\text{br}}\)) that run parallel to the [001] direction. The Ru\(_{\text{cus}}\) and O\(_{\text{br}}\) atoms each lack a bonding partner compared with the bulk and thus expose single coordination vacancies toward the vacuum. From the RuO\(_2\)(110) unit cell, one finds that the areal densities of Ru\(_{\text{cus}}\) atoms and O\(_{\text{br}}\) atoms are each equal to 0.32 ML\(_{\text{Ru}(0001)}\). For convenience, we specify absolute coverages for the RuO\(_2\)(110) surface such that 1 ML (monolayer) equals the Ru\(_{\text{cus}}\) surface atom density of \( 5.02 \times 10^{14} \text{ cm}^{-2} \) of s-RuO\(_2\)(110). Lastly, we use the symbol "ot" to describe atoms or molecules that bind “on-top” of the Ru\(_{\text{cus}}\) atoms, such as O\(_{\text{ot}}\) atoms (Fig. 4-1).

We estimate atomic oxygen coverages by scaling integrated O\(_2\) TPD spectra with those obtained after exposing s-RuO\(_2\)(110) at 300 K to a saturation dose of O\(_2\) and assuming that the O\(_2\) exposure generates an atomic oxygen coverage of 0.86 ML, which is equal to 86% of Ru\(_{\text{cus}}\).
We restored the stoichiometric surface termination after each TPRS experiment by exposing the surface to 5 L of O₂ at 750 K supplied through a tube doser. This restoration approach is effective because the final temperature reached during TPRS measurements lies below that at which the RuO₂(110) layer begins to thermally decompose.

We studied the reactivity of CH₃OH (Alfa Aesar, 99.9%) and CD₃OH (Acros, 99.5%) on the s-RuO₂(110) surface using TPRS. We used a calibrated beam doser to deliver methanol to the sample at an incident flux of approximately 0.047 ML s⁻¹ (CH₃OH) and 0.044 ML s⁻¹ (CD₃OH). The sample-to-doser distance was set to about 15 mm to ensure uniform impingement of methanol across the sample surface and minimize reactions of methanol with the chamber walls. Both CH₃OH and CD₃OH were purified by several freeze-pump-thaw cycles before admission into the UHV chamber. We collected TPRS spectra after methanol exposures by positioning the sample in front of a shielded mass spectrometer at a distance of about 8 mm and then heating the sample to 800 K at a constant rate of 1 K s⁻¹. Initially, we monitored each mass between 1 and 100 amu using a short dwell time to identify the main products that are generated from reactions of methanol on s-RuO₂(110). These experiments reveal that the only species desorbing from the methanol-exposed s-RuO₂(110) sample are methanol, formaldehyde, water, CO₂ and small amounts of CH₃OCHO. In subsequent experiments we only monitored mass fragments that allowed these species to be readily distinguished, which include m/z = 2, 18, 28, 29, 30, 31, 32, 44 and 60. The 60 amu trace uniquely represents desorption rate of only methyl formate, as none of the other products generate this mass fragment in the ionizer of the mass spectrometer.

To estimate CO desorption yields, we scaled integrated CO desorption spectra by an integrated TPD spectrum collected from a saturation coverage of CO on Ru(0001) prepared at 300 K and assuming that the saturation coverage is 0.68 MLRu(0001). To estimate H₂O
desorption yields, we conducted TPRS experiments after exposing RuO$_2$(110) to varying amounts of H$_2$ followed by a saturation dose of O$_{ot}$ atoms and monitored the desorption yields of H$_2$O and the O$_2$ resulting from the recombination of O$_{ot}$ atoms. In these experiments, the adsorbed hydrogen is completely converted to water during TPRS by reacting with O$_{ot}$ atoms, and the H$_2$O yield is thus equal to the decrease in the O$_{ot}$ recombination yield relative to its value on the O$_{ot}$ saturated surface.$^{95}$ To estimate CO$_2$ desorption yields we scaled integrated CO$_2$ desorption spectra by an integrated TPD spectrum collected from a saturated monolayer of CO on Ru(0001) and using a relative sensitivity factor relating the CO and CO$_2$ signal intensities measured with the mass spectrometer at an electron energy of 100 eV (Hiden Analytical).

We estimate the absolute desorption yields of CH$_3$OCHO, CH$_3$OH and CH$_2$O by applying a procedure described by Ko et al.$^{96}$ These authors describe an approach to estimate 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).$^{96}$ This approach has also been used to quantitatively explain product evolution resulting from methanol oxidation on PdO(101).$^{13}$ The normalization factors are calculated by accounting for 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.$^{96}$ to the methanol signal intensity and applied these factors to rescale the methanol, methyl formate and formaldehyde signals. The CH$_2$O and CH$_3$OH traces in our results are obtained from the 29 and 31 amu traces, respectively, after correcting for relevant species in the ionizer. We used fragmentation patterns reported in NIST database to deconvolute mass spectrometer signals.$^{97}$ Since methyl formate also generates 31 amu fragments in the ionizer, we
corrected the 31 amu signal by subtracting 31 amu signal appeared due to methyl formate to obtain absolute methanol signal. Similarly, 29 amu trace was corrected to remove traces generated in the mass spectrometer by methanol to obtain formaldehyde signal. Based on reproducibility of our results, we estimate that the absolute coverages and yields determined from our TPRS results are accurate to within ~15% of the stated values.

4.3 Results

4.3.1 CH₃OH oxidation on s-RuO₂(110)

Figure 4-2a shows TPRS spectra obtained after adsorbing 0.33 ML of CH₃OH on the s-RuO₂(110) surface at 88 K. The TPRS data shows that all of the adsorbed methanol reacts with the surface to produce CO₂, H₂O and small amounts of CH₂O. Most of the adsorbed methanol (~0.26 ML) is completely oxidized to CO₂ that evolves in a sharp TPRS peak centered at 490 K, while the remainder of the methanol dehydrogenates to produce CH₂O (~0.06 ML) in a TPRS peak at 385 K with a small shoulder at 440 K. The small CO₂ peak near 300 K arises from the oxidation of CO that adsorbed from the UHV background. The H₂O TPRS feature exhibits a predominant peak at 575 K in addition to smaller features centered at 390 K and 490 K, where the latter peaks coincide with the CH₂O and CO₂ peaks, respectively. We estimate that at least 67% (~0.38 ML) of the water desorbs in the feature at 575 K (between 510 K and 750 K), while the two lower temperature features account for total of ~0.19 ML of H₂O. Previous studies show that the hydrogenation of s-RuO₂(110) by H₂ produces HO₆br groups that recombine during heating to generate a H₂O TPRS peak near 575 K. Since all of the carbon-containing products desorb below ~500 K after methanol adsorption, we conclude that the high-temperature H₂O peak (~575 K) results from the recombination of HO₆br groups in the absence of other adsorbed species, i.e., after species such as CH₃O have vacated the Ru₆cat sites. The coincidence of the H₂O peaks at 390 K and 490 K with the CH₂O and CO₂ peaks suggests that reactions
which produce CH$_2$O and CO$_2$ promote the formation and desorption of H$_2$O below the temperatures at which HO$_{br}$ recombination occurs readily on the adsorbate-free RuO$_2$(110) surface. The presence of adsorbed species such as CH$_3$O on the Ru$_{cus}$ may also facilitate the formation of H$_2$O from HO$_{br}$ groups. Researchers have presented evidence that adsorbed CH$_3$O groups facilitate the low-temperature formation of water on ceria\textsuperscript{100} and terbia.\textsuperscript{101} A key finding is that the s-RuO$_2$(110) surface is highly reactive toward methanol, and that complete oxidation to CO$_2$ is the dominant reaction pathway at low coverages of CH$_3$OH.

Figure 4-2b shows TPRS spectra obtained after adsorbing about 1.1 ML of CH$_3$OH on s-RuO$_2$(110) at 88 K. Compared with the results obtained at low methanol coverage, we observe an increase in the CH$_2$O and H$_2$O desorption yields and also CH$_3$OH desorption with increasing methanol coverage. At saturation of the methanol monolayer, we estimate that the yield of partially oxidized products (CH$_2$O and a small amount of methyl formate) is ~0.31 ML and that about 0.37 ML of CH$_3$OH desorbs from the monolayer. The CO$_2$ desorption yield remains approximately constant at a value of ~0.25 ± 0.02 ML as the initial CH$_3$OH coverage increases from about 0.33 to 1.0 ML. These results show that the methanol monolayer saturates at a coverage of ~0.94 ML, which is very close to the density of Ru$_{cus}$ sites, and that desorption, complete oxidation and partial oxidation pathways produce similar product yields when the monolayer is initially saturated; we estimate that 39% of the methanol desorbs, 33% partially oxidizes to CH$_2$O and methyl formate and 28% completely oxidizes. These results agree well with behavior reported previously for methanol oxidation on s-RuO$_2$(110)\textsuperscript{15}; however, we do not observe CO production in our experiments.

The CH$_3$OH TPRS trace exhibits well-defined peaks at 155 K and 385 K and also a broad region of desorption that spans the temperatures separating these peaks (~190 to 300 K). The
peak at 155 K arises from a small amount (~0.12 ML) of methanol desorbing from a multilayer state and/or associated with O_{br} atoms, and the TPRS features above about 190 K are consistent with methanol desorbing from Ru_{cus} sites likely through the hydrogenation of CH_{3}O groups via HO_{br} groups. We estimate that about 0.20 ML of CH_{3}OH desorbs in the peak centered at 385 K, and about 0.17 ML of CH_{3}OH desorbs in the region between 190 K and 300 K, resulting in a total of 0.37 ML of CH_{3}OH desorbing from the monolayer. The CH_{2}O TPRS trace also exhibits a peak centered at 385 K and a small shoulder at ~450 K, with negligible desorption at temperatures below 300 K.

The concurrent desorption of CH_{2}O and CH_{3}OH in peaks at 385 K indicates a coupling in the reactions that produce these peaks. A possibility is that CH_{3}O groups undergo disproportionation and generate CH_{2}O and CH_{3}OH in a single reaction step, resulting in the simultaneous desorption of these species. Similar behavior in the oxidation of methanol on TiO_{2}(110) has been reported and attributed to a disproportionation reaction of neighboring methoxy groups.\textsuperscript{87, 88} Another possibility is that O_{br} atoms mediate the dehydrogenation of CH_{3}O groups to CH_{2}O and that this step is coupled to the hydrogenation of CH_{3}O groups to CH_{3}OH. We estimate that a total of 0.25 ML of CH_{2}O desorbs when the methanol monolayer is initially saturated and that the CH_{2}O and CH_{3}OH yields evolving in the 385 K peak are nearly equal at ~0.20 ML. This comparison suggests that disproportionation may account for the evolution of CH_{2}O and CH_{3}OH in the peak at 385 K since disproportionation would produce equal quantities of these species. We conducted TPRS experiments of CD_{3}OH oxidation on s-RuO_{2}(110) to further investigate the concurrent desorption of these products at 385 K.

The H_{2}O and CO_{2} TPRS features exhibit mainly quantitative changes with increasing methanol coverage above 0.33 ML, suggesting that the reaction processes which produce these
species are only weakly influenced by the methanol coverage. After saturating the methanol monolayer, the H₂O TPRS trace exhibits three main features centered at 390, 490 and 575 K and we estimate a total H₂O desorption yield of 0.90 ML. The measured H₂O TPRS yields agree to within 7% of the amounts estimated from the stoichiometry of the reactions observed. The H₂O TPRS peak at 575 K is dominant and accounts for about 0.49 ML (54%) of the H₂O desorption yield at saturation of the methanol monolayer. Comparing the data obtained at CH₃OH coverages of 0.33 vs. 1.1 ML, the intensities of the lower temperature H₂O TPRS features exhibit a larger relative increase compared with the higher temperature peak. This behavior likely indicates that the adsorbate or reaction-assisted production of H₂O is more effective when more HO₇br groups are present on the surface.

We find that the CO₂ yields are nearly the same at ~0.26 ML for initial methanol coverages equal to 0.33 and 1.1 ML, and that CO₂ desorbs in a relatively sharp peak at 490 K in both cases, with the CO₂ peak exhibiting only slight broadening at the leading edge for the higher initial methanol coverage. This similarity suggests that the production of CO₂ occurs by the same pathways and in similar local environments, regardless of the initial methanol coverage. Such a finding is interesting considering that the amount of O₇br atoms removed prior to the onset of CO₂ production is more than three times greater for the higher initial methanol coverage. Specifically, we estimate that 0.06 vs. 0.19 ML of H₂O desorbs below 400 K for these low vs. high methanol coverages. Possible implications are that the reactions which generate CO₂ are largely insensitive to the presence of O₇br-vacancies or that exchange of subsurface O-atoms and O₇br-vacancies is facile and restores a large quantity of the O₇br atoms prior to CO₂ production during TPRS.
4.3.2 Product Yields as a Function of Methanol Coverage

The evolution of the TPRS product yields demonstrates that complete oxidation is strongly favored for methanol coverages up to ~0.33 ML, and that the selectivity toward partial oxidation increases with increasing methanol coverage thereafter. Figure 4-3 shows the yields of carbon-containing reaction products obtained during TPRS as a function of the initial methanol coverage on s-RuO$_2$(110). The CO$_2$ yield increases rapidly to ~0.25 ML as the methanol coverage initially increases, and effectively plateaus at this value once the methanol coverage reaches ~0.33 ML. The CH$_2$O yield increases only slowly with increasing methanol coverage to 0.33 ML but increases sharply thereafter, reaching a value of 0.25 ML at saturation of the methanol monolayer. The yield of methyl formate also appears to increase more sharply above methanol coverage of 0.33 ML, though the maximum yield is only about 0.03 ML. At saturation of the monolayer, we estimate that ~60% of the adsorbed methanol oxidizes during TPRS and that the combined yield of CH$_2$O and CH$_3$OCHO is 1.2 times higher than the CO$_2$ yield. The trends in the product yields observed here are similar to those reported previously for methanol oxidation on the PdO(101) surface.$^{13}$ Those researchers present evidence that CH$_3$OH oxidation to CO$_2$ on PdO(101) occurs through a dioxymethylene (CH$_2$O$_2$) intermediate and that formation of the CH$_2$O$_2$ species occurs up to 33% of the O$_{cus}$ density due to stoichiometric constraints.

4.3.3 Oxidation of CD$_3$OH on s-RuO$_2$(110)

We conducted TPRS experiments of CD$_3$OH oxidation on s-RuO$_2$(110) to further investigate the concurrent desorption of methanol and formaldehyde at 385 K. The main idea is that CD$_2$O production via disproportionation of CD$_3$O groups would only cause the desorption of CD$_3$OD in the 385 K methanol peak, whereas a coupling of CD$_3$O dehydrogenation and hydrogenation steps could cause both CD$_3$OH and CD$_3$OD to desorb concurrently in the high temperature peak. Figure 4-4 shows TPRS spectra of CO$_2$, CD$_3$OH, CD$_3$OD and CD$_2$O obtained
after adsorbing ~1.0 ML of CD$_3$OH on s-RuO$_2$(110) at 88 K. The TPRS spectra show that both CD$_3$OH and CD$_3$OD desorb concurrently with CD$_2$O in peaks at 385 K, demonstrating that hydrogenation of CD$_3$O groups from HO$_{br}$ groups occurs rapidly as CD$_2$O is produced. We estimate that the CD$_3$OH yield in the sharp TPRS peak at ~385 K is about 1.6 times higher than the CD$_3$OD yield (~0.16 vs. 0.10 ML), and that the CD$_2$O yield is about 0.23 ML. The higher yield of CD$_3$OH vs. CD$_3$OD clearly demonstrates that hydrogenation of CD$_3$O groups from neighboring HO$_{br}$ groups is the predominant pathway for methanol desorption in the peak at 385 K.

The data also shows that at least 57% (i.e., 0.13/0.23 ML) of the CD$_2$O is produced from the dehydrogenation of CD$_3$O groups likely via D-atom transfer to O$_{br}$ atoms. We reach this conclusion by recognizing that disproportionation must produce the same quantities of CD$_2$O and CD$_3$OD, but that the yields of these products in the high-temperature peaks are 0.23 ML and 0.10 ML, respectively. Furthermore, coupling of the hydrogenation and dehydrogenation reactions could also generate CD$_3$OD, thus making it difficult to unambiguously confirm the relative importance of the disproportionation pathway. The general picture that emerges from this data is that dehydrogenation is the dominant pathway for the conversion of methoxy to formaldehyde on s-RuO$_2$(110) and that this reaction is triggered by the generation of O$_{br}$ atoms resulting from the hydrogenation of adsorbed methoxy groups.

4.3.4 CH$_3$OH oxidation on O-rich RuO$_2$(110)

Figures 4-5a-d show TPRS spectra of CH$_3$OH, CO$_2$, CH$_2$O and H$_2$O obtained from RuO$_2$(110) as a function of the O$_{ot}$-atom pre-coverage, after generating a methanol coverage of 1 ± 0.1 ML on each O-rich surface. The TPRS results demonstrate that O$_{ot}$ atoms enhance the selectivity toward the complete rather than partial oxidation of methanol in addition to modifying
the methanol-surface interaction and the evolution of H₂O. The CH₃OH TPRS spectra show that methanol desorption at temperatures above the low-temperature peak (>~ 225 K) diminishes significantly with increasing Oₜₜ coverage, while the low-temperature peak intensifies and shifts toward higher temperature. The increase (decrease) in the low (high) temperature CH₃OH desorption yields with increasing Oₜₜ coverage provides evidence that CH₃OH molecules adsorb directly on Oₜₜ atoms and do not displace the Oₜₜ atoms under the conditions studied. The low-temperature CH₃OH peak also resolves into at least two distinct components. For example, components at 177 K and 189 K are evident in the CH₃OH TPRS peak obtained from the O-rich RuO₂(110) surface with an Oₜₜ-atom pre-coverage of 60%. The upshift in the low-temperature CH₃OH desorption peak with increasing Oₜₜ coverage suggests that adsorbed methanol molecules interact more strongly with Oₜₜ atoms compared with Oₜb atoms or other methanol molecules. The CH₂O desorption yield also diminishes with increasing Oₜₜ-atom coverage, closely tracking the decrease in the yield of CH₃OH that desorbs above ~225 K. The correlation between these product yields supports the idea that coupling between CH₃O dehydrogenation and hydrogenation steps is mainly responsible for CH₂O production. Notably, a small CH₂O feature at ~330 K initially emerges with increasing Oₜₜ coverage but starts to diminish as the Oₜₜ coverage increases beyond ~50%.

The TPRS data further reveals that pre-adsorbed Oₜₜ atoms strongly promote the complete oxidation of methanol to CO₂. The CO₂ TPRS trace exhibits a single peak that intensifies sharply as the Oₜₜ coverage initially increases to ~50%. The CO₂ yield diminishes with increasing Oₜₜ coverage beyond ~50% but remains higher than that obtained from the s-RuO₂(110) surface. The CO₂ TPRS peak also shifts from 490 K to 515 K with increasing Oₜₜ coverage.
coverage, possibly indicating that reaction with O$_{ot}$ atoms enhances the stability of a key intermediate to CO$_2$ formation.

The H$_2$O TPRS spectra demonstrate that O$_{ot}$ atoms facilitate the desorption of water resulting from methanol dehydrogenation on RuO$_2$(110). An H$_2$O desorption peak below ~400 K develops in the TPRS spectra obtained after adsorbing CH$_3$OH on O$_{ot}$ pre-covered RuO$_2$(110). By comparison with TPD spectra obtained from H$_2$O exposed RuO$_2$(110),$^{74, 93}$ we attribute this low-temperature peak to the desorption-limited evolution of H$_2$O$_{ot}$ species that form by the hydrogenation of O$_{ot}$ atoms. The desorption-limited H$_2$O feature exhibits a maximum at ~338 K as well as a small shoulder near 360 K at low O$_{ot}$ pre-coverages (< 25%), and subsequently intensifies and shifts toward higher temperature with increasing O$_{ot}$ coverage, reaching a peak temperature of ~390 K for an O$_{ot}$ coverage of 86%. The H$_2$O$_{ot}$ peak temperature observed at the highest O$_{ot}$ coverage agrees well with that observed for a pure H$_2$O layer adsorbed on s-RuO$_2$(110).$^{74, 93}$ The upshift in the H$_2$O$_{ot}$ peak temperature with increasing O$_{ot}$ coverage suggests that H$_2$O$_{ot}$ molecules interact more strongly with one another than they do with neighboring CH$_3$OH and CH$_3$OH-derived species. A smaller H$_2$O TPRS peak between 490 K and 515 K also intensifies with increasing O$_{ot}$ coverage to ~60% while the H$_2$O TPRS peak at ~570 K diminishes slightly, with both of these features diminishing sharply above an O$_{ot}$ coverage of 60%. The H$_2$O TPRS peak near 500 K is consistent with the reaction-limited desorption of H$_2$O during CO$_2$ formation. The key characteristic of the H$_2$O TPRS spectra is the facile desorption of H$_2$O below 400 K resulting from the hydrogenation of O$_{ot}$ atoms. We speculate that the low-temperature H$_2$O desorption plays a decisive role in promoting the complete oxidation of methanol on O-rich RuO$_2$(110) because the reaction efficiently removes H-atoms from the surface and should thus increase the coverage of surface O-atoms relative to HO groups.
4.3.5 Desorption Yields vs. O_{ot} Coverage on RuO$_2$(110)

Figure 4-6a shows the TPRS yields of CO$_2$, CH$_2$O and CH$_3$OCHO measured as a function of the O_{ot} pre-coverage on RuO$_2$(110) for an initial CH$_3$OH coverage of ~1 ML. The CH$_2$O yield decreases steadily from 0.25 ML to 0.10 ML as the O_{ot} coverage increases to 86%, corresponding to a factor of 2.6 decrease. In contrast, the CO$_2$ yield increases from 0.26 to 0.43 ML with increasing O_{ot} coverage to ~50% and decreases thereafter to a final value of 0.28 ML at 86% O_{ot} coverage. We estimate that the ratio of the CO$_2$:CH$_2$O yields increases from about 1.0 to 3.0 with increasing O_{ot} coverage to saturation, with this ratio rising to a maximum value of 3.3 at 60% O_{ot} coverage. The methyl formate yield also appears to pass through a maximum with increasing O_{ot} coverage. Our results demonstrate that O_{ot} atoms strongly promote the complete oxidation of methanol on RuO$_2$(110) over partial oxidation.

Evaluation of the product yields also provides evidence that methanol adsorbed on both Ru$_{cus}$ atoms and O$_{ot}$ atoms are oxidized during the TPRS experiments. We assert that each Ru$_{cus}$ atom and O$_{ot}$ atom binds with a single CH$_3$OH molecule when the CH$_3$OH monolayer is saturated at ~1.0 ML. In this case, the initial coverages of methanol (MeOH) adsorbed on Ru$_{cus}$ atoms and O$_{ot}$ atoms are equal to [MeOH]$_{Ru}$ = [Ru$_{cus}$] and [MeOH]$_{O_{ot}}$ = [O$_{ot}$], respectively, where [O$_{ot}$] is the initial coverage of O$_{ot}$ atoms and [Ru$_{cus}$] is the coverage of initially available Ru$_{cus}$ atoms and is equal to 1 − [O$_{ot}$].

Figure 4-6b compares [MeOH]$_{Ru}$ (= [Ru$_{cus}$]) with the total yield of reacted methanol, [MeOH]$_{rxn}$, during TPRS, and also compares [MeOH]$_{O_{ot}}$ (= [O$_{ot}$]) with the yield of methanol that desorbs in the low-temperature peak below ~225 K, [MeOH]$_{des, lo}$. We define the total yield of reacted methanol as the sum of the yields of CO$_2$, CH$_2$O and CH$_3$OCHO (x2). The comparison shows that [MeOH]$_{rxn}$ is higher than [MeOH]$_{Ru}$ at O$_{ot}$ coverages greater than ~0.30 ML, with the difference between [MeOH]$_{rxn}$ and [MeOH]$_{Ru}$ increasing with increasing O$_{ot}$ coverage. This
result demonstrates that the amount of methanol that reacts becomes increasingly greater than 
\([\text{MeOH}]_{\text{Ru}}\), and thus indicates that methanol molecules initially adsorbed on other types of sites 
(e.g., O_{ot} atoms) also react in significant quantities during TPRS. The graph also shows that 
\([\text{MeOH}]_{\text{Oot}}\) is greater than \([\text{MeOH}]_{\text{des, lo}}\) for O_{ot} coverages above \(~0.25\) ML, and that the 
difference between \([\text{MeOH}]_{\text{Oot}}\) and \([\text{MeOH}]_{\text{des, lo}}\) increases with increasing O_{ot} coverage, 
mirroring the difference between \([\text{MeOH}]_{\text{rxn}}\) and \([\text{MeOH}]_{\text{Ru}}\). We assert that the difference 
between \([\text{MeOH}]_{\text{Oot}}\) and \([\text{MeOH}]_{\text{des, lo}}\) is approximately equal to the amount of CH_{3}OH-O_{ot} 
pecies that react during TPRS, \([\text{MeOH}]_{\text{Oot, rxn}}\), and conclude that a large fraction of methanol 
molecules adsorbed on the O_{ot} atoms reacts during TPRS.

We consider an approximate model of the desorption and reaction yields to compare the 
reactivity of the MeOH-Ru_{cus} and MeOH-O_{ot} species. As an approximation, we neglect 
interconversion between MeOH adsorbed on Ru_{cus} and O_{ot} atoms, and assume that the initially 
adsorbed MeOH either reacts or desorbs. This approximation provides a reasonable way to 
distinguish the reaction yields of the MeOH-Ru_{cus} and MeOH-O_{ot} species, because the branching 
between desorption and the initial reaction step(s) of the MeOH-O_{ot} species occurs below \(~225\) 
K, i.e., the trailing edge of the low temperature CH_{3}OH TPRS peak (Figure 4-5a), prior to the 
desorption of other reaction products. We then define separate yields of reacted and desorbed 
MeOH by the following equations, 
\([\text{MeOH}]_{\text{Ru}} = [\text{MeOH}]_{\text{Ru, rxn}} + [\text{MeOH}]_{\text{Ru, des}}\) and 
\([\text{MeOH}]_{\text{Oot}} = [\text{MeOH}]_{\text{Oot, rxn}} + [\text{MeOH}]_{\text{Oot, des}}\). We assume that the yields of MeOH that desorb below vs. above 
\(~225\) K are equal to \([\text{MeOH}]_{\text{Oot, des}}\) and \([\text{MeOH}]_{\text{Ru, des}}\), respectively. Under these assumptions, we 
estimate the reacted yields using the equations, 
\([\text{MeOH}]_{\text{Ru, rxn}} = [\text{MeOH}]_{\text{Ru}} - [\text{MeOH}]_{\text{des, hi}}\) and 
\([\text{MeOH}]_{\text{Oot, rxn}} = [\text{MeOH}]_{\text{Oot}} - [\text{MeOH}]_{\text{des, lo}}\). We find that the sum of \([\text{MeOH}]_{\text{Ru, rxn}}\) and 
\([\text{MeOH}]_{\text{Oot, rxn}}\) agrees with the value of \([\text{MeOH}]_{\text{rxn}}\) to within better than 20% at all O_{ot} coverages.
(Table 4-1). These differences occur because the model calculations assume a total CH$_3$OH coverage of 1 ML for each data set whereas the actual CH$_3$OH coverage varies among the data sets over a range from 0.92 to 1.06 ML. Our analysis suggests that the yield of CH$_3$OH-O$_{ot}$ species that react during TPRS increases to a value of 0.48 ML at an O$_{ot}$ coverage of 0.86 ML, and that reaction of the CH$_3$OH-O$_{ot}$ species accounts for 100% of the observed reactivity at this coverage.

The last two columns of Table 4-1 show estimates of the reaction probabilities of the MeOH-Ru$_{cus}$ and MeOH-O$_{ot}$ species as a function of the O$_{ot}$ coverage, defined as the percentage of the species that reacts rather than desorbs. The reaction probability for the MeOH-Ru$_{cus}$ species increases from 65% to ~80% with increasing O$_{ot}$ coverage to 0.70 ML, while the reaction probability of the MeOH-O$_{ot}$ species increases to a steady value of about 55%. Our estimates provide evidence that the MeOH-O$_{ot}$ species is highly reactive at O$_{ot}$ coverages above ~20% but that the MeOH-Ru$_{cus}$ species is more reactive than the MeOH-O$_{ot}$ species, and that O$_{ot}$ atoms enhance the reactivity of the MeOH-Ru$_{cus}$ species. Overall, our results provide evidence that each O$_{ot}$ and Ru$_{cus}$ atom binds with approximately one CH$_3$OH molecule at saturation of the methanol monolayer and that CH$_3$OH molecules are ineffective at displacing O$_{ot}$ atoms from the surface during adsorption at 88 K. According to the analysis, the reaction yield initially increases with O$_{ot}$ coverage because the reaction probability of the MeOH-Ru$_{cus}$ species increases in the presence of O$_{ot}$ atoms, possibly indicating that a fraction of the MeOH-Ru$_{cus}$ species react directly with O$_{ot}$ atoms. The analysis further suggests that the reactivity decreases as the O$_{ot}$ coverage increases beyond ~50% because the MeOH-O$_{ot}$ species become more prevalent and are less reactive than the MeOH-Ru$_{cus}$ species. Further study is needed to determine why the reactivities of the MeOH-Ru$_{cus}$ and particularly the MeOH-O$_{ot}$ species appear to initially increase
with the O_{ot} coverage. A possibility is that the branching between desorption and reaction of adsorbed CH$_3$OH depends on the local adsorbate arrangement, such as whether CH$_3$OH-O_{ot} species are adsorbed in the interior of O_{ot}-rich domains or at the boundaries, next to CH$_3$OH-Ru$_{cua}$ species.

4.4 Discussion

4.4.1 Mechanism for CH$_3$OH oxidation on s-RuO$_2$(110)

A key finding from the present study is that the complete oxidation of methanol is strongly favored on s-RuO$_2$(110) at low coverage and that the selectivity toward CH$_2$O formation increases sharply above methanol coverages close to ~33% of the Ru$_{cua}$ density. The variation in reaction selectivity with the methanol coverage on s-RuO$_2$(110) is similar to behavior reported previously for methanol oxidation on PdO(101). In that study, Hakanoglu et al. present evidence that a CH$_2$O$_2$ species mediates the complete oxidation of methanol and that formation of the CH$_2$O$_2$ intermediate is effectively irreversible, in that this species always converts to CO$_2$ and H$_2$O during TPRS.$^{13}$ Those authors identified the CH$_2$O$_2$ species from X-ray photoelectron spectra (XPS) and also showed that the intermediate to reaction-limited H$_2$O and CO$_2$ formation on PdO(101) has a C:H ratio of unity, consistent with the CH$_2$O$_2$ species. They further demonstrate that CH$_2$O$_2$ formation is facile on PdO(101) but depends sensitively on the availability of reactive O-atoms at the surface. Overlap between the Ru 3d and C 1s peaks prevented us from confirming CH$_2$O$_2$ formation on RuO$_2$(110) using XPS. Despite this limitation, we contend that a similar mechanism is operative during methanol oxidation on s-RuO$_2$(110) as identified for PdO(101), and that the stoichiometric requirement for CH$_3$O conversion to CH$_2$O$_2$ plays a decisive role in determining the branching between complete and partial oxidation. Our interpretation is based mainly on the variation of reaction selectivity with initial CH$_3$OH coverage, and indeed provides a consistent description of the observed reactivity.
of methanol on s-RuO$_2$(110). Additional studies to spectroscopically identify the CH$_2$O$_2$ species and other adsorbed intermediates would aid in confirming the mechanism that we propose here.

Following the work of Hakanoglu et al.,$^{13}$ we propose that the steps leading to CH$_2$O$_2$ formation involve the deprotonation of methanol followed by conversion of methoxy to the CH$_2$O$_2$ intermediate. We expect that methanol deprotonation occurs readily at low temperature, generating equal quantities of CH$_3$O-Ru$_{\text{cus}}$ species and HO$_{\text{br}}$ groups via the reaction,$^{102,103}$

$$\text{CH}_3\text{OH} - \text{Ru}_{\text{cus}} + \text{O}_{\text{br}} \rightarrow \text{CH}_3\text{O} - \text{Ru}_{\text{cus}} + \text{HO}_{\text{br}} \quad 4-1$$

We further assert that the conversion of the methoxy species to CH$_2$O$_2$ requires two O$_{\text{br}}$ atoms and may be represented generally by the following reaction equation,

$$\text{CH}_3\text{O} - \text{Ru}_{\text{cus}} + 2\text{O}_{\text{br}} \rightarrow \text{O}_{\text{br}} - \text{CH}_2\text{O} - \text{Ru}_{\text{cus}} + \text{HO}_{\text{br}} \quad 4-2$$

where the representation “O$_{\text{br}}$ - CH$_2$O - Ru$_{\text{cus}}$” depicts the dioxymethylene intermediate as a bidentate species that bonds to both an O$_{\text{br}}$ and a Ru$_{\text{cus}}$ atom. According to the proposed mechanism, three O$_{\text{br}}$ atoms are needed to convert a CH$_3$OH molecule to the CH$_2$O$_2$ species. All adsorbed methanol molecules can thus convert to CH$_2$O$_2$ species and HO$_{\text{br}}$ groups at methanol coverages below 0.33 ML. The strong preference for complete oxidation below 0.33 ML suggests that the conversion of CH$_3$O groups to CH$_2$O$_2$ is intrinsically facile on s-RuO$_2$(110) compared with other reactions such as CH$_2$O desorption.

Methanol molecules adsorbed in excess of 0.33 ML are unable to convert to the CH$_2$O$_2$ species due to the stoichiometric constraint, and thus react by other pathways. Our results show that the main reactions of the excess CH$_3$O groups are hydrogenation and dehydrogenation to CH$_3$OH and CH$_2$O via reaction with HO$_{\text{br}}$ and O$_{\text{br}}$ species, respectively, and that a relatively small quantity also converts to methyl formate. The hydrogenation and dehydrogenation reactions may be represented by the equations,
\[ \text{CH}_3\text{O} - \text{Ru}_\text{cus} + \text{HO}_{\text{br}} \rightarrow \text{CH}_3\text{OH} - \text{Ru}_\text{cus} + \text{O}_{\text{br}} \] 4-3

\[ \text{CH}_3\text{O} - \text{Ru}_\text{cus} + \text{O}_{\text{br}} \rightarrow \text{CH}_2\text{O} - \text{Ru}_\text{cus} + \text{HO}_{\text{br}} \] 4-4

Our experiments with CD$_3$OH demonstrate that coupling between these methoxy hydrogenation and dehydrogenation reactions is mainly responsible for the concurrent desorption of methanol and formaldehyde at 385 K.

It is instructive to consider the sequence of reactions that occur when the methanol layer on s-RuO$_2$(110) is saturated at ~100% coverage. In this case, facile methanol deprotonation would convert all of the O$_{\text{br}}$ atoms to HO$_{\text{br}}$ groups at low temperature, with a CH$_3$O-Ru$_\text{cus}$ species adsorbed next to each HO$_{\text{br}}$ group. Assuming that the HO$_{\text{br}}$ groups are inactive as H-atom acceptors under the conditions studied, then additional dehydrogenation of methoxy groups requires that a fraction of the HO$_{\text{br}}$ groups release hydrogen and revert to O$_{\text{br}}$ atoms. Our results provide evidence that hydrogenation of methoxy groups via reaction Eq. 4-3 regenerates O$_{\text{br}}$ atoms that promote methoxy dehydrogenation by reaction Eq. 4-4, with the rates of these reactions increasing sharply at about 330 K and generating the CH$_3$OH and CH$_2$O TPRS peaks at 385 K. We find that 0.37 ML of monolayer CH$_3$OH and 0.25 ML of CH$_2$O evolve during TPRS when the methanol monolayer is saturated, meaning that ~0.62 ML of the CH$_3$O groups react via reaction Eq. 4-3 and 4-4. In addition, our results show that ~0.26 ML of the methoxy groups completely oxidize to CO$_2$ when the monolayer is initially saturated. This finding suggests that the conversion of CH$_3$O groups to CH$_2$O$_2$ occurs in parallel to the hydrogenation and dehydrogenation steps that yield CH$_3$OH and CH$_2$O.
The conversion of CH$_3$O groups to CH$_2$O$_2$ in parallel with the hydrogenation and dehydrogenation steps requires the regeneration of large quantity O$_{br}$ atoms, according to the proposed mechanism. Specifically, the stoichiometry of reaction Eq. 4-2 indicates that ~0.52 ML of O$_{br}$ atoms are needed to convert 0.26 ML of CH$_3$O to CH$_2$O$_2$. Below 400 K, the desorption of CH$_3$OH and H$_2$O can both regenerate O$_{br}$ atoms that are needed to convert CH$_3$O to CH$_2$O$_2$. However, we estimate that only 0.12 ML of O$_{br}$ atoms are generated by reaction Eq. 4-3 and 4-4 at saturation of the methanol monolayer, where the value of 0.12 ML is equal to the amount of monolayer CH$_3$OH that desorbs in excess of CH$_2$O. This estimate suggests that H$_2$O formation accounts for the majority of O$_{br}$ atoms that are regenerated below 400 K. We assume that water formation occurs by the recombination of HO$_{br}$ groups and may be represented generally by the following reaction equation,

$$2HO_{br} \rightarrow H_2O(g) + O_{br} + V_{br} \quad 4-5$$

where $V_{br}$ represents a bridging oxygen vacancy. For the initially saturated CH$_3$OH monolayer, we estimate that 0.19 ML of H$_2$O desorbs below 400 K and would thus generate 0.19 ML of O$_{br}$ atoms according to reaction Eq. 4-5. These estimates suggest that a total of 0.31 ML of O$_{br}$ atoms are regenerated during CH$_3$O hydrogenation and dehydrogenation as given by reaction Eq. 4-3 and 4-4. This value of the O$_{br}$ coverage is less than that needed to account for the conversion of 0.52 ML of CH$_3$O groups to CH$_2$O$_2$ species based on the stoichiometry of reaction Eq. 4-2, suggesting that other processes restore O$_{br}$ atoms as well.

The exchange of subsurface O-atoms with surface $V_{br}$ sites may provide a mechanism for replacing O$_{br}$ atoms during the formation of H$_2$O below ~400 K. Such healing of surface $V_{br}$ sites could generate an additional 0.19 ML of O$_{br}$ atoms, bringing the total quantity of O$_{br}$ atoms generated below 400 K into excellent agreement (0.50 vs. 0.52 ML) with that needed to satisfy
the stoichiometric requirement for CH₂O₂ formation. Notably, the CO₂ TPRS trace obtained from the methanol-covered s-RuO₂(110) surface exhibits a single peak at ~490 K for all initial methanol coverages, and the peak only broadens slightly with increasing methanol coverage from ~0.33 to 1 ML. These characteristics suggest that the reaction-limited production of CO₂ resulting from methanol oxidation on s-RuO₂(110) occurs through a common intermediate and in a similar local environment for initial methanol coverages above 0.33 ML. We assert that the regeneration of O_{br} atoms from subsurface oxygen provides a viable explanation of the relative invariance of the CO₂ TPRS peak with increasing methanol coverage. The reason is that such O_{br} atom regeneration can allow the same quantity of CH₂O₂ species to form, and establishes a similar reaction environment for the formation and complete oxidation of the CH₂O₂ species at all initial methanol coverages above 0.33 ML.

Prior studies demonstrate that lattice oxygen restores O_{br} atoms of mildly-reduced RuO₂(110) during heating, lending supporting to our interpretation. For example, scanning tunneling microscopy (STM) experiments provide evidence that the thermal restoration of mildly-reduced RuO₂(110) surfaces, generated via oxide reduction by CO, H₂ or CH₃OH, occurs by a mechanism wherein threefold-coordinated surface O-atoms convert to O_{br} atoms, causing the release of Ru_{cus} atoms and the formation of metallic Ru pits after heating to above ~600 K.⁸,⁸²,⁸⁹ A more recent investigation using reflection-absorption infrared spectroscopy (RAIRS) of adsorbed CO demonstrates that lattice oxygen begins to replace O_{br} atoms of RuO₂(110) at temperatures as low as 370 K.¹⁰⁴ Similarly, we have shown that subsurface oxygen atoms regenerate O_{cus} atoms of the PdO(101) surface during CO oxidation, and that the regeneration becomes highly facile only after nearby CO molecules desorb from the surface at temperatures near ~400 K.¹⁰⁵,¹⁰⁶ An analogous process could provide a mechanism for the partial restoration
of O$_{ot}$-atoms on RuO$_2$(110) during chemical reduction, but additional investigations are needed to test this idea. We expect that the kinetics of the restoration process could depend sensitively on the presence and nature of adsorbed species.

Our results demonstrate that the branching between complete oxidation and partial oxidation to CH$_2$O depends on the initial CH$_3$OH coverage on s-RuO$_2$(110). Prior studies show that the product distribution also depends sensitively on the extent of reduction of the RuO$_2$(110) surface. *In situ* measurements conducted during the steady-state oxidation of methanol show that complete oxidation to CO$_2$ and H$_2$O is favored on RuO$_2$(110) at high O$_2$:CH$_3$OH ratio. Blume et al. also show that the RuO$_2$(110) surface partially reduces at moderate O$_2$:CH$_3$OH ratio, resulting in mixtures of metallic Ru, an intermediate RuO$_x$ phase and RuO$_2$(110) at the surface. They show that partial oxidation of methanol to CO, H$_2$ and H$_2$O is favored on metallic Ru domains, while conversion to CH$_2$O is preferred on the RuO$_x$ phase. These findings demonstrate that the selectivity of Ru catalysts toward methanol oxidation can depend sensitively on the temperature and reactant partial pressures due to the effect of these parameters on the distribution of surface phases at steady state as well as the adsorbate coverages. Based on prior STM studies, we expect that small quantities of metallic Ru develop on the RuO$_2$(110) surface during our TPRS experiments, but only at temperatures above ~600 K after nearly all of the adsorbed species have desorbed. We thus conclude that the reactivity observed during TPRS results entirely from methanol reaction on RuO$_2$(110) and that metallic Ru domains have a negligible influence. The absence of CO and H$_2$ desorption features during our TPRS experiments supports this conclusion.

**4.4.2 Mechanism for CH$_3$OH oxidation on O-rich RuO$_2$(110)**

Our results show that O$_{ot}$ atoms promote the complete oxidation of methanol on RuO$_2$(110) and that the activity of the O-rich surface increases up to high O$_{ot}$ coverages. Adding
O$_{ot}$ atoms to the surface increases the quantity of reactive surface O-atoms that are available for oxidizing methanol, causing the selectivity toward complete oxidation to increase with increasing O$_{ot}$ coverage. For an initial methanol coverage of about 1 ML, the yield of CO$_2$ increases from 0.26 ML on the s-RuO$_2$(110) surface to a maximum value of 0.43 ML with increasing O$_{ot}$ coverage to 0.50 ML. The CO$_2$ percentage of the total reaction yield for methanol saturated surfaces increases from 45% to 60% with increasing initial O$_{ot}$ coverage to 0.50 ML, and the selectivity toward CO$_2$ formation remains at 60% with further addition of O$_{ot}$ atoms. Given that CO$_2$ evolves in a single TPRS peak irrespective of the O$_{ot}$ coverage (Figure 4-5b), we assert that CH$_2$O$_2$ species serve as the key intermediates for complete oxidation of methanol on stoichiometric and O-rich RuO$_2$(110) surfaces and that formation of CH$_2$O$_2$ species can involve O$_{ot}$ as well as O$_{br}$ atoms.

On-top oxygen atoms may promote CH$_3$OH dehydrogenation by both direct and indirect pathways. For example, an adsorbed methanol molecule could directly transfer an H-atom to an O$_{ot}$ atom via O-H or C-H bond cleavage. We expect that methanol adsorbed on a Ru$_{cus}$ atom would tend to react directly with an adjacent O$_{ot}$ atom via O-H bond cleavage, as represented by the following reaction equation,

$$\text{CH}_3\text{OH} - \text{Ru}_{cus} + O_{ot} \rightarrow \text{CH}_3\text{O} - \text{Ru}_{cus} + H\text{O}_{ot}$$  

We discuss possible reactions of CH$_3$OH-O$_{ot}$ species below. The O$_{ot}$ atoms can also indirectly promote the dehydrogenation of methanol and methanol-derived species by removing H-atoms from the surface via water formation and desorption, thereby regenerating reactive surface O-atoms. The desorption of one H$_2$O molecule results in the conversion of two surface OH groups to one and possibly two surface O-atoms, the latter depending on the rate at which subsurface O-atoms can shift to the surface.
Prior studies show that H$_2$O formation via reaction of HO$_{ot}$ species is a desorption-limited process, meaning that HO$_{ot}$ species react readily to produce H$_2$O$_{ot}$ species at temperatures below that for H$_2$O desorption from the Ru$_{cus}$ sites during TPRS. In contrast, the recombination rate of HO$_{br}$ species is reaction-limited in the absence of other adsorbed species, and gives rise to H$_2$O desorption during TPRS at temperatures above that of the H$_2$O$_{ot}$ species. Researchers have also shown that H transfer from HO$_{br}$ groups to O$_{ot}$ atoms occurs readily on the RuO$_2$(110) surface, and can provide a pathway for regenerating reactive O$_{br}$ atoms that can continue to participate in adsorbate dehydrogenation. Low-temperature H$_2$O desorption appears to play a significant role in promoting the complete oxidation of methanol on O-rich RuO$_2$(110). As seen in Figure 4-5, the H$_2$O TPRS intensity below ~400 K increases markedly from the methanol-saturated surfaces as the initial O$_{ot}$ coverage increases. We specifically estimate that the low-temperature (< 400 K) H$_2$O TPRS yield increases from 0.19 to 0.49 ML with increasing initial O$_{ot}$ coverage to saturation. The enhancement in low-temperature H$_2$O desorption caused by O$_{ot}$ atoms appears to be an important factor in promoting the complete oxidation of methanol on O-rich RuO$_2$(110).

Our results provide evidence that a large fraction of CH$_3$OH species that are initially adsorbed in O$_{ot}$-rich domains undergo complete oxidation on RuO$_2$(110), in parallel with the oxidation of CH$_3$OH molecules that bind initially on Ru$_{cus}$ sites. Although further study is needed to clarify the nature of methanol species adsorbed on O-rich RuO$_2$(110), it is reasonable to expect that the CH$_3$OH-O$_{ot}$ and CH$_3$OH-Ru$_{cus}$ species experience distinct binding mechanisms and follow different pathways for initial bond activation. The CH$_3$OH-Ru$_{cus}$ species likely achieves favorable bonding through a dative interaction between a lone pair on the O-atom of CH$_3$OH and empty states localized on the Ru$_{cus}$ atom. The CH$_3$OH-Ru$_{cus}$ species would then
undergo O-H bond cleavage via H-transfer to a neighboring O-atom, resulting in adsorbed OH and CH$_3$O-Ru$_{cus}$ species. Either an O$_{br}$ or O$_{ot}$ atom could serve as the H-atom acceptor. In this case, the Ru$_{cus}$ atom acts as an acid site and binds strongly with the conjugate CH$_3$O base.

The CH$_3$OH-O$_{ot}$ species is likely to bind and react by different mechanisms than the CH$_3$OH-Ru$_{cus}$ species because the acidic Ru$_{cus}$ sites are occupied by O$_{ot}$ atoms and should thus be unavailable to coordinate with a CH$_3$OH molecule or a CH$_3$O product. We expect that non-bonding interactions dominate the binding of the CH$_3$OH-O$_{ot}$ species, particularly H-bonding between the OH group and surface O-atoms. The upshift in the low-temperature CH$_3$OH desorption peak with increasing O$_{ot}$ coverage (Figure 4-5a) suggests that H-bonding is more favorable when methanol adsorbs in the presence of both O$_{ot}$ and O$_{br}$ atoms compared with only O$_{br}$ atoms. Because methoxy formation appears unlikely, we speculate that initial activation of the CH$_3$OH-O$_{ot}$ species occurs by C-H bond cleavage to produce O-CH$_2$OH and OH species. For example, a reaction where H-O$_{ot}$ and C-O$_{br}$ bond formation occur concurrently may be represented by the following equation,

$$\text{CH}_3\text{OH} - \text{O}_{ot} + \text{O}_{br} \rightarrow \text{O}_{br} - \text{CH}_2\text{OH} + \text{HO}_{ot}$$

Such an initial activation step might also occur with different pairs of surface O-atoms, though we expect that at least one O$_{ot}$ atom participates. Our results suggest that initial C-H bond cleavage of the CH$_3$OH-O$_{ot}$ species occurs below ~225 K during TPRS, i.e., below the trailing edge of the low-temperature CH$_3$OH peak, since the bond cleavage must occur before all of the CH$_3$OH-O$_{ot}$ species desorb. The initial C-H bond cleavage step that we propose for the CH$_3$OH-O$_{ot}$ species is reasonable because the CH$_2$OH leaving group can form a strong C-O bond with a surface O-atom whereas Ru$_{cus}$ sites are unavailable in O$_{ot}$-rich regions to bind with a CH$_3$O leaving group. Also, prior studies show that O$_{ot}$ atoms on RuO$_2$(110) are more active than O$_{br}$.
atoms in promoting intramolecular bond cleavage of adsorbed species that results in H-atom transfer. For example, O_{ot} atoms are significantly more reactive than O_{br} atoms toward the initial bond activation of adsorbed C_2H_4, NH_3 and HCl.\textsuperscript{2,3}

The strong preference for complete oxidation to CO_2 as well as the persistence of a single CO_2 TPRS peak with increasing O_{ot} coverage suggest that the CH_3OH-O_{ot} and CH_3OH-Ru_{cus} species transform to a common intermediate prior to completely oxidizing. As discussed above, we assert that CH_3OH reacts on the s-RuO_2(110) to generate a bidentate CH_2O species that may be represented as O_{br}-CH_2O-Ru_{cus}. We speculate that O_{ot} atoms and HO_{ot} groups promote O-H bond cleavage of the O_{br}-CH_2OH (or O_{ot}-CH_2OH) species, and that facile conversion of O_{ot} atoms to H_2O and H_2O desorption creates Ru_{cus} sites needed for CH_2O formation. The following equation represents the net reaction that we propose,

\[
\text{O}_{br} - \text{CH}_2\text{OH} + \text{HO}_{ot} \rightarrow \text{O}_{br} - \text{CH}_2\text{O} - \text{Ru}_{cus} + \text{H}_2\text{O} (\text{gas}) \quad 4-8
\]

This general scenario is reasonable since O_{ot} atoms convert readily to H_2O and are strong H-atom acceptors. Reaction Eq. 4-7 and 4-8 represent a viable pathway by which CH_3OH-O_{ot} species can transform to the same CH_2O intermediate as proposed for the CH_3OH-Ru_{cus} species. From the present data, we cannot exclude other forms of the CH_2O intermediate, such as an O_{ot}-CH_2O-Ru_{cus} species. Again, however, the CO_2 TPRS spectra provide compelling evidence to conclude that a common intermediate governs the complete oxidation of methanol on the stoichiometric and O-rich surfaces, irrespective of the initial O_{ot} coverage.

4.5 Summary

We used TPRS to investigate the adsorption and oxidation of methanol on stoichiometric and O-rich RuO_2(110) surfaces. Our results show that methanol dissociates efficiently on the s-RuO_2(110) surface, and reacts with the surface oxygen atoms to produce CO_2, CH_2O, H_2O and small quantities of methyl formate during TPRS. We find that the complete oxidation of CH_3OH
to CO$_2$ and H$_2$O is strongly favored for initial CH$_3$OH coverages below ~0.33 ML, with CO$_2$
evolving in a single TPRS peak at ~500 K and H$_2$O desorbing in a broad TPRS feature from
~300 to 750 K. The CO$_2$ TPRS yield remains constant and partial oxidation to mainly CH$_2$O
becomes increasingly favored as the initial CH$_3$OH coverage increases from 0.33 to 1.0 ML. We
find that CH$_2$O and CH$_3$OH desorb concurrently in a TPRS peak at ~385 K for CH$_3$OH
coverages above 0.33 ML. We present evidence that an adsorbed CH$_2$O$_2$ species serves as the
key intermediate to complete oxidation and that CH$_2$O$_2$ formation is intrinsically facile on the s-
RuO$_2$(110) surface, but becomes limited by the availability of O$_{br}$ atoms at CH$_3$OH coverages
above 0.33 ML. We assert that the stoichiometric constraint for CH$_2$O$_2$ formation causes
methanol molecules adsorbed in excess of 0.33 ML to dehydrogenate to mainly CH$_2$O and
desorb. Experiments with CD$_3$OH show that the concurrent desorption of methanol and
formaldehyde arises predominantly from a kinetic coupling between the hydrogenation and
dehydrogenation of adsorbed CH$_3$O groups via reaction with HO$_{br}$ groups and O$_{br}$ atoms,
respectively.

We find that O$_{ot}$ atoms strongly promote the complete oxidation of CH$_3$OH on
RuO$_2$(110) and that O-rich RuO$_2$(110) surfaces exhibit high activity toward methanol oxidation.
Our results show that the ratio of CO$_2$ to partially oxidized products (CH$_2$O + CH$_3$OCHO)
generated during TPRS doubles with increasing O$_{ot}$ coverage to 50%, and that the total quantity
of reacted CH$_3$OH increases slightly above that obtained on the s-RuO$_2$(110) surface. We present
evidence that CH$_3$OH species adsorbed within O$_{ot}$-rich domains react to a significant extent
during TPRS in parallel with reaction of CH$_3$OH adsorbed on Ru$_{cus}$ sites of partially O-rich
RuO$_2$(110). We suggest that the hydrogenation of O$_{ot}$ atoms and resulting desorption of H$_2$O
below 400 K provides a facile pathway for regenerating reactive O-atoms at the surface that promote the complete oxidation of adsorbed methanol.
Table 4-1. TPRS yields of reacted MeOH shown as a function of the initial O_{ot} coverage on RuO_{2}(110). The second column shows the total TPRS yield of reacted MeOH, and the third and fourth columns give estimates of the yields of MeOH-Ru_{cus} and MeOH-O_{ot} species that react as determined from the model discussed in the text. The fifth column shows estimates of the percentage of the total reaction yield resulting from reaction of MeOH-O_{ot} species, and the last two columns give estimates of the reaction probabilities of the MeOH-Ru_{cus} and MeOH-O_{ot} species. We estimate an uncertainty of ~15% for the reported TPRS yields.

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Figure 4-1. Ball-and-stick model of RuO$_2$(110) surfaces. Model representation of (a) stoichiometric RuO$_2$(110) and (b) O-rich RuO$_2$(110) surfaces. Bridging (O$_{br}$) and on-top (O$_{ot}$) O-atoms are indicated.
Figure 4-2. TPRS spectra after CH$_3$OH adsorption on s-RuO$_2$(110) surface at 88 K. TPRS spectra of CO$_2$, CH$_3$OH, CH$_2$O, H$_2$O and CH$_3$OCHO obtained from s-RuO$_2$(110) surface after adsorbing (a) ~0.33 ML (low coverage) and (b) ~1.1 ML (high coverage) CH$_3$OH at a substrate temperature of 88 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 
Figure 4-3. Yields of carbon-containing reaction products obtained as a function of the initial methanol coverage on s-RuO$_2$(110). The yields were estimated from integrated TPRS spectra obtained after adsorbing methanol on s-RuO$_2$(110) layer at 88 K.
Figure 4-4. TPRS spectra after CD$_3$OH adsorption on s-RuO$_2$(110) surface at 89 K. TPRS spectra of CD$_3$OH, CD$_3$OD, CD$_2$O and CO$_2$ obtained from s-RuO$_2$(110) surface after adsorbing 1.0 ML CD$_3$OH at a substrate temperature of 89 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 
Figure 4-5. TPRS spectra after CH$_3$OH adsorption on O-rich RuO$_2$(110) surface at 88 K. TPRS spectra of a) CH$_3$OH, b) CO$_2$, c) CH$_2$O and d) H$_2$O, obtained from O-rich RuO$_2$(110) surfaces after dosing ~1.0 ML CH$_3$OH at a substrate temperature of 88 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 
Figure 4-6. TPRS yields after CH₃OH oxidation on O-rich RuO₂(110). a) TPRS yields of carbon-containing reaction products and b) TPRS yields of both reacted CH₃OH and low-temperature desorbed CH₃OH plotted as a function of the Oₜ coverage on O-rich RuO₂(110) surface after adsorbing ~1 ML of CH₃OH at 88 K. The dashed lines correspond to the nominal coverages of exposed Ruₗₘₙ atoms (red) and Oₜ atoms (blue) at the RuO₂(110) surfaces prior to methanol adsorption.
CHAPTER 5
SUPPRESSION OF COMPLETE OXIDATION PATHWAY DURING METHANOL
OXIDATION BY SELECTIVE CHLORINATION OF RuO$_2$(110) SURFACE

5.1 Motivation

Environmental and monetary concerns are strong motivation for developing selective
catalytic processes in industrial applications in order to reduce waste by-products. Partial
oxidation catalysis is one of the critical processes in a wide variety of industrial applications
ranging from large-scale production of commodities to synthesis of minute amounts of
pharmaceuticals and chemicals. However, the chemistry of selective oxidation is especially
challenging because complete oxidation is typically favored over partial oxidation due to
thermodynamic consequences. RuO$_2$ is known as a powerful catalyst for promoting many
oxidation processes such as CO oxidation$^7$ and HCl oxidation to Cl$_2$.$^{109}$ The strong catalytic
activity of the RuO$_2$(110) surface is attributed to the presence of coordinatively unsaturated Ru
(Ru$_{\text{cus}}$) and oxygen (O$_{\text{br}}$) atoms. The O$_{\text{br}}$ atoms act as Brønsted base sites, i.e. they are strong H-
atom receptors. CO and HCl molecules bind strongly on the Ru$_{\text{cus}}$ sites, and surface can release
the O$_{\text{br}}$ atoms that oxidize the adsorbate molecules. The RuO$_2$(110) surface acts a stable catalyst
in the oxidation of HCl in presence of oxygen to produce Cl$_2$ and H$_2$O.$^{109,110}$ Crihan et al.
demonstrate that the extraordinary stability of RuO$_2$(110) surface for HCl oxidation stems from
the selective and self-limiting replacement of bridging O atoms (O$_{\text{br}}$) by Cl atoms.$^{16}$ Upon HCl
exposure on RuO$_2$(110) surface, O$_{\text{br}}$ atoms leave the surface as H$_2$O by reacting with H atoms
from HCl and adsorbed Cl atoms fill in the bridging oxygen vacancies, leading to formation of
RuO$_{2-x}$Cl$_x$(110) surface.$^{16,111}$ Chlorination of RuO$_2$(110) surface is a dynamic process and the
degree of chlorination can be controlled by varying the HCl supply to the surface. Experimental
and computation studies further report that CO oxidation to CO$_2$ is considerably suppressed upon
chlorination of the RuO$_2$(110) surface relative to stoichiometric RuO$_2$(110) surface.$^{111}$ These
findings present the RuO$_{2-x}$Cl$_x$(110) surface as an interesting model system to explore selective oxidation reactions.

Methanol is the simplest alcohol consisting of C-H, C-O, and O-H bonds, which makes it an excellent probe molecule to study reactivity of a surface and selective activation of chemical bonds of polyatomic molecules. In our recent work$^{112}$, we demonstrated that methanol readily deprotonates on stoichiometric (s-) and O-rich RuO$_2$(110) surfaces at very low temperatures forming methoxy (CH$_3$O-) groups and HO$_{br}$. At monolayer saturation, ~60% of adsorbed methanol on s-RuO$_2$(110) oxidizes to form CH$_2$O, CO$_2$ and H$_2$O with equal branching between partial oxidation (CH$_2$O) and complete oxidation (CO$_2$). Our results show that CH$_2$O desorbs from the s-RuO$_2$(110) prior to CO$_2$ desorption, and low temperature H$_2$O desorption creates free O$_{br}$ sites on the surface which are essential for complete oxidation to CO$_2$ by removing H-atoms from the HO$_{br}$ species. We presented evidence that product selectivity in methanol oxidation on RuO$_2$(110) is strongly dependent on availability of reactive O-atoms on the surface. Presence of O$_{ot}$ atoms on the RuO$_2$(110) surface preferentially promote complete oxidation of methanol to CO$_2$. In the present study, we employed temperature programmed reaction spectroscopy (TPRS) to investigate oxidation of methanol on RuO$_{2-x}$Cl$_x$(110) surface with different Cl$_{br}$ coverages. We will show that RuO$_{2-x}$Cl$_x$(110) surface selectively suppresses complete oxidation of methanol into CO$_2$ without severely affecting CH$_2$O yield via partial oxidation or promoting any additional chemical reactions.

5.2 Experimental Details

We prepared stoichiometric RuO$_2$(110) surface (‘s-RuO$_2$(110)’) by exposing a clean Ru(0001) surface to gas-phase atomic oxygen beam at 750 K. The procedure generates a conformal s-RuO$_2$(110) layer consisting of ~18 ML$_{Ru(0001)}$ O-atoms, where 1 ML$_{Ru(0001)}$ unit is defined as Ru surface atom density of $1.57 \times 10^{15}$ cm$^{-2}$ on Ru(0001). Growth and
characterization of the conformal s-RuO$_2$(110) film are detailed in Appendix A (also in Chapter 4). Selective replacement of bridging oxygen sites by Cl atoms was achieved by exposing the s-RuO$_2$(110) surface to varying amounts of HCl at 700 K to obtain RuO$_{2-x}$Cl$_x$(110) surface (Figure 5-1). HCl molecules adsorb on the Ru$_{cus}$ sites and release their hydrogen to adjacent O$_{br}$ atom to form HO$_{br}$ and Cl$_{tot}$ species. The HO$_{br}$ groups recombine to form H$_2$O that readily desorbs from the surface under the exposure conditions leaving behind an oxygen vacancy at bridging positions. Cl$_{tot}$ atoms then diffuse into these bridging vacancies to form Cl$_{br}$ groups. Prior investigations show that the excess Cl$_{tot}$ atoms recombine and desorb in form of Cl$_2$ gas, and Cl$_{br}$ saturation is achieved after 80% of the bridging O atoms are replaced with Cl atoms.\textsuperscript{113, 114} We measured Cl 2p spectrum using x-ray photoelectron spectroscopy (XPS) after preparing various RuO$_{2-x}$Cl$_x$(110) surfaces to estimate the degree of surface chlorination. Figure 5-2 shows Cl 2p XPS spectra obtained at 300 K from RuO$_{2-x}$Cl$_x$(110) surface with different Cl$_{br}$ coverages. We observed Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ peaks in the XPS spectra near 198 and 199 eV, respectively, which is in good agreement with previously reported results.\textsuperscript{16, 113, 114} We assumed that the maximum Cl 2p signal to correspond to 0.80 ML Cl$_{br}$ concentration to estimate Cl$_{br}$ coverages on the chlorinated surface, where the unit monolayer (ML) expresses absolute coverages and equals Ru$_{cus}$ surface atom density of $5.02 \times 10^{14}$ cm$^{-2}$ on the s-RuO$_2$(110) surface. Additionally, we find that HCl adsorption on Ru(0001) produces a sharp ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern at saturation coverage. To evaluate the accuracy of Cl$_{br}$ coverages estimation, we also estimated Cl$_{br}$ coverage on RuO$_{2-x}$Cl$_x$(110) surface by assuming HCl saturation coverage on Ru(0001) to be equal to 0.33 ML. This approach provides good agreement with our earlier assumption that Cl$_{br}$ saturated RuO$_{2-x}$Cl$_x$(110) surface consists of 0.80 ML Cl$_{br}$ and 0.20 ML O$_{br}$. Lastly, we prepared O-rich RuO$_{2-x}$Cl$_x$(110) surfaces by exposing the surface to 1 L of O$_2$ at 300 K supplied through a tube
doser, followed by annealing to various temperatures in order to obtain desired \( \text{O}_{\text{ot}} \) coverage by desorbing the excess \( \text{O}_{\text{ot}} \). More details about O-rich surface preparation are provided in Appendix A.

We performed successive \( \text{CH}_3\text{OH} \) TPRS experiments on \( \text{RuO}_{2-x}\text{Cl}_x(110) \) surface to explore the stability of the chlorinated surface under reducing conditions and its effect on the product yields. We find that \( \text{RuO}_{2-x}\text{Cl}_x(110) \) surfaces with \( \text{Cl}_{\text{br}} \) coverages below 50% are stable and \( \text{Cl}_{\text{br}} \) coverage remains within 20% of original coverage after repeated \( \text{CH}_3\text{OH} \) exposures. On the other hand, \( \text{RuO}_{2-x}\text{Cl}_x(110) \) surfaces with \( \text{Cl}_{\text{br}} \) coverages above 50% lose \( \text{Cl}_{\text{br}} \) atoms after three \( \text{CH}_3\text{OH} \) exposures and \( \text{Cl}_{\text{br}} \) coverage decreases to \( \sim50-60\% \). Interestingly, we do not observe any chlorine containing products during TPRS at any \( \text{Cl}_{\text{br}} \) coverage. A possible explanation could be that \( \text{Cl} \) atoms desorb from the surface as \( \text{Cl}_2 \) gas but \( \text{Cl}_2 \) yield is well below detection limit of the mass spectrometer. We performed three saturation exposures of \( \text{CH}_3\text{OH} \) on the \( \text{RuO}_{2-x}\text{Cl}_x(110) \) surfaces with \( \sim50\% \) \( \text{Cl}_{\text{br}} \) coverages, and find that product (\( \text{CH}_2\text{O}, \text{CO}_2, \text{H}_2\text{O} \) and \( \text{CH}_3\text{OH} \)) yields remain same during all three exposures (see Appendix B).

5.3 Results and Discussion

5.3.1 \( \text{CH}_3\text{OH} \) oxidation on s-\( \text{RuO}_{2-x}\text{Cl}_x(110) \)

Figures 5-3a-d show TPRS spectra of \( \text{CH}_3\text{OH}, \text{CO}_2, \text{CH}_2\text{O} \) and \( \text{H}_2\text{O} \) obtained from \( \text{RuO}_{2-x}\text{Cl}_x(110) \) as a function of the \( \text{Cl}_{\text{br}} \) coverage, after generating a methanol coverage of \( \pm 0.15 \) ML on each chlorinated surface. The TPRS data from oxidation of \( \text{CH}_3\text{OH} \) on the \( \text{RuO}_{2-x}\text{Cl}_x(110) \) surface shows that all oxidative products desorb prior to 600 K, and we find that none of the products contain \( \text{Cl} \) atoms. This observation is consistent with prior work which demonstrates that \( \text{Cl}_{\text{br}} \) species of the \( \text{RuO}_{2-x}\text{Cl}_x(110) \) surface are thermally and chemically stable up to 800 K.\(^{16}\) TPRS spectra corresponding to 0 ML \( \text{Cl}_{\text{br}} \) (black) in Figure 5-3 represent methanol oxidation on the stoichiometric \( \text{RuO}_2(110) \) surface. By integrating the TPRS spectra,
we estimate that ~1.1 ML CH$_3$OH initially adsorbs on the s-RuO$_2$(110) at 88 K, and ~0.94 ML CH$_3$OH adsorbs in the monolayer that either desorbs or oxidizes above 190 K. TPRS results show that methanol binds strongly on the s-RuO$_2$(110) and readily reacts with the surface. We estimate that ~60% of the adsorbed methanol oxidizes to primarily produce CH$_2$O, CO$_2$ and H$_2$O with almost equal branching between partial oxidation (CH$_2$O) and complete oxidation (CO$_2$) of methanol on the s-RuO$_2$(110) surface. CH$_3$OH TPRS trace (Figure 5-3a, black) exhibits a multilayer peak at 155 K and two sub-monolayer CH$_3$OH TPRS peaks centered at 268 K and 386 K, respectively. In the previous chapter, we assert that the broad CH$_3$OH desorption peak at 268 K stems from recombination of CH$_3$O and H atoms from HO$_{br}$ species. By integrating of CH$_3$OH TPRS spectra, we estimate that the low temperature CH$_3$OH peak contributes ~0.17 ML CH$_3$OH, while CH$_3$OH peak centered at 385 K contributes 0.20 ML. The CH$_2$O TPRS trace (Figure 5-3c, black) reveals that ~0.25 ML CH$_2$O desorbs in a single desorption peak centered at 380 K. In Chapter 4, we demonstrated that the concurrent desorption of CH$_2$O and CH$_3$OH results primarily from coupled hydrogenation and dehydrogenation of CH$_3$O groups, and that the complete oxidation of CH$_3$OH to CO$_2$ on s-RuO$_2$(110) surface involves formation of CH$_2$O$_2$ species as a critical and irreversible intermediate step.$^{112}$ We also observe small amount of CH$_3$OCHO desorption in a small peak at 385 K indicating coupling reaction between two adjacent CH$_3$O groups. We estimate that ~0.26 ML CH$_3$OH is completely oxidized to CO$_2$, which produces a sharp CO$_2$ TPRS peak centered at 490 K (shown in Figure 5-3b, black) after CH$_2$O and CH$_3$OH desorption is complete. H$_2$O TPRS trace (Figure 5-3d, black) exhibits three main features centered at 390, 490 and 575 K with an estimated total of 0.90 ML H$_2$O desorption. The dominant H$_2$O TPRS peak at 575 K accounts for 54% (~0.49 ML) of the total H$_2$O desorption yield. Previous studies attribute the H$_2$O TPRS peak at 575 K to H$_2$O evolution
by recombination of HO$_{br}$ groups, while the adsorbate or reaction-assisted formation of H$_2$O produces the low-temperature H$_2$O TPRS features.

The TPRS results shown in Figure 5-3 further reveal that surface chlorination of RuO$_2$(110) alters the oxidative product distribution in favor of partial oxidation of methanol without promoting any additional chemistry, however, the overall reactivity of the surface diminishes due to chlorination. The CH$_3$OH TPRS spectra (Figure 5-3a) show that the total CH$_3$OH desorption increases with increasing Cl$_{br}$ coverage. For instance, total CH$_3$OH desorption increases by ~30% on the RuO$_{2-x}$Cl$_x$(110) with 0.78 ML Cl$_{br}$ coverage relative to the s-RuO$_2$(110). We find that the CH$_3$OH yield from the high temperature peak (>~ 325K) remains almost constant (~0.20 ML) though the peak temperature slightly shifts toward lower temperature with increasing Cl$_{br}$ coverage. The multilayer and low temperature CH$_3$OH peaks, on the other hand, increase with increasing Cl$_{br}$ coverage resulting in increased methanol desorption. We estimate that CH$_3$OH desorption yield below 325 K increases by ~60% (0.45 ML vs 0.28 ML) relative to s-RuO$_2$(110) when Cl$_{br}$ coverage reaches 0.78 ML Cl$_{br}$ coverage. The increase in the low temperature CH$_3$OH desorption yields and the downshift in corresponding CH$_3$OH peak temperatures indicate that the interaction of CH$_3$OH molecules with Ru$_{cus}$ atoms is weakened due to presence of Cl$_{br}$ atoms. Note that unlike O$_{br}$ atoms, Cl$_{br}$ atoms on RuO$_{2-x}$Cl$_x$(110) are coordinatively saturated and do not participate in the reaction since we do not observe any chlorine containing products during TPRS. Furthermore, Cl$_{br}$ atom will reduce the acidity of adjacent Ru$_{cus}$ site, so it is likely that Ru$_{cus}$ sites adjacent to Cl$_{br}$ atoms only molecularly adsorb CH$_3$OH molecules resulting in increased CH$_3$OH desorption at low temperature. By integrating the CH$_2$O TPRS spectra (Figure 5-3c), we estimate that the CH$_2$O desorption yield decreases very slightly (~8%) as the Cl$_{br}$ coverage increases to 0.47 ML, but
diminishes significantly as the Cl_{br} coverage increases beyond ~50%. Notably, CH_{2}O TPRS peaks broaden and shift to temperatures below 370 K with increasing chlorination as opposed to CH_{2}O TPRS peak at 380 K on s-RuO_{2}(110). The downward shift in the CH_{2}O desorption peak suggests that the surface chlorination either affects the local reaction environment for CH_{2}O formation or reduces the binding energy of CH_{2}O produced via CH_{3}O dehydrogenation or both. Note that the high temperature CH_{3}OH peak centered near 380 K now only partially overlaps with the CH_{2}O desorption peak. The separation of CH_{2}O and CH_{3}OH peaks at high temperature further affirms that a coupled dehydrogenation and hydrogenation of CH_{3}O groups is the primary pathway for CH_{2}O and CH_{3}OH formation on the RuO_{2}(110) surface above 300 K, rather than disproportionation of CH_{3}O groups. TPRS results (not shown here) from CD_{3}OH oxidation on RuO_{2-x}Cl_{x}(110) also confirm that the coupled hydrogenation and dehydrogenation of CH_{3}O groups remains the dominant pathway for methanol oxidation on chlorinated RuO_{2}(110).

The CO_{2} TPRS spectra (Figure 5-3b) reveal that CO_{2} desorbs in a single peak near 490 K and Cl_{br} atoms on RuO_{2-x}Cl_{x}(110) strongly suppress complete oxidation of methanol to CO_{2}. In fact, we observe the CO_{2} yield decreases by ~30% at 0.30 ML Cl_{br} coverage relative to the s-RuO_{2}(110) and it further decreases by ~70% as the Cl_{br} coverage approaches saturation. In Chapter 4, we demonstrated that complete oxidation of CH_{3}OH to CO_{2} requires at least three free neighboring O_{br} atoms, and the reaction pathway for CO_{2} formation is independent of methanol coverage on the surface. The CO_{2} yields obtained from RuO_{2-x}Cl_{x}(110) are in excellent agreement with these assertions. For instance, RuO_{2-x}Cl_{x}(110) surface with 0.47 ML Cl_{br} atoms will have 0.53 ML free O_{br} atoms suggesting that maximum CO_{2} yield after complete oxidation of CH_{3}OH should be ~0.14 ML, which agrees well with the estimated CO_{2} yield of ~0.13 ML on RuO_{2-x}Cl_{x}(110) with 0.47 ML Cl_{br} atoms. These results combined together strongly indicate that
selective replacement of O\textsubscript{br} atoms by Cl\textsubscript{br} atoms on the RuO\textsubscript{2} surface essentially alters the local oxidative environment by reducing the number of O\textsubscript{br} trimer ensembles required to form key intermediate CH\textsubscript{2}O\textsubscript{2}, thereby leading to a sharp decrease in CO\textsubscript{2} yield. Formation of CH\textsubscript{2}O, on the other hand, has a lower stoichiometric dependency on O\textsubscript{br} sites, therefore, replacement of the bridging O atoms with Cl atoms suppresses CO\textsubscript{2} yield more than it does the CH\textsubscript{2}O yield. We find that CH\textsubscript{2}O:CO\textsubscript{2} yield ratio steadily increases with increasing Cl\textsubscript{br} coverage, however, the amount of reacted CH\textsubscript{3}OH decreases significantly above 50\% bridging site chlorination. For example, only 36\% of CH\textsubscript{3}OH in the monolayer reacts at 0.78 ML Cl\textsubscript{br} coverage and the CH\textsubscript{2}O:CO\textsubscript{2} yield ratio increases by a factor of 2.1, while 60\% of CH\textsubscript{3}OH in the monolayer reacts on s-RuO\textsubscript{2}(110) with CH\textsubscript{2}O:CO\textsubscript{2} ratio of 0.9. H\textsubscript{2}O TPRS spectra (Figure 5-3d) show that the H\textsubscript{2}O TPRS peak centered at 490 K observed during CH\textsubscript{3}OH oxidation on s-RuO\textsubscript{2}(110) severely diminishes due to chlorination and the H\textsubscript{2}O TPRS peaks centered at 370 and 575 K shift to lower temperatures with increasing Cl\textsubscript{br} coverage. Notably, the H\textsubscript{2}O desorption yield via low temperature peak (370 K) matches well with the CH\textsubscript{2}O desorption yield below 410 K, which suggests that dehydrogenation of CH\textsubscript{3}O groups on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) may promote increased formation of H\textsubscript{2}O at low temperature. The drop in the total H\textsubscript{2}O TPRS yield is obviously because of the decrease in the amount of CH\textsubscript{3}OH reacted on the surface.

5.3.2 Oxidation Selectivity vs. Cl\textsubscript{br} Coverage on s-RuO\textsubscript{2-x}Cl\textsubscript{x}(110)

Figure 5-4a shows the product yields of CO\textsubscript{2} and CH\textsubscript{2}O as a function of Cl\textsubscript{br} coverage after adsorbing 1 \pm 0.15 ML CH\textsubscript{3}OH on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surfaces at 89 K. We find that methanol reactivity on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) decreases with increasing Cl\textsubscript{br} coverage. CO\textsubscript{2} and CH\textsubscript{2}O yields decrease with increasing Cl\textsubscript{br} coverage but the decrease in CO\textsubscript{2} yield is much sharper than that the decrease CH\textsubscript{2}O yield. We estimate that the selectivity to CH\textsubscript{2}O increases by a factor of ~2 relative to s-RuO\textsubscript{2}(110) as Cl\textsubscript{br} coverage approaches saturation. Figure 5-4b shows fraction of
methanol oxidized per adsorbed CH$_3$OH molecule in the monolayer, fractional yields of CO$_2$ and CH$_2$O shown on the left ordinate axis and CH$_2$O:CO$_2$ ratio on the right ordinate axis plotted as function of Cl$_{br}$ coverage. The fractional yields of CO$_2$ and CH$_2$O are defined as the amount of CO$_2$ and CH$_2$O produced per CH$_3$OH molecule adsorbed on the RuO$_{2-x}$Cl$_x$(110) surface, respectively. All values are obtained after adsorbing 1 ± 0.15 ML CH$_3$OH on RuO$_{2-x}$Cl$_x$(110) surfaces at 89 K. It is evident that the fraction of adsorbed methanol that undergoes oxidation steadily decreases with increasing chlorination of the bridging sites. We find that methanol oxidation drops by ~30% compared with the s-RuO$_2$(110) surface after replacing 78% of bridging sites with Cl$_{br}$ atoms on the RuO$_{2-x}$Cl$_x$(110) surface. Fractional CO$_2$ yield steadily drops with the increasing chlorination as well, while the fractional CH$_2$O yield remains almost the same irrespective of the extent of chlorination. We find that 78% chlorination of the bridging sites on the RuO$_2$(110) surface reduces the CO$_2$ yield by 67% relative to the s-RuO$_2$(110) surface, while the CH$_2$O yield drops only by 35% leading to increased product selectivity toward CH$_2$O. Our experiments indicate that CH$_2$O:CO$_2$ ratio almost linearly increases with increasing chlorination. We find that the CH$_2$O:CO$_2$ yield ratio increases from ~0.9 to 1.9 as Cl$_{br}$ coverage increases to ~78%. Variation in oxidation selectivity with surface coverages may arise mainly from different dependencies of CH$_2$O formation vs. CH$_3$O dehydrogenation on the local O$_{br}$-atom coverage and distribution. These results show that oxidation selectivity can be varied over a wide range (CH$_2$O:CO$_2$ from 0.9 to 1.9) by changing surface composition.

5.3.3 CH$_3$OH oxidation on O-rich RuO$_{2-x}$Cl$_x$(110)

Figure 5-5 shows the TPRS spectra obtained after exposing 3.0 ML methanol on a 0.48 ML O$_{ot}$ atoms pre-covered RuO$_{2-x}$Cl$_x$(110) surface with 0.47 ML Cl$_{br}$ coverage. The TPRS data is representative of observed surface behavior due to presence of O$_{ot}$ species on the RuO$_{2-x}$Cl$_x$(110) surface. These TPRS results reveal that CH$_3$OH oxidation on the O-rich
RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface is similar to that on O-rich RuO\textsubscript{2}(110)\textsuperscript{112} and that the O\textsubscript{ot} atoms promote the evolution of H\textsubscript{2}O at low temperature and increase the selectivity toward the complete oxidation of methanol. CH\textsubscript{3}OH trace shows that the multilayer peak develops a shoulder at its trailing edge in presence of O\textsubscript{ot} atoms and CH\textsubscript{3}OH peak at 385 K has nearly disappeared. CH\textsubscript{2}O TPRS trace shows that the CH\textsubscript{2}O yield also decreases with increasing O\textsubscript{ot} coverage and the peak temperature shifts to lower temperatures. We estimate that ~0.14 ML CH\textsubscript{2}O desorbs in a small peak centered at 326 K on 0.48 ML O\textsubscript{ot} pre-covered RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface with 0.47 ML Cl\textsubscript{br} atoms. By integrating the CO\textsubscript{2} TPRS trace, we estimate that ~0.37 ML CO\textsubscript{2} desorbs in a sharp feature near 506 K. Interestingly, the CO\textsubscript{2} yield obtained from the 0.48 ML O\textsubscript{ot} pre-covered RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface is much higher than that obtained from s-RuO\textsubscript{2}(110) surface indicating that the pre-adsorbed O\textsubscript{ot} atoms nullify the effect of selective surface chlorination, and promote the formation of dioxyymethylene (CH\textsubscript{2}O\textsubscript{2}), the essential intermediate for complete oxidation of methanol. The CH\textsubscript{2}O:CO\textsubscript{2} ratio decreases to 0.4 as opposed to 1.7 on the RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface with 0.47 ML Cl\textsubscript{br} atoms. H\textsubscript{2}O TPRS trace shows that low temperature H\textsubscript{2}O desorption features centered at 362 K and 502 K are significantly enhanced in presence of O\textsubscript{ot} atoms. The H\textsubscript{2}O TPRS peak at 362 K is consistent with desorption-limited formation of H\textsubscript{2}O\textsubscript{ot} species via hydrogenation of O\textsubscript{ot} atoms.\textsuperscript{74,112} The H\textsubscript{2}O TPRS peak at 502 K is consistent with the reaction-limited desorption of H\textsubscript{2}O during CO\textsubscript{2} formation.

5.3.4 CH\textsubscript{3}OH oxidation on s-RuO\textsubscript{2-x}Cl\textsubscript{x}(110) at Low Coverage

We investigated CH\textsubscript{3}OH oxidation at 0.33 ML initial coverage on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) using TPRS. The idea behind the investigation is to understand the effect of Cl\textsubscript{br} atoms on kinetics of CH\textsubscript{3}OH oxidation on RuO\textsubscript{2-x}Cl\textsubscript{x}(110). In our recent work\textsuperscript{112}, we demonstrated that complete oxidation is strongly favored for low methanol coverages on s-RuO\textsubscript{2}(110), and almost all of the adsorbed methanol reacts with the surface up to 0.33 ML initial CH\textsubscript{3}OH coverages. The CO\textsubscript{2}
yield effectively saturates at 0.26 ML once the methanol coverage reaches ~0.33 ML on s-RuO$_2$(110). These results make the low coverage oxidation of methanol a great tool to observe changes in oxidation selectivity due to selective replacement of O$_{br}$ atoms by Cl atoms. Figure 5-6 shows TPRS spectra of CH$_3$OH, CH$_2$O, CO$_2$ and H$_2$O and product yields obtained after adsorbing ~0.33 ML CH$_3$OH on various RuO$_{2-x}$Cl$_x$(110) surfaces. The CH$_2$O TPRS spectra show that the CH$_2$O yield initially increases and reaches its maximum (~0.12 ML) at 0.47 ML Cl$_{br}$ coverage and then starts to decrease as Cl$_{br}$ coverage increases up to 50%. The CH$_2$O TPRS peak shifts toward lower temperature with increasing Cl$_{br}$ coverage. The H$_2$O TPRS spectra show that high temperature H$_2$O peak at 575 K diminishes and shifts toward lower temperature, while a low temperature peak start to appear below 375 K with increasing chlorination. Interestingly, the low temperature H$_2$O TPRS peaks coincide with corresponding CH$_2$O TPRS peak, and the H$_2$O desorption yield below 410 K is same as CH$_2$O yield suggesting that the evolution of CH$_2$O and the low temperature H$_2$O may involve common reaction steps. The CO$_2$ TPRS spectra show that CO$_2$ yield sharply decreases with increasing surface chlorination even at such low methanol coverages. As shown in Figure 5-6b, we estimate that the selectivity to partial oxidation of CH$_3$OH to CH$_2$O increases by almost a factor of 6 as the Cl$_{br}$ coverage approaches saturation, however the amount of reacted CH$_3$OH decreases by ~44% near Cl$_{br}$ saturation.

5.3.5 Atomic Arrangement of Bridging O and Cl atoms on s-RuO$_{2-x}$Cl$_x$(110)

TPRS results presented above demonstrate that product selectivity for oxidation of methanol on RuO$_{2-x}$Cl$_x$(110) strongly depends on availability of reactive O-atoms on the surface and Cl$_{br}$ atoms selectively suppress complete oxidation of methanol on s-RuO$_{2-x}$Cl$_x$(110). So, it is instructive to develop an understanding of the distribution of O and Cl atoms in bridging rows of RuO$_{2-x}$Cl$_x$(110) surface at different Cl$_{br}$ coverages because any change in local arrangement of O$_{br}$ and Cl$_{br}$ atoms will affect yields of CO$_2$ and CH$_2$O. We employed DFT and Monte Carlo
(MC) calculations to investigate the atomic arrangement of O and Cl atoms in bridging rows of s-RuO$_{2-x}$Cl$_x$(110) surface as a function of Cl$_{br}$ coverage. Preliminary DFT calculations predict that adjacent Cl$_{br}$ atoms (Cl-Cl configurations) within a row strongly repel (estimated configurational energy $E_{11} \sim 25$ kJ/mol) each other, while Cl-O-Cl configurations are moderately stabilized by $\sim 3-4$ kJ/mol suggesting that Cl$_{br}$ atoms will more likely be separated by an oxygen atom than paired up together. Preliminary DFT calculations further predict weak interaction across the chlorinated rows indicating that bridging rows can be modelled as one dimensional array by neglecting the interaction among bridging rows. We performed Monte Carlo simulations on a 1D periodic array consisting of total 5000 sites of O and Cl atoms using these approximates energies to determine the energetically preferred atomic arrangement of O and Cl atoms in a bridging row of s-RuO$_{2-x}$Cl$_x$(110). Figure 5-7 shows probability of various trimer configurations of Cl$_{br}$ and O$_{br}$ atoms on RuO$_{2-x}$Cl$_x$(110) surface as function of Cl$_{br}$ coverage after optimizing the 1D periodic array at 700 K using MC method. We denote O and Cl atom with digits 0 and 1, respectively. To improve the statistical accuracy and simplify the calculations, 1000 samples were collected to estimate trimer probabilities for each Cl$_{br}$ coverage assuming negligible interactions between bridging rows.

We find that probability of O$_{br}$ trimers ($P_{000}$) sharply decreases with increasing Cl$_{br}$ coverage and becomes zero above 0.50 ML Cl$_{br}$ coverage. Probability of oxygen dimer next to a Cl atom ($P_{100}$) slightly increases up to 0.5 ML Cl$_{br}$ coverage and essentially becomes zero above 0.5 ML. Probability of Cl trimers ($P_{111}$) remains zero up to 0.50 ML and begins to sharply increase above 0.50 ML Cl$_{br}$ coverage suggesting that Cl$_{br}$ atoms are less likely to cluster together at low Cl$_{br}$ coverage. These results are obvious because Cl-O-Cl configurations more stable than Cl-Cl paired configurations. Probability of O-Cl-O and Cl-O-Cl configurations ($P_{010}$
and $P_{101}$, on the other hand, increases as $Cl_{br}$ coverage reaches 0.50 ML, and decreases above 0.5 ML $Cl_{br}$ coverage. Notably, $P_{010}$ decreases much faster than $P_{101}$ because of increasing Cl concentration in the bridging row. Cl-Cl-O configurations are scarce up to 0.5 ML but increase sharply above 0.5 ML $Cl_{br}$ coverage reaching maximum at 0.7 ML followed by a sharp decrease. Overall, we find that the probability of alternating configuration (Cl-O-Cl and O-Cl-O) is enhanced significantly, causing a decrease in number of trimer containing adjacent oxygen atoms. These results provide important insight into preferred atomic arrangement of bridging rows due to surface chlorination because the availability of free $O_{br}$ atoms strongly affects the product distribution of methanol oxidation on s-RuO$_2$(110). Complete oxidation of methanol to CO$_2$ requires at least three free $O_{br}$ sites, which demands presence of two $O_{br}$ dimers (in adjacent rows) or trimers next to adsorbed methanol molecule. Partial oxidation of methanol to CH$_2$O, on the other hand, has much lower oxygen dependency and requires only a pair of free $O_{br}$ sites for the reaction to occur.

Increased desorption of methanol at high $Cl_{br}$ coverages suggests that surface chlorination weakens the interaction of methanol with Ru$_{cus}$ sites. However, the evolution of products from methanol oxidation on RuO$_2$-$x$Cl$_x$(110) is qualitatively similar to that on s-RuO$_2$(110) indicating that initial reaction steps for methanol adsorption are same on both surfaces. Following the reaction mechanism described in Chapter 4, we propose that CH$_3$OH molecule will deprotonate via following reaction if the neighboring bridge site is occupied by an oxygen atom,

$$\text{CH}_3\text{OH} - \text{Ru}_{cus} + O_{br} \rightarrow \text{CH}_3\text{O} - \text{Ru}_{cus} + \text{HO}_{br} \quad 5-1$$

CH$_3$OH molecule is more likely to molecularly adsorb on Ru$_{cus}$ next to a Cl$_{br}$ site resulting in low temperature CH$_3$OH TPRS peak during TPRS. Dehydrogenation and hydrogenation of CH$_3$O
groups via reaction with HO$_{br}$ and O$_{br}$ species will produce CH$_2$O, CH$_3$O and H$_2$O (at low temperature).

$$\text{CH}_3\text{O} - \text{Ru}_{\text{cus}} + \text{O}_{br} \rightarrow \text{CH}_2\text{O} - \text{Ru}_{\text{cus}} + \text{HO}_{br} \quad 5-2$$

$$2\text{HO}_{br} \rightarrow \text{H}_2\text{O}(g) + \text{O}_{br} + \text{V}_{br} \quad 5-3$$

$$\text{CH}_3\text{O} - \text{Ru}_{\text{cus}} + \text{HO}_{br} \rightarrow \text{CH}_3\text{OH} - \text{Ru}_{\text{cus}} + \text{O}_{br} \quad 5-4$$

Desorption of CH$_2$O, however, strongly depends on availability of free O$_{br}$ sites in its neighborhood. The adsorbed CH$_2$O species can diffuse along the Ru$_{\text{cus}}$ row until they find a free O$_{br}$ site to form CH$_2$O$_2$ intermediate leading to CO$_2$ formation. Therefore, presence of free O$_{br}$ site leads to competition between CH$_2$O desorption and CH$_2$O$_2$ intermediate formation,

$$\text{CH}_2\text{O} - \text{Ru}_{\text{cus}} \rightarrow \text{CH}_2\text{O}(g) + \text{Ru}_{\text{cus}} \quad 5-5$$

$$\text{CH}_2\text{O} - \text{Ru}_{\text{cus}} + \text{O}_{br} \rightarrow \text{O}_{br} - \text{CH}_2\text{O} - \text{Ru}_{\text{cus}} \quad 5-6$$

Formation of CH$_2$O$_2$ intermediate via reaction Eq. 5-6 becomes the rate limiting step for complete oxidation to CO$_2$. Using Eq. 5-2 to 5-6, we can scale CH$_2$O and CH$_2$O$_2$ yields with O$_{br}$ concentration on RuO$_{2-x}$Cl$_x$(110) surface via following equations,

$$[\text{CH}_2\text{O}] \sim [\text{O}_{br}] \sim (1 - [\text{Cl}_{br}] - [\text{HO}_{br}]) \quad 5-7$$

$$[\text{CH}_2\text{O}_2] \sim [\text{O}_{br}]^2 \sim (1 - [\text{Cl}_{br}] - [\text{HO}_{br}])^2 \quad 5-8$$

Note that Eq. 5-7 and 5-8 are simplified expressions to explain the dependency of oxidation kinetics on availability of O$_{br}$ and do not consider the kinetics of diffusion of species along the Ru$_{\text{cus}}$ row, local site distribution of O$_{br}$ and Cl$_{br}$ atoms and unsteady state conditions of TPRS. The scaling relationships in Equations 5-7 and 5-8 qualitatively describe the sharp decrease in CO$_2$ yield but fail to explain the increase in CH$_2$O yield at low methanol coverages. The reason is that in order to simplify the kinetics, we neglected many unsteady state reaction parameters such as change in coverage, temperature, removal of H-atom oxygen vacancy healing
process and local distribution of O\textsubscript{br} and Cl\textsubscript{br} atoms etc. Further theoretical analysis such as kinetic Monte Carlo simulations is required to investigate the effect of unsteady state oxidation of methanol and predict the ensemble effects of O\textsubscript{br} and Cl\textsubscript{br} atoms on methanol oxidation. CO\textsubscript{2} TPRS peaks obtained from methanol oxidation on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) and s-RuO\textsubscript{2}(110) are very similar which indicates that production of CO\textsubscript{2} via complete oxidation of methanol occurs via same reaction mechanism on both surfaces.

5.4 Summary

In conclusion, the RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface can efficiently adsorb and oxidize CH\textsubscript{3}OH despite the decrease in available O\textsubscript{br} sites on the surface. Although overall reactivity of RuO\textsubscript{2-x}Cl\textsubscript{x}(110) is decreased due to surface chlorination, selective replacement of bridging oxygen sites by Cl atoms on the RuO\textsubscript{2-x}Cl\textsubscript{x}(110) suppresses complete oxidation of CH\textsubscript{3}OH to CO\textsubscript{2}, while CH\textsubscript{2}O formation via partial oxidation of CH\textsubscript{3}OH is less affected even at high Cl\textsubscript{br} coverages. Our experiments show that CH\textsubscript{2}O yield remains almost unchanged relative to the s-RuO\textsubscript{2}(110) surface up to ~50\% Cl\textsubscript{br} coverage and decreases as Cl\textsubscript{br} coverage approaches saturation. CO\textsubscript{2} yield, on the other hand, sharply decreases with increasing Cl\textsubscript{br} coverage. Monte Carlo calculations for site arrangement of O and Cl atoms in the bridging row show that the number of trimers containing adjacent O\textsubscript{br} atoms decreases with increasing Cl\textsubscript{br} coverage, while probabilities of alternating configurations such as Cl-O-Cl and O-Cl-O are enhanced significantly. These alterations in local bridging site arrangement due to surface chlorination cause sharp decrease in CO\textsubscript{2} yield via complete oxidation of CH\textsubscript{3}OH without severely affecting partial oxidation to CH\textsubscript{2}O. We demonstrate that partial surface chlorination can modify reaction selectivity when the site requirements differ among competing reaction channels.
Figure 5-1. Schematic representation of chlorination process of RuO$_2$(110) surface. The s-RuO$_2$(110) surface, upon exposure to HCl at 700 K, transforms into RuO$_{2-x}$Cl$_x$(110) surface (right) where O$_{br}$ atoms are replaced by Cl atoms (Cl$_{br}$). The RuO$_{2-x}$Cl$_x$(110) surface is thermally stable up to 800 K.
Figure 5-2. XPS Cl 2p spectra obtained from RuO$_{2-x}$Cl$_x$(110) surface with various Cl$_{br}$ coverages. We prepared various RuO$_{2-x}$Cl$_x$(110) surfaces by performing HCl exposures ranging from 0.05 L to 2.5 L on RuO$_2$(110) surface at 700 K. An exposure of 2.5 ML HCl yields Cl$_{br}$ saturation at 0.80 ML.
Figure 5-3. TPRS spectra after CH$_3$OH adsorption on RuO$_2$:Cl$_x$(110) surface at 89 K. TPRS spectra of (a) CH$_3$OH, (b) CO$_2$, (c) CH$_2$O and (d) H$_2$O obtained from RuO$_2$:Cl$_x$(110) surfaces after dosing ~1.0 ML CH$_3$OH at a substrate temperature of 89 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 

![Graphs showing TPRS spectra for CH$_3$OH, CO$_2$, CH$_2$O, and H$_2$O adsorption on RuO$_2$:Cl$_x$(110) surface.](image-url)
Figure 5-4. Oxidation selectivity as a function of Cl\textsubscript{br} coverage. (a) Product yields as function of Cl\textsubscript{br} coverage and (b) Fractional yields of CO\textsubscript{2} and CH\textsubscript{2}O, and fraction of methanol oxidized per adsorbed methanol molecule (left ordinate axis) and CH\textsubscript{2}O/CO\textsubscript{2} ratio (right ordinate axis) as function of percentage Cl\textsubscript{br} coverage on chlorinated RuO\textsubscript{2}(110) surface.
Figure 5-5. TPRS spectra after CH$_3$OH adsorption on O-rich RuO$_2$-$\alpha$Cl$_x$(110) surface at 89 K. TPRS spectra of CH$_3$OH, CH$_2$O, H$_2$O, CO$_2$, and CH$_3$OCHO obtained after adsorbing saturation coverage of methanol on the 0.48 ML O$_{\alpha}$ pre-covered RuO$_2$-$\alpha$Cl$_x$(110) surface with 0.47 ML Cl$_{br}$ at substrate temperature of 88 K. The TPRS spectra were obtained using a constant heating rate of 1 K s$^{-1}$. 
Figure 5-6. TPRS spectra obtained after adsorbing 0.33 ML CH₃OH on various RuO₂₋ₓClₓ(110) surfaces at 89 K. (a) TPRS spectra and (b) product yields plotted as a function Clbr coverages obtained after adsorbing 0.33 ML CH₃OH on various RuO₂₋ₓClₓ(110) surfaces at 89 K. The TPRS spectra were obtained using a constant heating rate of 1 K s⁻¹.

(a) TPRS
CH₃OH + RuO₂₋ₓClₓ(110)
[CH₃OH]₀ = 0.33 ML
Tₛ = 89 K

Desorption rate (a.u.)

(b) TPRS Yields
CH₃OH + RuO₂₋ₓClₓ(110)
[CH₃OH]₀ = 0.33 ML
Tₛ = 89 K

TPRS
Yield (ML)

Total CH₃OH reacted

CO₂

CH₂O

CH₃OH

H₂O

Desorption rate (a.u.)

Temperature (K)

H₂O₂₀s_s-RuO₂
CH₃OH₂₀s_s-RuO₂
CH₂O₂₀s_s-RuO₂
CO₂₂₀s_s-RuO₂
H₂O₂₀s_RuO₂₀.₃₀ML_Clbr
CH₃OH₂₀s_RuO₂₀.₃₀ML_Clbr
CH₂O₂₀s_RuO₂₀.₃₀ML_Clbr
CO₂₂₀s_RuO₂₀.₃₀ML_Clbr
H₂O₂₀s_RuO₂₀.₄₇ML_Clbr
CH₃OH₂₀s_RuO₂₀.₄₇ML_Clbr
CH₂O₂₀s_RuO₂₀.₄₇ML_Clbr
CO₂₂₀s_RuO₂₀.₄₇ML_Clbr
H₂O₂₀s_RuO₂₀.₇₈ML_Clbr
CH₃OH₂₀s_RuO₂₀.₇₈ML_Clbr
CH₂O₂₀s_RuO₂₀.₇₈ML_Clbr
CO₂₂₀s_RuO₂₀.₇₈ML_Clbr
Figure 5-7. Probability of various trimer configurations of Cl\textsubscript{br} and O\textsubscript{br} atoms on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface as function of Cl\textsubscript{br} coverage. A 1D Lattice with total 5000 sites consisting of Cl\textsubscript{br} and O\textsubscript{br} atoms was optimized at 700 K using Monte Carlo method to obtain trimer probabilities at different Cl\textsubscript{br} coverages. 1000 samples were collected to estimate trimer probabilities for each Cl\textsubscript{br} coverage. 1: Cl-atom and 0: O-atom.
CHAPTER 6
CONCLUSION

We investigated growth and properties of multilayer oxide layers prepared by oxidizing Ir and Ru single crystals using gas-phase atomic oxygen beam. We employed temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) and ion scattering spectroscopy (ISS) to explore the structural properties of prepared oxygen phases. TPRS investigations after adsorbing probe molecules such as H\textsubscript{2}O, CO and CH\textsubscript{3}OH provide insights into oxidative properties of these surfaces.

Oxidation of Ir(100) surface between 300 K and 625 K using gas-phase oxygen atom beam in UHV environment shows that oxygen coverages as high as 3.4 ML (monolayers) can be developed on Ir(100) surface at substrate temperatures up to 500 K. Our results indicate that adsorption of oxygen and subsequent development of various oxygen phases on the Ir(100) are relatively insensitive to the surface temperature up to 500 K. A meta-stable 2D surface oxide with (4 × 4) periodicity develops on the Ir(100) substrate above 0.8 ML oxygen coverage that kinetically stabilized at surface temperatures up to 673 K. The surface oxide phase transforms into a new structure upon heating to 673 K that yields a (2 × 1) pattern overlapping with a unique square pattern around each substrate spot that is rotated at ~45° relative to the substrate spots. Oxygen coverages above 2.1 ML produce sharp and explosive O\textsubscript{2} TPD desorption features near 725 K that is consistent with decomposition of a multilayer oxide, however this peak temperature is significantly lower than the decomposition temperature of IrO\textsubscript{2}(100) or IrO\textsubscript{2}(110) layers reported in literature. LEED observations from these high concentration phases exhibit only a (1 × 1) pattern similar to chemisorbed oxygen layer on an unreconstructed Ir(100) surface. The (1 × 1) LEED pattern from these high coverages also transforms into the (2 × 1) pattern overlapping with the square pattern around each substrate spot rotated at ~45° relative to the substrate spots.
after annealing to 673 K. Our experiments indicate that these high concentration oxygen phases are chemically inactive toward adsorption and oxidation of CO and propane. The observed behavior of oxidized Ir(100) surface in our experiments is similar to chemisorbed oxygen overlayers on the Ru(0001) surface with dissolved oxygen, however TPD and LEED data indicates formation of multilayer IrO$_x$ structures. Additional studies such as low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM) can shed light on the exact structure of these oxygen phases on Ir(100).

We also investigated the oxidation of Ir(111) by gas-phase oxygen atoms at temperatures between 500 and 625 K using temperature programmed desorption (TPD), low energy electron diffraction (LEED), low energy ion scattering spectroscopy (LEISS) and density functional theory (DFT) calculations. We find that a well-ordered surface oxide with $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity relative to Ir(111) develops prior to the formation of a rutile IrO$_2$(100) layer. The IrO$_2$(100) layer saturates at thickness of about four oxide layers under the oxidation conditions employed, and decomposes during TPD to produce a single, sharp O$_2$ desorption peak at ~770 K. Favorable lattice matching at the oxide-metal interface is likely responsible for the preferential growth of the IrO$_2$(100) facet during the initial oxidation of Ir(111), with the resulting coincidence lattice generating a clear $(6 \times 1)$ moiré pattern in LEED. Temperature programmed reaction spectroscopy (TPRS) experiments reveal that CO and H$_2$O molecules bind only weakly on the IrO$_2$(100) surface and LEISS measurements show that the oxide surface is highly enriched in O-atoms. These characteristics provide strong evidence that the rutile IrO$_2$(100) layer is oxygen-terminated, and thus lacks reactive Ir atoms that can strongly bind molecular adsorbates. Oxygen binding energies predicted by DFT suggest that on-top O-atoms will remain adsorbed on IrO$_2$(100) at temperatures up to ~625 K, thus supporting the conclusion that the rutile IrO$_2$ layer
grown in our experiments is oxygen-terminated. As such, the appearance of only a single O2 TPD peak indicates that the singly coordinate, on-top O-atoms remain stable on the IrO2(100) surface up to temperatures at which the oxide layer begins to thermally decompose. LEED also provides evidence of formation of small domains of IrO2(110) that coexist with IrO2(100) structure prepared at 625 K.

Interestingly, IrO2(110) formation is observed only after formation of IrO2(100) on the Ir(111) surface. It is likely that IrO2(100) may act as nucleation centers for the growth of IrO2(110) during the early phases of oxidation. Our investigation into oxidation of Ir(100) and Ir(111) surfaces under UHV conditions using gas-phase atomic oxygen beam indicates that preparation of well-defined IrO2(110) with exposed Ir\text{cux} and O\text{br} atoms on metallic Ir surface requires surface temperature above 650 K and much higher oxidant flux than employed in our experiments in order to overcome the kinetic limitations of oxidation. In fact, our group has recently demonstrated that a high-quality IrO2(110) layer can be grown by oxidizing Ir(100) at 775 K and an O2 partial pressure of 5 torr.\textsuperscript{26} The IrO2(110) layer in these experiment readily promotes C-H bond cleavages in CH4 at temperatures as low as 150 K, however detailed mechanism of IrO2(110) formation is still unknown. A future work can be dedicated to investigate the oxidation process to establish minimum temperature and oxygen partial pressure to produce a conformal IrO2(110) layer. More work will be required to explore the physical and chemical properties of this surface. DFT can a useful tool to predict the reactivity of IrO2(110) toward various molecules such as methanol, H2O, alkanes etc.

We employed temperature-programmed reaction spectroscopy (TPRS) to investigate the adsorption and oxidation of methanol on stoichiometric and O-rich RuO2(110) surfaces as well as RuO2-xClx(110) surface. We find that the complete oxidation of CH3OH is strongly preferred
on stoichiometric RuO$_2$(110) during TPRS for initial CH$_3$OH coverages below ~0.33 ML and that partial oxidation to mainly CH$_2$O becomes increasingly favored with increasing CH$_3$OH coverage from 0.33 to 1.0 ML. Our supports formation of an intrinsically facile adsorbed CH$_3$O$_2$ species as the key intermediate to complete oxidation that becomes limited by the availability of bridging O-atoms on stoichiometric RuO$_2$(110) at initial CH$_3$OH coverages above 0.33 ML. We show that methanol molecules adsorbed in excess of 0.33 ML dehydrogenate to mainly CH$_2$O and desorb during TPRS, with adsorbed CH$_3$O groups mediating the evolution of both CH$_2$O and CH$_3$OH. We find that O-rich RuO$_2$(110) surfaces are also highly active toward methanol oxidation and that selectivity toward the complete oxidation of methanol increases markedly with increasing coverage of on-top O-atoms (O$_{ot}$) on RuO$_2$(110). CH$_3$OH species adsorbed within O$_{ot}$-rich domains react efficiently during TPRS, in parallel with reaction of CH$_3$OH adsorbed initially on Ru sites. The data suggests that the facile hydrogenation of O$_{ot}$ atoms and the resulting desorption of H$_2$O at low-temperature provides an efficient pathway for restoring reactive O-atoms and thereby promoting complete oxidation of methanol on the O-rich RuO$_2$(110) surface. Our results demonstrate that O$_{ot}$ is more strongly adsorbed on the surface, and therefore instead of displacing the on-top O-atoms, CH$_3$OH (weakly) binds with O$_{ot}$ species above 50% O$_{ot}$ coverages resulting in increased low temperature CH$_3$OH desorption peaks and low CO$_2$ yield.

We find that availability of free O$_{br}$ atoms plays a crucial role in oxidation of CH$_3$OH, and CH$_3$OH:(O$_{br}$ and/or O$_{ot}$) ratio on the surface determines yields of various oxidation products. TPRS experiments to explore CH$_3$OH adsorption and oxidation on RuO$_{2-x}$Cl$_x$(110) surface demonstrate that product selectivity (CH$_2$O:CO$_2$ ratio) can be altered by regulating the RuO$_2$(110) surface composition. Selective replacement of bridging O atoms by Cl atoms
remarkably suppresses complete oxidation of methanol without strongly affecting partial oxidation. The data suggests that surface chlorination alters local oxidative environment for complete oxidation by reducing the number of available O$_{br}$ atoms required to form key intermediate CH$_2$O$_2$, thereby leading to a sharp decrease in CO$_2$ yield. Additional investigation is needed to identify reaction mechanism of methanol oxidation on chlorinated RuO$_2$. DFT can provide valuable insights into the oxidation methanol on the chlorinated RuO$_2$ surface. We demonstrate in chapter 4 and 5 that the CH$_2$O:CO$_2$ ratio from CH$_3$OH oxidation on RuO$_2$-$_x$Cl$_x$(110) surface can be altered from 0 to ~2 by changing the concentration of various surface species such as O$_{br}$, Cl$_{br}$, O$_{ot}$ and CH$_3$OH. We demonstrate that partial chlorination can modify reaction selectivity when competing reaction channels have different site requirements. Further work is required to explain unsteady state conditions of oxidation and obtain additional information the oxidative properties of the RuO$_2$-$_x$Cl$_x$(110) surface. Additionally, we can investigate the prospects of preparing IrO$_2$-$_x$Cl$_x$(110) surface and explore the effects of surface chlorination of IrO$_2$(110) surface. Results presented in Chapter 4 and 5 may provide insightful comparisons about the growth and surface chemistry of these IrO$_2$-$_x$Cl$_x$(110) surfaces.
APPENDIX A
PREPARATION OF STOICHIOMETRIC AND OXYGEN-RICH RuO$_2$(110) SURFACES

A.1 Preparation of a Stoichiometric RuO$_2$(110) thin film on Ru(0001) by Gaseous O-Atoms

We prepared conformal RuO$_2$(110) thin films on Ru(0001) surface under UHV conditions using gas-phase atomic oxygen as oxidant. In order to find the optimal substrate temperature for oxidation, we initially oxidized the Ru(0001) surface at different substrate temperatures using a constant amount of atomic oxygen. O$_2$ TPD experiments show that oxidation of Ru(0001) below 700 K is limited by diffusion of sufficient oxygen atoms into the lattice to react with the lattice Ru atoms. Ru oxidation increases significantly at 800 K but LEED images reveal that the RuO$_2$(110) layer produced at 800 K has extremely rough morphology. We find that oxidation of Ru(0001) at 750 K generates highly crystalline and conformal RuO$_2$(110) film that is suitable for our experiments.

Figure A-1 shows O$_2$ TPD spectrum obtained after oxidizing Ru(0001) at 750 K using ~76 ML$_{Ru(0001)}$ gaseous O-atoms supplied by the atomic oxygen beam. Oxygen desorbs in sharp explosive peak at 1042 K that is consistent with formation of rutile RuO$_2$ layer. By integrating the O$_2$ TPD spectrum, we estimate that the RuO$_2$ layer consists of ~18 ML$_{Ru(0001)}$ oxygen atoms. LEED observations (Figure A-1 inset) combined with the O$_2$ TPD show that such exposure repeatedly produces a stoichiometrically-terminated (s-) RuO$_2$(110) film without any observable (1 × 1) domain indicating a conformal RuO$_2$(110) layer across the Ru(0001) substrate.

A.2 Restoration of reduced RuO$_2$(110) thin film

Oxidation of adsorbed methanol on s-RuO$_2$(110) reduces the oxide surface by consuming the O$_{br}$ atoms. We restored the reduced oxide surface by exposing it to 5 L O$_2$ at 750 K. CO adsorption and oxidation experiments on s-RuO$_2$(110), heavily reduced and restored s-
RuO$_2$(110) surfaces demonstrate that this method effectively fills the bridging oxygen vacancies and the restored s-RuO$_2$(110) surface is as reactive as the original s-RuO$_2$(110).$^{93}$

### A.3 Preparation of a O-rich RuO$_2$(110) thin films

We employed procedures available in literature to prepare O-rich RuO$_2$(110) surfaces with various on-top oxygen (O$_{ot}$) coverages.$^{8,115}$ Figure A-2 shows the O$_2$ TPD spectra obtained after preparing O$_{ot}$ coverages ranging between 11 to 86% on the RuO$_2$(110) surface. We first exposed the s-RuO$_2$(110) surface to 1 L O$_2$ at 300 K which produces a saturation O$_{ot}$ coverage$^8$ of 0.86 ML ($1 \text{ ML} = \text{Ru}_{\text{cub}}$ surface atom density = $5.024 \times 10^{14} \text{ cm}^{-2}$). The O$_{ot}$ saturated RuO$_2$(110) surface is then annealed to various temperatures in order to obtain desired O$_{ot}$ coverage by desorbing the excess O$_{ot}$. Table A-1 lists O$_{ot}$ coverages prepared on RuO$_2$(110) surface as function of the annealing temperatures.

<table>
<thead>
<tr>
<th>$T_{\text{anneal}}$ (K)</th>
<th>O$_{ot}$ (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>455</td>
<td>0.11</td>
</tr>
<tr>
<td>430</td>
<td>0.22</td>
</tr>
<tr>
<td>415</td>
<td>0.32</td>
</tr>
<tr>
<td>400</td>
<td>0.48</td>
</tr>
<tr>
<td>390</td>
<td>0.60</td>
</tr>
<tr>
<td>380</td>
<td>0.71</td>
</tr>
<tr>
<td>No annealing</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Figure A-1. O₂ TPD and LEED image of s-RuO₂(110) layer prepared on Ru(0001) surface. O₂ TPD and LEED image (inset) obtained after oxidizing Ru(0001) at 750 K using plasma generated atomic oxygen beam to generate 18 ML_Ru(0001) oxygen coverage. LEED observations confirms formation of a conformal RuO₂(110) layer under these conditions.
Figure A-2. O$_2$TPD obtained from various O$_{ot}$ coverages on RuO$_2$(110) surface. We prepared O-rich RuO$_2$(110) surfaces by 1 L O$_2$ exposure (black) at 300 K, followed by annealing to different temperatures to obtain desired O$_{ot}$ coverage by desorbing excess O$_{ot}$. 

<table>
<thead>
<tr>
<th>O$_{ot}$ (ML)</th>
<th>T$_{anneal}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td>0.71</td>
<td>380</td>
</tr>
<tr>
<td>0.60</td>
<td>390</td>
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<tr>
<td>0.48</td>
<td>400</td>
</tr>
<tr>
<td>0.32</td>
<td>415</td>
</tr>
<tr>
<td>0.22</td>
<td>430</td>
</tr>
<tr>
<td>0.11</td>
<td>455</td>
</tr>
</tbody>
</table>
APPENDIX B

STABILITY OF Cl\textsubscript{br} ATOMS ON RuO\textsubscript{2-x}Cl\textsubscript{x}(110) SURFACE

We performed repeated cycles of methanol adsorption and oxidation on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface to investigate the stability of RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surfaces. We find that RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surfaces with Cl\textsubscript{br} coverage above 0.5 ML lose Cl atoms with successive CH\textsubscript{3}OH exposures and Cl\textsubscript{br} coverage decreases to \sim 0.5 ML after 3 CH\textsubscript{3}OH exposures (Figure B-1). Figure B-2a shows a series TPRS spectra obtained after adsorbing 1 ML CH\textsubscript{3}OH on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) with 0.44 ML Cl\textsubscript{br} atoms at 89 K. It is evident from TPRS spectra that surface behavior remains unaltered after multiple TPRS cycles. We measured Cl\textsubscript{br} concentration on the surface before and after TPRS cycles by collecting Cl 2p XPS spectra. We estimate using the Cl 2p XPS spectra (Figure B-2b) that Cl\textsubscript{br} coverage decreases by from 0.44 ML to 0.36 ML after four consecutive TPRS cycles. These results indicate that Cl\textsubscript{br} atoms on RuO\textsubscript{2-x}Cl\textsubscript{x}(110) are stable below 0.5 ML coverage under the conditions explored.

![Cl 2p XPS spectra of RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface before and after successive CH\textsubscript{3}OH exposures. XPS spectra show that the original RuO\textsubscript{2-x}Cl\textsubscript{x}(110) surface with 0.78 ML Cl\textsubscript{br} atoms loses \sim40\% of Cl\textsubscript{br} atoms after 3 successive CH\textsubscript{3}OH exposures.](image)
Figure B-2. Stability of Cl$_{br}$ atoms on RuO$_{2-x}$Cl$_x$(110) surface. (a) Three consecutive TPRS spectra obtained after adsorbing 1 ML CH$_3$OH on RuO$_{2-x}$Cl$_x$(110) with 0.44 ML Cl$_{br}$ atoms at 89 K with 1 K/s heating rate. (b) Cl 2p XPS spectra of RuO$_{2-x}$Cl$_x$(110) before and after multiple cycles of CH$_3$OH adsorption and TPRS.
APPENDIX C
PYTHON SCRIPT TO OBTAIN TRIMER PROBABILITIES AT DIFFERENT Clbr COVERAGES USING MONTE CARLO METHOD

import numpy as np
import numpy.random as ran
import matplotlib.pyplot as plt
import sympy as sym
from IPython import get_ipython
get_ipython().run_line_magic('matplotlib', 'inline')

#matplotlib inline
sym.init_printing()
#plt.rc('text', usetex=True)
#plt.rc('font', family='serif')
fig, trimercnt = plt.subplots(figsize=(16,8))

def lattice(S0, Clcov):
    A = [0] * S0
    if Clcov <= S0/2:
        n=0
        for i in range(Clcov):
            if n < 2*Clcov:
                A[n] = 1
                n+=1
    else:
        n=0
        halfCl = S0/2
        for i in range(halfCl):
            if n < 2*halfCl:
                A[n] = 1
                n+=2
        Clrest = Clcov - halfCl
        m =1
        for i in range(Clrest):
            if m < 2*Clrest:
                A[m] = 1
                m+=2
    return A

def energy(Ai, S, Cl):
    """energy of a specific 1D configuration""
    E11 = 25
    E101 = -3
    # E111 = 45
    Ai = lattice(S, Cl)
    Enet = 0
    for j in range(S):
        print j, Enet
        xl = Ai[j]
        if j == 0:
            l1 = Ai[0]
            l2 = Ai[1]
if j+2 < S:
    x3 = Ai[j + 2]
    x2 = Ai[j + 1]
elif j+1 < S:
    x2 = Ai[j + 1]
    if j+2 == S:
        x3 = l1
else:
    if j == S-1:
        x2 = l1
        x3 = l2
if x1 == 1 and x2 == 1:
    Enet += E11
elif x1 == 1 and x2 == 0 and x3 == 1:
    Enet += E101
else:
    # print "final else j = ", j, "(j + 1)th atom is x1 = ", x1
    Enet += 0
    # print "ENERGY LOOP: Ai IS ", Ai, "energy: Enet = ", Enet
return Enet

# calculate number of trimers for a given lattice"
def trimers(Ax):
    s= len(Ax)
    N111 = 0
    N110 = 0
    N101 = 0
    N011 = 0
    N100 = 0
    N010 = 0
    N001 = 0
    N000 = 0
    for j in range(s):
        x1 = Ax[j]
        if j == 0:
            l1 = Ax[0]
            l2 = Ax[1]
        if j+2 < s:
            x3 = Ax[j + 2]
            x2 = Ax[j + 1]
        elif j+1 < s:
            x2 = Ax[j + 1]
            if j+2 == S:
                x3 = l1
        else:
            if j == S-1:
                x2 = l1
                x3 = l2
        if x1 == 1 and x2 == 1:
N111 += 1
elif x1 == 1 and x2 == 0 and x3 == 1:
    N101 += 1
elif x1 == 1 and x2 == 1 and x3 == 0:
    N110 += 1
elif x1 == 0 and x2 == 1 and x3 == 1:
    N011 += 1
elif x1 == 1 and x2 == 0 and x3 == 0:
    N100 += 1
elif x1 == 0 and x2 == 1 and x3 == 0:
    N010 += 1
elif x1 == 0 and x2 == 0 and x3 == 1:
    N001 += 1
elif x1 == 0 and x2 == 0 and x3 == 0:
    N000 += 1

#    print "TRIMER LOOP: Ai IS - ", Ax
#    print "N111 =", N111
#    print "N110 =", N110
#    print "N101 =", N101
#    print "N011 =", N011
#    print "N100 =", N100
#    print "N010 =", N010
#    print "N001 =", N001
#    print "N000 =", N000

return N111, N101, N110, N011, N100, N010, N001, N000

########################################################

#    def mcloop(A, S0, Clcov, T, M):
#    # Begin MC Loop
#    acc = 0
#    ind = 0
#    for k in range(M):
#        print "MC step# =", k
#        E1 = energy(A, S0, Clcov)
#        E2 = E1
#        p = ran.randint(0, S0)
#        q = ran.randint(0, S0)
#        print "p =", p, "q =", q
#        s1 = A[p]
#        s2 = A[q]
#        if A[p] != A[q]:
#            if A[p] == 1:
#                A[p] = 0
#                A[q] = 1
#                ind = 1
#            else:
#                A[p] = 1
#                A[q] = 0
#                ind = 1
#        print "A[p] changed to 0 and A[q] changed to 1"
#        else:
#            A[p] = 1
#            A[q] = 0
#            ind = 1
#        print "A[p] changed to 1 and A[q] changed to 0"
#        E2 = energy(A, S0, Clcov)
# dE = E2 - E1
# print "MC step# =", k, "dE =", dE, "E2 = ", E2, "E1 = ", E1
else:
    dE = E2 - E1
#
# n = ran.random()
#
# if dE <= 0 and ind == 1:
#     A = A2
#     E = E2
#     acc += 1
#     print "MC step# =", k, "A2 and E2 accepted; dE<=0; dE =", dE,
#            "E2 = ", E2, "E1 = ", E1, "E = ", E
# elif np.exp(-1 * dE/(1.38E-23*T)) > n and ind == 1:
#     A = A2
#     E = E2
#     acc += 1
#     print "MC step# =", k, "A2 and E2 accepted; random acceptance
else:
    if ind == 1:
        A[p] = s1
        A[q] = s2
        Ex = energy(A, S0, Clcov)
        if Ex == E1:
            E = E1
            ind = 0
            print "Total accepted MC steps", acc, "out of", M

return A, E

def main():
    S0 = input("Enter 1D lattice size: ")
    Clcov = input("Enter a number for Cl coverage smaller than lattice size: ")
    T = input("Enter the temperature in K: ")
    M = input("Enter the number of Monte Carlo steps: ")
    S = input("Enter the number of samples: ")
    lstN111 = []
lstN110 = []
lstN101 = []
lstN011 = []
lstN100 = []
lstN010 = []
lstN001 = []
lstN000 = []
lstEnergy = []
    A = lattice(S0, Clcov)
    A0 = A
    print "Original 1D lattice: ", A0
    E = energy(A, S0, Clcov)
    print "Original lattice energy E0 = ", E
firstM = S0*100
if firstM < 1000:
    firstM = 1000
A, E = mcloop(A, S0, Clcov, T, firstM)
print "Sample# =1"
print "Lattice A:", A, "Energy =", E

# print "populating list for trimers"
N111, N101, N110, N011, N100, N010, N001, N000 = trimers(A)
lstN111.append(N111)
lstN110.append(N110)
lstN101.append(N101)
lstN011.append(N011)
lstN100.append(N100)
lstN010.append(N010)
lstN001.append(N001)
lstN000.append(N000)
lstEnergy.append(E)

for s in range(S-1):
    A, E = mcloop(A, S0, Clcov, T, M)
    print "Sample# =", s+2,
    print "Lattice A:", A, "Energy =", E
    # print "populating list for trimers"
    N111, N101, N110, N011, N100, N010, N001, N000 = trimers(A)
    lstN111.append(N111)
lstN110.append(N110)
lstN101.append(N101)
lstN011.append(N011)
lstN100.append(N100)
lstN010.append(N010)
lstN001.append(N001)
lstN000.append(N000)
lstEnergy.append(E)

##
print "lstN111 =", lstN111
print "lstN110 =", lstN110
print "lstN101 =", lstN101
print "lstN011 =", lstN011
print "lstN100 =", lstN100
print "lstN010 =", lstN010
print "lstN001 =", lstN001
print "lstN000 =", lstN000
print "lstEnergy =", lstEnergy

xE = [x for x in lstEnergy]
yN111 = [x for x in lstN111]
yN101 = [x for x in lstN101]
yN110 = [x for x in lstN110]
yN011 = [x for x in lstN011]
yN100 = [x for x in lstN100]
yN010 = [x for x in lstN010]
yN001 = [x for x in lstN001]
yN000 = [x for x in lstN000]

xmin = min(lstEnergy)
xmax = max(lstEnergy)
ymax = max(lstN111 + lstN101 + lstN110 + lstN011 + lstN100 + lstN010 + lstN001 + lstN000)

trimercnt.plot(xE, yN111, 'ks', markersize=10, label=r'$N_{111}$')
trimercnt.plot(xE, yN101, 'rs', markersize=10, label=r'$N_{101}$')
trimercnt.plot(xE, yN110, 'r^', markersize=15, label=r'$N_{110}$')
trimercnt.plot(xE, yN011, 'r*', markersize=15, label=r'$N_{011}$')
trimercnt.plot(xE, yN010, 'g*', markersize=15, label=r'$N_{010}$')
trimercnt.plot(xE, yN100, 'gs', markersize=10, label=r'$N_{100}$')
trimercnt.plot(xE, yN001, 'g^', markersize=15, label=r'$N_{001}$')
trimercnt.plot(xE, yN000, 'bs', markersize=10, label=r'$N_{000}$')
trimercnt.legend(loc='best', fontsize=18)
trimercnt.set_ylim(-100, ymax + 100)
trimercnt.set_xlim(xmin-10, xmax +10)
trimercnt.grid(b=True, color='k', linestyle='-.')
trimercnt.set_xlabel('Configurational energy (kJ/mol Cl)', fontname="Times New Roman", fontweight="bold", fontsize=18)
trimercnt.set_ylabel('Counts (a.u.)', fontname="Times New Roman", fontweight="bold", fontsize=18)
title = "1D lattice with %s Cl-atoms and %s O-atoms" % (Clcov, S0-Clcov)
plt.title(title, fontname="Times New Roman", fontweight="bold", fontsize=18)

plt.show()
REFERENCES


97. NIST Mass Spec Data Center and d. S.E. Stein.


BIOGRAPHICAL SKETCH

Rahul (Rai) was born in Azamgarh (now Mau), India to Vidya and Sheshnath Rai. He was raised in Barmer, Rajasthan, where he graduated top of his high school class in 1999. After receiving his undergraduate degree in chemical engineering from Sardar Vallabhbhai National Institute of Technology, Surat in 2005, he went on to work as Senior Consultant for IT multinational Capgemini in its credit cards and banking domain. He enrolled for his master’s degree in chemical engineering at University of Florida in spring of 2012. During his tenure as a master’s student, he investigated \( \text{H}_2\text{O} \) formation pathways after \( \text{H}_2 \) chemisorption on \( \text{PdO}(101) \) surface using \textit{ab initio} quantum mechanical methods (DFT-D3) under the guidance of Dr. Jason F. Weaver. Rahul earned his M.S. (thesis) degree in chemical engineering in August 2013. He was offered an opportunity to investigate the growth and reactivity of iridium oxide surfaces under ultra-high vacuum conditions, while pursuing his doctoral degree in chemical engineering at UF. He received his PhD degree in August 2017.