The Partial Oxidation of Propene to Acrolein
Over Single-Crystal Cu$_2$O

by

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(ABSTRACT)

The partial oxidation of propene (CH$_2$=CHCH$_3$) to acrolein (CH$_2$=CHCHO) has been studied over Cu$_2$O(100) and (111) single crystal surfaces. Propene adsorption under ultra-high vacuum conditions yields no significant oxidation products, but the propene desorption temperatures are sensitive to the structural differences in the surfaces.

Propene adsorption at atmospheric pressure followed by thermal desorption in ultrahigh vacuum demonstrates that propene may be activated at higher pressures. Over the nonpolar Cu$_2$O(111) surface, lattice oxygen insertion occurs at 300 K and 1 atm. with the formation of the σ-bonded allyl intermediate. Once formed, this specie is stable in ultrahigh vacuum and produces acrolein during TDS via a reaction-limited process. A comparison of these data with studies of allyl alcohol decomposition over Cu$_2$O surfaces indicate that the σ-bonded intermediate is surface allyloxy (CH$_2$=CH-CH$_2$O·) which dehydrogenates to acrolein via hydride elimination on the carbon α to the oxygen. Thus, oxygen insertion precedes the final hydrogen abstraction in the partial oxidation pathway. Propene is also observed during allyl alcohol decomposition indicating that the transformation of the π-allyl to the σ-allyl (allyloxy) during propene oxidation is reversible.

The structure sensitivity of the propene oxidation reaction is demonstrated by the lack of acrolein production from the Cu-terminated, Cu$_2$O(100) surface following 1 atm. propene exposures. The origin of the structure sensitivity is related to the absence of coordinately-unsaturated lattice oxygen anions on the (100) surface.
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Chapter 1

Introduction

1.1 Background

The partial oxidation of propene (CH$_2$=CHCH$_3$) to acrolein (CH$_2$=CHCHO) is a useful model for the class of allylic oxidation reactions of olefins. Several mixed oxides catalyze propene partial oxidation to acrolein, but Cu$_2$O is the only reported single component oxide catalyst [1]-[3]. There is evidence that some details of the reaction pathway are similar over the bismuth-molybdate [4], tin-antimony oxide [5], uranium-antimonate [6], and single component Cu$_2$O catalysts [4]. Thus, mechanistic information obtained over Cu$_2$O may be applicable to more complex mixed oxide systems [2]-[7].

The basic steps in the reaction pathway of propene oxidation to acrolein have been widely studied, and are shown in Figure 1.1. In the rate determining step over Cu$_2$O and bismuth-molybdate catalysts, a methyl hydrogen is abstracted from propene producing a symmetric π-allyl intermediate [4, 8]. The order in which the second and third steps occur is not well understood, but involves a second hydrogen abstraction and lattice oxygen insertion into the symmetric π-allyl to form an oxygen-containing σ-allyl species. Grasselli and coworkers [3] advocate the formation of a σ-allyl on bismuth-molybdate catalysts where oxygen insertion occurs prior to a final hydrogen abstraction (i.e., an allyloxy intermediate). However, several groups advocate the formation of a σ-allyl species on bismuth-molybdate [1] and Cu$_2$O [7] catalysts where lattice oxygen insertion occurs after a final hydrogen abstraction.

The primary focus of this dissertation is on the nature of the oxygen containing σ-allyl and the order in which the second and third steps in the propene oxidation pathway occur. This problem was studied for propene oxidation to acrolein using different compounds to
Figure 1.1: Propene oxidation pathway.
simulate the various postulated surface species involved in the pathway shown in Figure 1.1.

A study of the reactivity and surface chemistry of molecules which simulate the two different $\sigma$-allyl intermediates proposed above could be used to gain a greater understanding of the propene oxidation pathway. Adsorbed acrolein has been used to study the $\sigma$-allyl species obtained by hydrogen abstraction from the $\pi$-allyl prior to oxygen insertion. A study of acrolein reactivity also gives information on any additional products formed from subsequent reactions of adsorbed acrolein. In addition to acrolein, propionaldehyde (CH$_3$CH$_2$CHO) has also been detected as a minor product in studies of propene oxidation over Cu$_2$O catalysts [8]. Thus, both acrolein and propionaldehyde surface chemistry and reactivity were studied on Cu$_2$O in an attempt to gain further understanding of the propene partial oxidation pathway. The study of propionaldehyde and acrolein adsorption and reactivity on the Cu$_2$O(100) surface is detailed in Chapter 5. Chapter 5 has been submitted to the Journal of Physical Chemistry [9].

In contrast, the dissociative adsorption of allyl alcohol to give a surface allyloxy (CH$_2$=CHCH$_2$O-) species has been used to study the $\sigma$-allyl intermediate obtained when oxygen insertion occurs prior to the final hydrogen abstraction. Additionally, allyl alcohol has been detected as a minor reaction product during propene oxidation studies over Cu$_2$O single crystals at atmospheric pressure and room temperature [Chapter 7]. In addition to allyl alcohol, a study of the reactivity of 1-propanol with Cu$_2$O and the comparison of these results with the decomposition of allyl alcohol gives information on the effects of the carbon-carbon double bond on C$_3$ alcohol reactivity. The study of allyl alcohol and 1-propanol adsorption and reactivity is given in Chapter 6. Chapter 6 has been submitted to the Journal of Physical Chemistry [10].

Surface carboxylate species have been observed as reaction intermediates in the decomposition of oxygenates on oxide surfaces. In studies of C$_3$ aldehyde [Chapter 5] and alcohol [Chapter 6] decomposition on the Cu$_2$O(100) surface, carboxylate species were detected in photoemission experiments. In order to better understand the role of carboxylate species in the alcohol and aldehyde decomposition pathways, a study of acrylic and propionic acids
on the Cu$_2$O(100) surface was undertaken. The results of these studies are detailed in Chapter 4. Chapter 4 has been submitted to the Journal of Physical Chemistry [11].

Finally, propene adsorption was studied on Cu$_2$O single crystal surfaces at low temperature and 300 K under both ultrahigh vacuum (UHV) and atmospheric pressure conditions. Chapter 3 details propene adsorption studies under UHV conditions on the Cu$_2$O(111) and (100) surfaces, while Chapter 7 details propene oxidation studies at atmospheric pressure and room temperature (300K). Chapter 3 has been submitted to Surface Science [12], and Chapter 7 has been submitted to the Journal of Catalysis [13].

In addition to the material covered in Chapters 1-7, some other background work was done which was necessary for interpretation of the results reported. CO, H$_2$O, and predissociated hydrogen adsorption was studied on the Cu$_2$O(100) surface. The CO [14] and H$_2$O [15] work have been published in Surface Science. The predissociated hydrogen work has been submitted for publication to the Journal of Chemical Physics [16].

1.2 Surfaces Investigated

The use of Cu$_2$O single crystal surfaces as model catalysts allows for the testing of site requirements for propene adsorption and oxidation. The two low-index surfaces investigated differ both in the availability of surface lattice oxygen and the Cu$^+$ coordination numbers. As with other cubic crystals, an ideal Cu$_2$O(111) surface possesses hexagonal symmetry. No single atomic layer parallel to the Cu$_2$O(111) surface contains both copper cations and oxygen anions. The copper planes parallel to the (111) surface contain four Cu$^+$ cations per surface unit cell with a 4+ charge. Each copper-containing plane is sandwiched between two oxygen containing planes. Each of these oxygen containing planes has one anion per surface unit cell and a 2- charge. Thus, a three plane repeat unit is necessary to satisfy stoichiometry and charge neutrality. Surface energy considerations dictate that the termination for an ideal, stoichiometric Cu$_2$O(111) surface be nonpolar [17]. Therefore, the ideal surface will be terminated by an outer atomic layer of oxygen anions, with a second atomic layer of Cu$^+$
cations, and a third atomic layer of oxygen anions. The ideal, stoichiometric, Cu$_2$O(111) surface exposes singly-and doubly-coordinate Cu$^+$ cations (bulk coordination = 2) in the second atomic layer in the ratio of 1 to 4, respectively. However, the top atomic layer is composed exclusively of threefold-coordinate oxygen anions (bulk coordination = 4). A ball model illustration of the ideal, stoichiometric (111) surface is shown in Figure 1.2(a).

An oxygen-deficient Cu$_2$O(111) surface may also be prepared by exposure to reducing gases. Such treatments lead to a ($\sqrt{3} \times \sqrt{3}$)R30° LEED periodicity due to an ordered one-third of a layer of oxygen vacancies [Chapter 3]. Each oxygen vacancy gives rise to a threefold site of singly-coordinate Cu$^+$ cations. A ball model of the oxygen deficient Cu$_2$O(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface is shown as Figure 1.2(b).

The ideal Cu$_2$O(100) surface is polar with square symmetry. As on the (111) surface, no single atomic layer parallel to the (100) surface contains both oxygen anions and copper cations. The bulk structural arrangement perpendicular to the [100] direction alternates between copper-containing and oxygen-containing planes. The oxygen planes parallel to the Cu$_2$O(100) surface contain one oxygen anion per (100) surface unit cell with a charge of 2-, while the copper planes are composed of two copper cations per unit cell with a total charge of 2+. Thus, a two plane repeat unit consisting of one plane of copper and one plane of oxygen is necessary to maintain stoichiometry and charge neutrality. The Cu$_2$O(100) surface used in this study was a polar, Cu-terminated, reconstructed surface which displayed a (3$\sqrt{2} \times \sqrt{2}$)R45° LEED periodicity with many missing spots [Chapter 2]. Although there is no definitive model of the structure of the reconstructed surface, the periodicity of the reconstruction suggests a relaxation of top atomic layer Cu$^+$ cations, possibly associated with a weak Cu$^+$-Cu$^+$ bonding interaction [Chapter 2]. In contrast to the (111) surface, the ideal, Cu-terminated (100) surface exposes no lattice oxygen in the top atomic layer. All top layer Cu$^+$ cations are singly coordinated. A ball model of the ideal, Cu-terminated, Cu$_2$O(100) surface is shown in Figure 1.3(a).

An ideal Cu$_2$O(100) surface should be either copper or oxygen terminated; if it is copper terminated on one side of the crystal, charge neutrality mandates that the opposite side of
Figure 1.2: Ball model illustrations of (a) the ideal, stoichiometric Cu$_2$O(111) surface, (b) the oxygen deficient ($\sqrt{3} \times \sqrt{3}$) Cu$_2$O(111) surface. The small solid circles represent Cu$^+$ cations, while the large open circles represent O$^{2-}$ anions. Drawings are based on the ionic radii of the ions, and assume no relaxation. Increased shading of the oxygen anions represents increasing distance away from the surface. For clarity, only the top four atomic layers of each surface are shown.
the crystal be oxygen terminated by analogy to the polar ZnO(0001)-Zn and ZnO(0001)-O surfaces [18]. An oxygen terminated surface can be prepared by $10^9$ L ($1 \text{ L} \equiv 10^{-6} \text{ Torr sec.}$) exposures to $O_2$. This preparation lifts the reconstruction on the (100) surface to form a (1 x 1) oxygen-terminated surface which is believed to contain doubly-coordinate oxygen in the outer atomic layer. The ball model illustration of the ideal, oxygen-terminated, Cu$_2$O(100) surface is shown in Figure 1.3(b). A more complete description of the characterization of clean Cu$_2$O(100) and (111) surfaces is given in Chapter 2. Chapter 2 has been published in Physics Review B: Solid State Physics [19].

1.3 Experimental

The experimental apparatus used in this study is a dual-chamber, stainless steel ultrahigh vacuum system. The analysis chamber (base pressure of $4 \times 10^{-11}$ Torr) is equipped with a Leybold EA-11 hemispherical energy analyzer, a dual anode Mg/Al x-ray source for x-ray photoelectron spectroscopy (XPS), and a differentially-pumped D.C. discharge lamp for ultraviolet photoelectron spectroscopy (UPS). XPS spectra were collected using Mg Kα radiation ($h\nu = 1253.6$ eV) exclusively, and run at a resolution of 1.03 eV FWHM on Ag 3$d_{5/2}$. UPS spectra were run with an analyzer resolution ($\Delta E$) of 0.15 eV, and referenced to the valence band maximum.

LEED experiments were performed in the preparation chamber using V.G. 3-grid reverse view optics. A broad beam ion gun in the preparation chamber was used for sample cleaning. A high-pressure reaction cell mounted on the preparation chamber was used for large gas exposures. The reaction cell is separated from the rest of the vacuum system by means of sliding seals, thus the sample can be transferred from the reaction cell to the preparation or analytical chambers without exposure to atmosphere. The base pressure of the preparation chamber is $7 \times 10^{-11}$ Torr.

The background pressure was less than $1.5 \times 10^{-10}$ Torr throughout the thermal desorption experiments. Dosing was accomplished by backfilling with a variable leak valve. For
Figure 1.3: Ball model illustrations of (a) the ideal, polar, Cu-terminated Cu$_2$O(100) surface, and (b) the O-terminated Cu$_2$O(100) surface. The small solid circles represent Cu$^{1+}$ cations, while the large open circles represent O$^{2-}$ anions. Drawings are based on the ionic radii of the ions, and assume no relaxation. Increased shading of the oxygen anions represents increasing distance away from the surface. For clarity, only the top four atomic layers of each surface are shown.
all thermal desorption experiments the sample was heated linearly at a rate of 2K/sec. An Inficon Quadrex 200 was used to monitor up to 6 masses simultaneously during the thermal desorption experiments. The mass spectrometer was equipped with a quartz skimmer to minimize the sampling of desorption products from the sample support hardware. All C₃ oxygenate doses reported in this paper have been corrected for ion gauge sensitivity [20]-[24], and all TDS traces have been corrected for mass spectrometer sensitivity.

The Cu₂O crystals used in this study were oriented by Laue backreflection and mechanically polished to within 1° of the (100) and (111) surfaces (unless otherwise noted). Sample dimensions were approximately 7×5×1 mm³. The samples were mechanically mounted (unless otherwise noted) on a tantalum holder which acted as an indirect heating and cooling source. A type K thermocouple was held in contact with the back of the sample through a small hole in the sample holder with Aremco type 509 ceramic cement. Hence, direct measurements of the crystal temperature were possible.

All XPS spectra were collected using Mg Kα radiation (hν = 1253.6 Ev) exclusively, and run at a resolution of 1.03 eV full width at half maximum (FWHM) on Ag 3d⁵/₂. Because of the width and asymmetry of the C 1s XPS spectra obtained from the C₃ oxygenates, peakfitting of the spectra was necessary. A Gauss-Newton curvefitting optimization routine using Gaussian peaks was used [25]. The variations in fitted peak positions which gave acceptable fits were ± 0.1 eV for the lowest and highest binding energy peaks, and ± 0.2 eV for peaks at intermediate binding energies. For all peakfits shown, the minimum number of peaks which gave acceptable fits was used. The peakfitting routine was used with a FWHM of 1.8 to 2.0 eV for the C 1s signals dependent on which FWHM value gave the best fit to a multilayer peak of a similar C₃ oxygenate on Cu₂O. For a given set of XPS experiments, the C 1s FWHM was not varied. All spectra reported were referenced to the Cu 2p₃/₂ binding energy of 932.4 eV [26].
Chapter 2
A Photoemission and Low-Energy Electron Diffraction Study of Clean and Oxygen-Dosed Cu$_2$O(111) and (100) Surfaces

2.1 Introduction

The surface properties of the oxygen/copper system have been investigated extensively for over twenty five years in an effort to understand the structure and electronic properties of both adsorbed and incorporated (oxide) oxygen [21 and references therein]. Recently, there has been a renewed interest in the electronic properties of copper oxides because of the advances in high $T_c$ copper-oxide superconductors. Cuprous oxide, Cu$_2$O, is a p-type semiconductor with the cuprite structure ($Pn3$). From a structural viewpoint, Cu$_2$O is interesting because it possesses unusual linear O—Cu—O bonds [28]. From an electronic viewpoint, bulk Cu$_2$O has been investigated because of interest in its Wannier exciton spectrum [29]. There are no previously reported photoemission or LEED studies for Cu$_2$O single crystal surfaces.

Herion et al. [30] studied the effects of electron irradiation on the Cu$_2$O(111) surface and noted that no degradation occurred during electron beam exposures in Auger electron spectroscopy (AES). They observed no preferential removal of oxygen during ion bombardment of the Cu$_2$O(111) surface, and suggested that clean, stoichiometric Cu$_2$O(111) surfaces could be prepared by ion bombardment and annealing [30]. Panzner et al. [31] examined the effect of Ar ion bombardment on Cu$_2$O layers prepared by oxidation of a copper single crystal. They found no detectable reduction of the surface for 3 keV Ar ion sputtering, but some Cu metal was observed following bombardment with 5 keV Ar ions [31].
Several groups have studied the conductivity of Cu$_2$O single crystals as a function of both annealing temperature and oxygen partial pressure [32]-[34]. A study of Cu$_2$O(111) showed that the surface conductivity changed as a function of exposure to air or heating in vacuum [32]. One study concluded that the conductivity of Cu$_2$O single crystals is associated with intrinsic crystal defects, and not due to the presence of oxygen at higher partial pressures [33]. However, Toth et al. reported that the conductivity of Cu$_2$O single crystals depends on the partial pressure of gas phase oxygen [34]. Assimos and Trivich examined the photoelectric threshold, work function, and surface barrier potential for Cu$_2$O(111) single crystal surfaces. They concluded that despite different surface preparation conditions, the bands for the Cu$_2$O(111) single crystal surface remained in a nearly flat band condition (-0.02 eV \leq qV_s \leq 0.13 eV) [35].

Several theoretical investigations of the band structure of Cu$_2$O have been reported due to interest in the exciton spectrum. Dahl and Switendick used a non-self-consistent APW method and concluded that the exciton spectrum was due to copper-derived electronic states [36]. Kleinman and Mednick [37] used a self-consistent expansion in Gaussian orbitals, and found that spin-orbit splitting puts the $\Gamma^+7(j = \frac{1}{2})$ level above the $\Gamma^+8(j = \frac{3}{2})$ level, in agreement with an earlier interpretation of exciton data [38]. Using a tight-binding Green's function method, Robertson's calculations gave a band structure more closely resembling the experimental optical gap and the O 2p band width than earlier calculations [39].

Previous studies of polycrystalline copper oxides have shown that Cu$^0$, Cu$^+$, and Cu$^{2+}$ can be distinguished using XPS [40]-[43]. Cu$^{2+}$ gives rise to intense shake up features in the Cu 2p spectrum. Cu$^0$ and Cu$^+$ may be distinguished by differences in the peak position and shape of the Cu L$_3$ VV Auger signal. In addition to differences in the core level spectra, UPS can also be used to distinguish between Cu valence states in copper oxide materials [44].

Rosencwiag and Wertheim examined oxygen and water adsorption on Cu$_2$O films and identified three different types of oxygen with XPS: lattice oxygen (O$^{2-}$, BE = 530.4 eV), surface hydroxide ion (OH$^-$, BE = 531.4 eV), and strongly chemisorbed oxygen (O$^-$, BE = 532.2 eV) [41]. In their work, no Cu$^{2+}$ was detected at the surface as a result of exposure
to gas phase oxygen or water vapor.

2.2 Experimental

The sample was clamped to a stainless steel stage with titanium shims and could be moved between the two chambers on a sample rod which passed through differentially-pumped sliding seals. The sample stage acted both as a mechanical support and an indirect heating and cooling source. A type-\(K\) thermocouple was fixed between the titanium clamp and the sample stage for temperature measurements. The stage temperature could be varied from 100 K to 1000 K. The sample stage and rod construction are such that the stage is permanently grounded. Hence, it was not possible to bias the sample during UPS, thus preventing accurate measures of changes in the sample work function.

The crystals used in this study were grown by a float zone technique using an arc image furnace [45]. The 1 mm thick single crystals were aligned using Laue backscattering and polished to give an optically smooth surface. An examination of the Cu\(_2\)O(111) crystal with LEED showed that the sample contained two rotationally misaligned (111) grains. The center of the crystal showed a superposition of the LEED pattern from each of the grains. One half of the crystal was azimuthally misaligned from the [111] direction by several degrees and often exhibited split spots suggesting a stepped surface. All LEED observations described in this paper were made on the opposite, non-stepped half of the Cu\(_2\)O(111) crystal which gave clear LEED patterns with no spot splitting. The (100) surface, in contrast, was a true single crystal aligned to within \(\pm 0.5^\circ\) of the [100] direction. All the experiments reported for the (100) surface were done only on one side of the crystal. Because of the mechanical mounting procedure, the back of the crystal was sufficiently scratched that it prevented characterization of the opposite side of the (100) polar face.

A variable leak valve was used to backfill the preparation chamber for exposures up to \(10^5\) L (1 L \(\equiv\) 1 Langmuir \(\equiv\) \(1 \times 10^{-6}\) Torr-sec.). Larger doses were done in flowing oxygen at atmospheric pressure in the high pressure cell. In an effort to minimize water
contamination in the oxygen, Matheson research grade oxygen (99.997% purity) was passed through a stainless steel coil immersed in liquid nitrogen before entry into a turbo-pumped stainless steel manifold (base pressure less than $10^{-8}$ Torr).

2.3 Results

2.3.1 Ion-bombardment and annealing experiments

Ion bombardment and consecutive annealing treatments were performed on both surfaces to examine changes in the structure and Cu-to-O ratio on recrystallization. After ion bombardment, the samples were heated to successively higher temperatures from 300 K to 1000 K in 100 K steps for photoemission and 25 K steps for LEED. All measurements were made after the samples cooled to 300 K.

XPS Cu-to-O ratios were determined from the areas under the Cu $2p_{3/2}$ and O 1s peaks and corrected using empirical sensitivity factors appropriate for our analyzer [46]. The major source of error in the XPS Cu-to-O ratios ($\pm 0.05$) was the determination of the O 1s peak area because of the small photoemission cross section relative to Cu. The quoted uncertainty in the Cu-to-O ratios ($\pm 0.05$) reflects only the variability in peak area determinations, not the variability of the sample for a given preparation. The Cu-to-O ratios are, therefore, taken to reflect trends in compositional changes at the surface, and not necessarily absolute measures of the surface composition or stoichiometry.

XPS

Variations in the XPS Cu-to-O ratio of the Cu$_2$O(111) surface are shown in Figure 2 for a set of ion-bombardment and consecutive annealing experiments. Several sets of data are shown, and although the points show some scatter, no consistent change with annealing temperature in the XPS Cu-to-O ratio is apparent. The data show an average value for the Cu-to-O ratio near 1.75. No change was observed in the Cu 2p and the Cu $L_3VV$ Auger signals from that expected for Cu$^+$. Thus, within the detection limits of XPS, no evidence
was seen for either the Cu$^{2+}$ or Cu$^{0}$ oxidation states.

Figure 2.1 also shows the XPS Cu-to-O ratios of the Cu$_2$O(100) surface for a set of ion-bombardment and consecutive annealing experiments. The Cu-to-O ratio falls in the range of 1.5 to 1.6, and shows little change ($\leq 5\%$) with annealing temperature up to 800 K. Upon heating to 900 K, the XPS Cu-to-O ratio decreased from an average value of about 1.57 to about 1.35, indicating an oxidation of the surface by the diffusion of oxygen from the bulk. The Cu-to-O ratio remained at this value, within experimental error, after further annealing to 1000 K. Ion bombardment of the Cu$_2$O(100) 1000 K-annealed surface with an XPS Cu-to-O ratio of 1.35 returned the XPS Cu-to-O ratio to near 1.60. However, these variations in surface composition proved to be history dependent. After approximately thirty ion-bombardment and annealing treatments, the drop in the Cu-to-O ratio (1.60 to 1.35) at 900 K was no longer observed, and a Cu-to-O ratio near 1.60 was maintained regardless of annealing temperature. The history dependence is apparently related to a depletion of bulk oxygen which significantly reduces the rate of oxygen diffusion to the surface. No change in the valence state of the Cu atoms at the surface was observed for any of the treatments described above. Thus, as on the (111) surface, no Cu$^{2+}$ or Cu$^{0}$ was observed.

LEED

After ion-bombarding the Cu$_2$O(111) surface, a faint (1$x$1) hexagonal LEED pattern on a diffuse background was observed, indicating substantial surface disorder. Upon annealing to 550 K, the diffuse background decreased, and faint fractional order spots were observed in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity. These faint fractional order spots would fade if left in the electron beam for 3 to 5 minutes. However, no corresponding intensity decrease was observed for the integral order beams. Further annealing to 950 K sharpened the integral order beams, and the fractional order spots disappeared completely. The (1$x$1) hexagonal pattern for a 1000 K-annealed Cu$_2$O(111) surface is shown in Figure 2.2.

Following ion bombardment of the Cu$_2$O(100) surface, a faint, square (1$x$1) LEED pattern on a diffuse background was observed, indicating a substantially disordered surface.
Figure 2.1: XPS Cu/O ratios for the Cu$_2$O(111) and (100) at a given temperature.
Figure 2.2: (a) (1×1) hexagonal LEED pattern ($E_b = 35$ eV) for the Cu$_2$O(111) surface following ion bombardment and annealing to 1000 K. (b) $(3\sqrt{2} \times \sqrt{2})R45^\circ$ LEED periodicity ($E_b = 35$ eV) for the Cu$_2$O(100) surface following ion bombardment and annealing to 800 K. (c) $(3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})R45^\circ$ pattern ($E_b = 40$ eV) formed by annealing the surface in (b) to 1000 K.
Upon annealing to 475 K the integral order beams became sharper, and faint fractional order spots became visible. The observed pattern, an apparent \((3\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity with many missing spots, became sharpest after annealing at 800 K, and is shown in Figure 2.2 (b). This periodicity, despite the missing spots, is hereafter referred to as \((3\sqrt{2} \times \sqrt{2})\) \(R45^\circ\) for notational convenience. For the initial runs, further annealing to 1000 K resulted in the appearance of an additional centered spot with a \((\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity (shown in Figure 2.2(c)) concurrent with the drop in Cu-to-O ratio from 1.60 to 1.35 observed in XPS. However, this high temperature behavior proved to be history dependent. After approximately thirty ion-bombardment and annealing treatments, the centered spot no longer appeared for annealing temperatures above 800 K. Additionally, the Cu-to-O ratio remained near 1.60 rather than decreasing to 1.35. Thus, the appearance of the centered spot in the LEED pattern was directly related to the change in the Cu-to-O ratio from near 1.60 to 1.35 observed in XPS. For notational purposes, the LEED periodicity shown in Figure 2.2(c) is hereafter referred to as a \((3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity.

UPS

UPS ion-bombardment and annealing sequences were performed to check for changes in the valence band structure as the surfaces reordered. For the Cu2O(111) surface, no significant changes in the valence band spectra were observed as a function of annealing temperature.

For the Cu2O(100) surface, the history dependence of the sample behavior observed in XPS and LEED was also found for UPS. The solid curve in Figure 2.3(a) is typical of previously reported He II spectra of Cu2O [44], and corresponds to a 1000 K-annealed surface following many ion-bombardment and annealing cycles (i.e., XPS [Cu]/[O] \(\approx\) 1.60, \((3\sqrt{2} \times \sqrt{2})\) \(R45^\circ\) LEED periodicity with no centered spot). Features in the photoemission spectrum from 5-8 eV are primarily O 2p derived, while the density of states in the 1-4 eV range are primarily Cu 3d bands [39, 44]. The low binding energy feature below 1 eV near the valence band maximum is associated with Cu d, s, p and O p interactions.
Figure 2.3: (a) He II UPS spectra of 1000 K-annealed Cu2O(100) surfaces. The solid line spectrum is characteristic of the surface following many ion bombardment and annealing cycles \([(3\sqrt{2} \times \sqrt{2}) \text{ R}45^\circ \text{ periodicity}]\), while the dashed spectrum was obtained early in the sample history \([(3\sqrt{2} \times \sqrt{2}) \text{ R}45^\circ \text{ periodicity}]\). (b) He II UPS spectrum of the Cu2O(100) surface following ion bombardment and annealing to 400 K (dashed) and 800 K (solid). The spectra correspond to the maximum variation in the 9.4 eV photoemission feature for a given ion bombardment and annealing cycle as shown in the inset. (c) UPS difference curve between the spectra in (b). All spectra are referenced to the valence band maximum, and N(E) spectra have been normalized on the feature below 1 eV.
An unusual feature not reported in earlier UPS investigations of polycrystalline Cu$_2$O [40, 44] was observed at a binding energy of 9.4 eV. The long term variability of this feature correlates with the behavior observed in XPS and LEED. Figure 2.3(a) shows a comparison of UPS spectra for two surfaces prepared by ion bombardment and annealing to 1000 K. The dashed curve in Figure 2.3(a) corresponds to an early 1000 K-annealed surface following only about ten ion-bombardment and annealing cycles (i.e., XPS Cu-to-O ≈ 1.35, (3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})R45° LEED periodicity.)

For the early runs where the decrease in Cu/O in XPS and the appearance of the centered spot in LEED were observed following high temperature annealing, the intensity of the 9.4 eV feature was found to vary significantly as a function of annealing temperature following ion bombardment. This behavior is illustrated in the inset in Figure 2.3. A maximum intensity of the 9.4 eV feature occurred after heating the ion-bombarded surface to 400 K. The intensity then decreased continually to zero upon heating to 800 K. Upon annealing to 900 K, the feature again appeared, coincident with a drop in the Cu/O ratio from 1.60 to 1.35 and the appearance of a centered spot in the LEED pattern. Figure 2.3(b) illustrates the maximum variation for a given ion-bombardment and annealing series between the 400 K (dashed curve) and 800 K (solid curve) annealed surfaces.

In an effort to identify the 9.4 eV photoemission feature, UPS difference curves were generated between spectra which exhibited a significant difference in intensity of the 9.4 eV feature. A representative difference curve, generated using the two He II spectra in Figure 2.3(b) is shown in Figure 2.3(c). Regardless of the sample history of the two curves used to generate a difference spectrum, the 9.4 eV feature was always found to be one feature of a difference spectrum like that shown in Figure 2.3(c). Agreement was found in the number and positions of the features regardless of whether He I or He II was used as the excitation source. Besides the 9.4 eV feature, a broad feature with a peak at 5.2 eV and a shoulder to higher binding energies (near 7 eV) is also apparent. This broad feature falls in the range of the O 2p emission in the N(E) spectrum. An additional feature is also apparent at about 2.3 eV binding energy regardless of data treatment. However, the shape of this
low binding energy feature is dependent on the shift employed to account for band bending
(0.2 eV max.) as well as any normalization of the spectra prior to taking the difference (ex.,
no normalization, normalization on the Cu 3d bands near 2.5 eV, or normalization on the
peak near the valence band maximum).

2.3.2 Oxygen adsorption

Photoemission and LEED were used to investigate the effects of oxygen adsorption at 300
K on both the Cu₂O(111) and Cu₂O(100) surfaces for several different surface preparations.
Oxygen doses were started at 0.1 L and increased in order-of-magnitude steps up to 10⁸ L.
He I and He II were used for UPS, and Cu/O ratios were determined with XPS for each
exposure. LEED observations were made as a function of annealing temperature following
a 10⁸ L oxygen dose on the annealed surfaces. All photoemission measurements and LEED
observations were made at 300 K. Figure 2.4 provides an illustrative set of UPS difference
curves which are characteristic of the observations made for all surfaces and preparation
conditions. For comparison, Figure 2.4(a) shows the gas-phase UPS spectrum for molecular
oxygen, O₂, reproduced from Ref. [47].

Oxygen on Cu₂O(111)

Two different Cu₂O(111) surface preparations were studied: a (1×1) surface prepared
by ion-bombardment and annealing to 1000 K for 20 minutes, and an ion-bombarded sur-
face. No adsorbate induced features were discernable in UPS on either the ion-bombarded
or 1000 K-annealed (1×1) surfaces for oxygen exposures of less than 10⁴ L. For 10⁴ L ex-_poses,
the hexagonal, 1000 K-annealed (1×1) surface exhibited a two-peaked UPS difference
spectrum with a peak separation of 4.6 eV as shown in Figure 2.4(b). In contrast, oxygen adsorption on the ion-bombarded surface gave rise to the difference spectrum shown in
Figure 2.4(c) with maxima at 9.4 eV, 5.2 eV, and 2.3 eV and a shoulder at about 7 eV.
For comparison purposes, the spectrum from Figure 2.3(c) is reproduced as Figure 2.4(d).
A comparison of Figure 2.4(c) and 2.4(d) demonstrates the electronic similarity between
Figure 2.4: (a) Gas phase O₂ UPS spectrum reprinted from Ref. [41] by permission of John Wiley & Sons, Ltd. (b) He I UPS difference spectrum of oxygen adsorbed on the (1×1), 1000 K-annealed, Cu₂O(111) surface. (c) He II difference spectrum following a 10⁴ L O₂ exposure on the ion bombarded Cu₂O(111) surface. Similar spectra to (c) are observed following oxygen adsorption on all Cu₂O(100) surface preparations investigated (see text for details). (d) Figure 2.3c; difference spectrum reproduced for comparison. All spectra except (a) are referenced to the valence band maximum.
the oxygen adsorption-induced features on the ion-bombarded (111) surface and the (100) surface under conditions when the 9.4 eV photoemission feature is observed.

**Oxygen on Cu$_2$O(100)**

Four different Cu$_2$O(100) surface conditions were studied: an ion-bombarded surface, an 800 K-annealed $(3\sqrt{2} \times \sqrt{2})$R45° surface, a 1000 K-annealed $(3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})$R45° surface, and a 1000 K-annealed $(3\sqrt{2} \times \sqrt{2})$R45° surface formed after more than 30 ion-bombardment and annealing treatments. The different (100) surface preparations were chosen because of the different XPS Cu/O ratios and LEED patterns observed for these conditions. No new valence band features were observed for any of the four Cu$_2$O(100) surface preparations for oxygen exposures up to $10^4$ L. For each of the four surface preparations investigated, a UPS difference spectrum essentially identical to the one obtained for oxygen adsorption on the ion-bombarded Cu$_2$O(111) surface (Figure 2.4(c)) was obtained. Further oxygen exposures to $10^9$ L and above gave similar difference spectra, with some increased intensity but no new features.

For each (100) surface preparation investigated except ion bombardment, a (1×1) square LEED pattern with diffuse background and a XPS Cu/O ratio of about 1.15 was observed after a $10^9$ L dose of oxygen. A representative (1×1) square LEED pattern is shown in Figure 2.5(a). When heated to 400-450 K in vacuum, the (1×1) surfaces formed by $10^9$ L oxygen exposures at 300 K exhibited $(\sqrt{2} \times \sqrt{2})$R45° LEED periodicities (shown in Figure 2.5(b)) with XPS Cu/O ratios of about 1.35. Annealing in vacuum to temperatures above 500 K led to complete removal of adsorbed oxygen as evidenced by a return to the original LEED periodicity and XPS Cu/O ratio for a given starting condition.
Figure 2.5: (a) Square ($1 \times 1$) pattern observed following $10^9$ L oxygen dose on an ordered Cu$_3$O(100) surface. (b) ($\sqrt{2} \times \sqrt{2}$)R45° periodicity observed following annealing of the surface in (a) to 400-450 K. All beam energies were 40 eV.
2.4 Discussion

2.4.1 Surface structure

Cu$_2$O(111)

The LEED observations for the (111) surface suggest the possibility of two different surface terminations corresponding to a hexagonal (1×1) periodicity and a (\(\sqrt{3} \times \sqrt{3}\))R30° LEED periodicity. While only a faint (\(\sqrt{3} \times \sqrt{3}\))R30° pattern was observed during the course of ion-bombardment and annealing studies, a much sharper and more distinct (\(\sqrt{3} \times \sqrt{3}\))R30° pattern has been observed during studies of the catalytic chemistry of Cu$_2$O(111) resulting from repeated exposures to propene (CH$_3$CH=CH$_2$) during thermal desorption studies (TDS) [12]. The observation of trace amounts of CO as a reaction-limited product in each TDS run suggests a net surface reduction (i.e., oxygen removal) associated with the (\(\sqrt{3} \times \sqrt{3}\))R30° periodicity [12].

A (\(\sqrt{3} \times \sqrt{3}\))R30° periodicity is typically associated with 1/3 monolayer of adsorbed species on hexagonal substrates [48]. For the Cu$_2$O(111) surface which exhibits a loss of oxygen, domains of (\(\sqrt{3} \times \sqrt{3}\))R30° periodicity could be indicative of the ordered loss of 1/3 or 2/3's of the terminating layer of oxygen anions from a stoichiometric surface. The change in LEED pattern from a (1×1) to a (\(\sqrt{3} \times \sqrt{3}\))R30° surface occurs gradually with faint fractional order spots appearing over the course of about twenty propene TDS runs. The slow rate of change to the new periodicity coupled with the observation of only trace amounts of CO per run suggests that 1/3 (rather than 2/3's) of the terminating oxygen layer is removed to form (\(\sqrt{3} \times \sqrt{3}\))R30° periodicity [12]. Oxygen vacancy formation is supported by the observation of an additional, higher temperature propene desorption channel in TDS from Cu$_2$O(111) surfaces exhibiting (\(\sqrt{3} \times \sqrt{3}\))R30° LEED periodicities [12].

Note that for the (\(\sqrt{3} \times \sqrt{3}\))R30° surface observed in the ion bombardment (Sec. 2.3.1) and surface chemistry [12] studies no significant increase in the XPS Cu/O ratio has been observed, in apparent conflict with the proposed model requiring an ordered 1/3 of an atomic layer of oxygen vacancies at the surface. However, numerical simulations of the
variation in XPS Cu/O ratio for normal emission based on the mean-free-path dependence of the photoelectrons (assuming no diffraction effects) gives a decrease in the XPS Cu/O ratio of only 0.05 for a surface with 1/3 of an atomic layer of oxygen vacancies [49, 50]. Because this variation is within experimental error, the use of normal-emission XPS data for evaluating this oxygen-vacancy model of the (111) surface is problematic.

The (1×1) LEED periodicity for the 1000 K-annealed Cu₂O(111) surface suggests a more nearly ideal, stoichiometric surface than the (\sqrt{3} \times \sqrt{3})R30° surface. A (1×1) LEED periodicity is characteristic of a simple, though not necessarily stoichiometric, termination of the bulk. An estimate of the defect (oxygen vacancy) density in the top atomic layer has been made via TDS experiments using propene as a probe molecule [12]. Assuming a sharp, well-defined, (\sqrt{3} \times \sqrt{3})R30° periodicity is characteristic of 1/3 of an atomic layer of oxygen vacancies, a comparison of the relative intensity of the high temperature propene desorption state for a (1×1) surface prepared by ion bombardment and annealing gives an estimate of about 3% oxygen vacancies in the top atomic layer. Thus, the (1×1) surface condition resulting from ion bombardment and annealing to 1000 K can be described as nearly stoichiometric, and the corresponding surface structure should be similar to the ideal stoichiometric surface shown in Figure 1.1(a), assuming no relaxation. Herion et al. [30] have reported that stoichiometric Cu₂O(111) surfaces can be prepared by ion-bombarding and annealing in vacuum to at least 425 K. However, our LEED observations (fractional order spots until 950 K) demonstrate that much higher temperatures are required to completely order the surface.

Cu₂O(100)

Four different LEED patterns have been observed on the (100) surface: (1×1), (\sqrt{2} \times \sqrt{2})R45°, (3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})R45°, and (3\sqrt{2} \times \sqrt{2})E45° periodicities. The observation of distinct and separate (3\sqrt{2} \times \sqrt{2})R45° and (\sqrt{2} \times \sqrt{2}) R45° periodicities (Figures 2.2(b) and 2.5(b), respectively) for different preparation conditions suggests that the (3\sqrt{2} \times \sqrt{2}) (\sqrt{2} \times \sqrt{2})R45° pattern (Figure 2.2(b)) is a combination of domains with the two different
periodicities. The XPS Cu/O ratios observed with the different periodicities vary in the order 
\((3\sqrt{2} \times \sqrt{2})R45^\circ > (3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})R45^\circ \approx (\sqrt{2} \times \sqrt{2})R45^\circ > (1\times1)\) with values of about 1.60, 1.35, and 1.15, respectively.

Calculations of the expected variation in XPS Cu/O ratio for the two ideal terminations of the polar (100) surface give values of 1.57 for the Cu-terminated surface (Figure 1.3(b)) and 1.23 for the O-terminated surface (Figure 1.3(c) [49, 50]). While there is much uncertainty in the appropriate values of mean-free paths to use for such calculations, the similarity between the experimentally measured extremes in the Cu/O ratio (1.60 and 1.15) and the calculated values for the two ideal surfaces (1.57 and 1.23) suggests that models compositionally similar to the ideal surfaces (i.e., copper and oxygen terminated) be considered to describe the \((3\sqrt{2} \times \sqrt{2})R45^\circ\) and \((1\times1)\) LEED periodicities.

The \((1\times1)\) LEED periodicity observed after a \(10^9\) L exposure of oxygen on the (100) surface is characteristic of a simple termination of the bulk, and demonstrates that oxygen adsorption lifts the \((3\sqrt{2} \times \sqrt{2})R45^\circ\) reconstruction observed for the most oxygen deficient (100) surface. The UPS data demonstrate that the adsorbed oxygen species on the (100) surfaces are atomic (see Section 2.3.2.), and therefore suggest a surface structurally and compositionally similar to an ideal, oxygen terminated (100) surface [49]. This assignment is further supported by the observation of a \((\sqrt{2} \times \sqrt{2})R45^\circ\) pattern formed by heating the \((1\times1)\) surface and partially desorbing the adsorbed oxygen layer. The \((\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity is suggestive of the presence (or absence) of 1/2 of a terminating oxygen layer, thus demonstrating that the \((1\times1)\) pattern is associated with a significantly higher surface oxygen coverage approaching that of a nearly complete terminating layer of oxygen atoms.

Annealing a (100) surface exhibiting a \((\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity (formed by a \(10^9\) L O\(_2\) exposure and heating in vacuum to 400-450 K) leads to the appearance of a \((3\sqrt{2} \times \sqrt{2})R45^\circ\) contribution in LEED. The final periodicity observed following high temperature annealing in vacuum is the same as the initial starting condition prior to oxygen dosing, and displays either a \((3\sqrt{2} \times \sqrt{2})(\sqrt{2} \times \sqrt{2})R45^\circ\) or \((3\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity depending on the sample history. Regardless of the method of preparation, (100) surfaces exhibiting a \((\sqrt{2} \times \sqrt{2})R45^\circ\)
contribution in the LEED periodicity have XPS Cu/O ratios which fall essentially midway between those of the (1x1) and (3√2 x √2)R45° surfaces. Based on the assumption of an O-terminated (1x1) surface, these observations support the model for a (√2 x √2)R45° periodicity associated with 1/2 a terminating oxygen layer, and a (3√2 x √2)R45° Cu-terminated, reconstructed surface.

The compositional arguments described above are somewhat circular, and depend on the assignment of the surface with the lowest(highest) Cu/O ratio to an oxygen(copper) termination. However, it is felt that the agreement between the compositional data from XPS and structural data from LEED is compelling. It would, however, be advantageous to confirm these structural/compositional models with a direct imaging technique such as scanning tunneling microscopy.

Describing the Cu₂O(100) Cu-terminated, reconstructed surface as a (3√2 x √2)R45° periodicity is notationally convenient, but not correct since there are many missing spots. The true periodicity is best described in terms of two rotational domains of an oblique lattice at 90° angles. One lattice vector is identical to that of the principal lattice vector of an unreconstructed surface (i.e., along the [010] or [001] directions), while the second lattice vector is oriented 45° off the first (i.e., along the [011] or [011] directions) with a magnitude of (3/2)√2. The oblique lattice vectors of the two domains map out all the spots in the observed LEED pattern without requiring additional unobserved spots. These oblique lattice vectors and the corresponding domains are shown superimposed on an ideal, Cu-terminated, Cu₂O(100) surface in Figure 2.6.

The observed reconstruction of the Cu-terminated Cu₂O(100) surface is not surprising since ideal polar surfaces exhibit high surface energies, and thus are often unstable [17]. For example, the relaxation of the Zn-terminated ZnO(0001) polar surface is well known [51]. One possible explanation for the oblique (i.e., (3√2 x √2)R45°) lattice on the Cu-terminated Cu₂O(100) surface is a relaxation of the singly coordinated surface copper cations. Such a model is suggested by the (3/2)√2 lattice vectors along the [011] and [011] directions. The (3/2)√2 dimension is an integer multiple of the (1/2)√2 separation between the Cu
Figure 2.26: Ball model drawing of the ideal Cu-terminated Cu2O(100) surface showing the two rotational domains of oblique periodicity corresponding to the (3√2×√2)R45° LEED pattern shown in Figure 2.26.
cations along these directions for the ideal, unreconstructed surface as shown in Figure 2.6, but is not an integer multiple of the \( \sqrt{2} \) spacing between anions along these directions. A relaxation between adjacent copper cations in neighboring rows along the [011] or [01\bar{1}] directions in steps of \((3/2)\sqrt{2}\) satisfies the oblique periodicity and requires only a single type of Cu\(^+\)-Cu\(^+\) interaction. No relaxation is suggested for copper cations along the same [011] or [01\bar{1}] rows because the periodicity would require two different Cu\(^+\)-Cu\(^+\) interactions: (1) between cations bound to the same second-layer oxygen anion and (2) cations bound to neighboring second layer oxygen anions.

Such a relaxation can be rationalized in terms of Cu\(^+\)-Cu\(^+\) bonding on the Cu\(_2\)O(100) surface similar to that observed between Cu\(^+\) centers in organometallic compounds, where a tendency for clustering is observed for Cu\(^+\) cations. Using molecular orbital calculations, Mehrotra and Hoffmann found that despite a closed shell d\(^{10}\) configuration, a small bonding interaction between bare Cu\(^+\) cations occurs because of hybridized 4s, 4p, and 3d orbitals \([52]\). They also report that typical Cu\(^+\)-Cu\(^+\) distances in organometallic compounds range from 3.58 \(\text{Å}\) to 2.42 \(\text{Å}\). The Cu\(^+\)-Cu\(^+\) distance for an ideal, unrelaxed, Cu terminated (100) surface is 3.01 \(\text{Å}\) \([28]\), which falls well within the ranges of separations reported for organometallic complexes.

Mehrotra and Hoffmann also report that bridging ligands play the dominant role in determining geometry and bond angles in copper-containing organometallic compounds \([52]\). The Cu-terminated Cu\(_2\)O(100) surface possesses a high concentration of unsaturated Cu\(^+\) cations essentially "missing" an oxygen ligand, thus supporting the possibility of a Cu\(^+\)-Cu\(^+\) interaction affecting the structure of a Cu-terminated Cu\(_2\)O(100) surface. The presence of Cu\(^+\)-Cu\(^+\) bonding to account for the oblique periodicity is also supported with the lifting of the reconstruction with 1/2 atomic layer of oxygen ligands in a \((\sqrt{2} \times \sqrt{2})R45^\circ\) surface. An ordered 1/2 monolayer of oxygen is enough to tie up at least one interacting Cu\(^+\) cation per Cu\(^+\)-Cu\(^+\) bonding pair, and hence play the dominant role in determining the surface structure.
2.4.2 Identification of surface oxygen species

Oxygen adsorption on the 1000 K-annealed Cu$_2$O(111) surface

Oxygen adsorption at 300 K gave a two-peaked UPS difference spectrum (Figure 2.4(b)) with a peak separation of 4.6 eV. In previous studies of room-temperature oxygen adsorption on metallic copper surfaces, Spitzer and Lüth [53] reported two UPS features for atomic oxygen with separations of 3.7 to 4.0 eV, depending on the surface under study. The significantly larger peak separation in the present work suggests that a different explanation is required.

Room temperature adsorption of oxygen on several other materials, primarily metal oxides, yields two-peaked UPS difference spectra with separations similar to those observed on the nearly stoichiometric Cu$_2$O(111) surface. Such two-peaked spectra have been observed on GaAs(100) [54], SrTiO$_3$(100) [55], NiO(100) [56], and MnO(100) [57] with peak separations of 4.6 eV, 4.5 eV, 5.0 eV, and 4.1 eV, respectively. In each case the adsorbed specie has been identified as molecular oxygen.

Neutral O$_2$ in the gas phase displays a characteristic UPS spectrum with four peaks as shown in Figure 2.4(a) [47]. The four photoemission features are due to $1\pi_u$ and $1\pi_g$ orbitals, and two different final states of $3\sigma_g$ emission [47]. It has been proposed that a two-peaked spectrum for adsorbed molecular oxygen may be due to overlap of $1\pi_u$ and $3\sigma_g$ orbitals giving the high binding energy peak, with the $1\pi_g$ orbital giving the low binding energy peak [54, 56]. McKay and Henrich [56] have attributed this overlap to a relaxation of the O–O bond associated with a negatively charged molecular adsorbate, possibly O$_2^2$–. The broadness of the peaks observed in the UPS difference spectrum for oxygen adsorption on nearly stoichiometric Cu$_2$O(111) (Figure 2.4(b)) is consistent with such an interpretation. The separation between the $3\sigma_g$ and $1\pi_u$ orbitals is slightly less than 2 eV in the gas phase. However, the width of the associated photoemission feature in the difference spectrum is also about 2 eV, implying that the two features observed in the gas phase are not resolved in the adsorbate. Thus, the two-peaked UPS difference spectrum in Figure 2.4(b) is assigned
to adsorbed molecular oxygen.

**Oxygen adsorbed on Cu$_2$O(100) and ion-bombarded Cu$_2$O(111)**

Oxygen adsorption at room temperature on all (100) surfaces and the ion-bombarded (111) surface results in UPS difference spectra with four features (Figure 2.4(c)). Essentially identical features were observed for the surface species formed by diffusion of bulk lattice oxygen to the Cu$_2$O(100) surface at elevated temperatures for the early sample treatments (Figure 2.4(d)). Despite the similar number of features, there is no clear correspondence with the four-peaked gas phase spectrum for molecular oxygen. Comparisons to data for oxygen adsorption on metallic copper show no clear correspondence in terms of peak separations or binding energies to the two and three-peaked spectra assigned to triplet atomic oxygen and singlet molecular oxygen, respectively [53, 58, 59].

Consideration of the oxygen-induced features at intermediate binding energies leads also to the conclusion that atomic oxygen species give rise to difference spectra in Figures 2.4(c) and 2.4(d). The peak at 5.2 eV and the shoulder near 7 eV show a strong correspondence in position and relative intensity with the O 2p features of the oxide substrate, indicating oxygen dissociation and at least partial incorporation as lattice oxygen, O$^{2-}$.

The low binding energy feature at 2.3 eV clearly is oxygen-induced, but its origins are unclear. Tight-binding calculations of the bulk electronic structure of Cu$_2$O have shown that a contribution of O 2p states is expected for lattice oxygen in this range of binding energies [39], consistent with the idea of at least partial incorporation of dissociated oxygen into the lattice. However, some charge redistribution may also be expected between copper 3d, 4s, and 4p states as a result of changes in hybridization upon adsorption. This explanation is appealing considering the proposed Cu$^+$.Cu$^+$ bonding interaction for the reconstructed, Cu-terminated (100) surface. Unfortunately, while there is clearly an increase in the density of states upon adsorption in this binding energy range, the variability in shape and intensity of the 2.3 eV feature with different forms of data manipulation (band bending corrections, normalization vs. no normalization, etc.) currently prevents a distinction between such
possibilities.

The high binding energy peak at 9.4 eV is clearly not associated with lattice oxygen, and suggests the presence of a nonincorporated form of adsorbed oxygen. Since this photoemission feature is observed following ion bombardment or diffusion of bulk oxygen to the (100) surface at high temperatures early in the sample history, it is unlikely that it is associated with a molecular adsorbate. Similarly, the ordering of annealed Cu$_2$O(100) surfaces to a (1×1) LEED periodicity following large oxygen exposures (10$^9$ L) is consistent with an atomic adsorbate which can assume the periodicity expected for a ideal O-terminated (100) surface. Thus, surface oxygen resulting from adsorption on the (100) and ion-bombarded (111) surface or diffusion from the bulk to the (100) surface at high temperature is believed to be atomic, with the photoemission showing characteristics of both adsorbed and incorporated (i.e., lattice) oxygen.

Interference from contaminant water

When oxygen adsorption studies require very large exposures such as those reported here, the possibility of interference from contaminant water must be seriously considered. For this reason, water adsorption on both the (111) and (100) surfaces of Cu$_2$O has been studied [12]. Water adsorption is dissociative at room temperature and is characterized by a two-peaked UPS difference spectrum with peak separation of 3.7 eV. The UPS results are clearly different than those observed following oxygen adsorption. It is also notable that H$_2$O adsorption on the reconstructed, Cu-terminated (100) surface does not result in either a lifting of the reconstruction to a (1×1) periodicity or a measurable increase in the Cu-to-O ratio as observed following oxygen adsorption. Thus, it is concluded that the reported results for oxygen adsorption are not merely due to contaminant water adsorption.
2.5 Conclusions

Ion bombardment and 1000-K annealing of the nonpolar Cu$_2$O(111) surface in vacuum produces a nearly stoichiometric surface. A ($\sqrt{3} \times \sqrt{3}$)R30° periodicity was observed also on the Cu$_2$O(111) surface, and is tentatively assigned to an ordered 1/3 of an atomic layer of oxygen vacancies. Oxygen adsorption at room temperature on the stoichiometric surface is molecular, and gives rise to a characteristic two-peaked UPS spectrum similar to that observed for other metal oxides. Oxygen adsorption on the defective (111) surface formed by ion bombardment was found to be dissociative. The atomic species on the defective surface show characteristics of both incorporated (i.e., lattice) and adsorbed oxygen.

Ion bombardment and vacuum annealing results for the polar Cu$_2$O(100) surface were history dependent. Annealing the ion-bombarded (100) surface to 800 K in vacuum gave an ordered, reconstructed, Cu-terminated surface with an apparent ($3\sqrt{2} \times \sqrt{2}$)R45° periodicity. The periodicity of the reconstruction suggests a relaxation of singly-coordinated, top-atomic-layer Cu$^+$ cations, possibly associated with weak Cu$^+$-Cu$^+$ bonding interactions. For the initial treatments, heating to 900 K resulted in the diffusion of oxygen from the bulk to the surface to form ($\sqrt{2} \times \sqrt{2}$)R45° domains associated with an ordered 1/2 of an outer atomic layer of oxygen atoms. This surface oxygen exhibited electronic characteristics of both incorporated (i.e., lattice) and adsorbed species. After approximately thirty ion-bombardment and annealing treatments, bulk oxygen was sufficiently depleted such that a ($3\sqrt{2} \times \sqrt{2}$)R45° Cu-terminated surface was retained for annealing temperatures of 900 K and above.

Oxygen adsorption on four differently prepared Cu$_2$O(100) surfaces was found to be atomic, with photoemission characteristics identical to those observed for oxygen which diffused from the bulk to the surface during high temperature annealing early in the sample history. Large oxygen exposures ($10^9$ L) lifted the observed ($3\sqrt{2} \times \sqrt{2}$)R45° reconstruction associated with the Cu-terminated surface, giving a (1 x 1) LEED periodicity and an O-terminated Cu$_2$O(100) surface. Heating at 400-450 K desorbed half of the terminating
layer leaving an ordered \((\sqrt{2} \times \sqrt{2})R45^\circ\) periodicity. Heating above 500 K removed the remainder of the adsorbed oxygen and returned the surface to its original condition from prior to the dose. Oxygen atoms in the outer atomic layer of the (100) surface, whether formed by adsorption or diffusion from the bulk, exhibited photoemission characteristics of both adatoms and lattice oxygen.
Chapter 3
Propene Adsorption on Cu$_2$O Single Crystal Surfaces

3.1 Introduction

No studies of propene adsorption in ultrahigh vacuum (UHV) on single-crystal metal oxide surfaces have been reported; however, several reports of propene adsorption on metal single crystal surfaces are available [60]-[65]. Propene adsorbed on the Cu(110) surface shows no evidence of hydrogenation on either clean or hydrogen-predosed surfaces in UHV [60]. Propene adsorbed on an oxygen-predosed Ag(110) surface yields water and carbon dioxide upon heating [61]. An allylic intermediate (C$_3$H$_5$) was proposed in the propene oxidation pathway on Ag(110); however, there was no direct experimental evidence for this surface specie. A different type of adsorbed propene was proposed on Pt(111) and Rh(111) surfaces. Using low energy electron diffraction (LEED) and thermal desorption, several studies advocate the formation of a surface propylidyne (CH$_3$CH$_2$C≡) specie [62]-[65] on Pt(111) and Rh(111) prior to breakup of the molecule into hydrocarbon fragments.

3.2 Experimental

Large propene doses (>10 L) at low temperature (100 - 120 K) resulted in desorption signals from the sample support hardware which overlapped the desorption signals from the Cu$_2$O surfaces. Hence, difficulty was encountered in determining the saturation coverages on the oxide surfaces. All propene doses have been corrected for ion gauge sensitivity [20].

Matheson polymer-grade propene (99.5%) containing 0.4% propane as the major contaminant was used. Matheson research grade O$_2$ (99.997%) was passed through a coiled
tube immersed in liquid nitrogen in an attempt to minimize the water content before use. Matheson research grade D₂ (99.5%) was used as received. Previous results have shown that D₂ does not dissociate on Cu₂O surfaces in UHV [16]. Therefore, a white hot platinum filament located approximately 15 mm from the sample was used to dissociate deuterium. The exposures to predissociated deuterium are reported as the equivalent D₂ dose.

3.3 Results

3.3.1 Propene Adsorption on Cu₂O(100)

Propene Adsorption, 100 K

Propene TDS traces following adsorption at 100 K are shown in Figure 3.1 as a function of dose. All the experiments described were done on a Cu-terminated (100) surface with a \((3\sqrt{2} \times \sqrt{2})R45^\circ\) LEED periodicity. For low doses, one coverage dependent desorption state was observed which shifted from 255 K at 0.02 L to 190 K at 0.6 L. A second feature was resolved at 140 K for coverages of 1.5 L and above. Assuming first-order desorption kinetics (vide infra) and applying the Redhead equation [66] with a preexponential of \(10^{13} \text{sec}^{-1}\) gives a range of activation energies of 12.5 to 14.9 kcal/mol for the coverage dependent desorption state (255 - 190 K), and 9.1 kcal/mol for the 140 K desorption state.

No products other than propene were observed during the thermal desorption experiments on the (100) surface. Some of the products specifically tested for include acrolein, propanaldehyde, allyl alcohol, propane, 1,5-hexadiene, benzene, acrylic acid, H₂O, CO₂ and CO. The lack of any products during propene thermal desorption suggests that propene adsorbs molecularly and does not dissociate on the (100) surface at 100 K in UHV.

In an effort to further characterize the adsorbed propene on the (100) surface, C 1s XPS measurements were carried out. For these experiments, 30 L of propene was dosed at 100 K, and then heated to successively higher temperatures. All XPS runs were made after the sample was cooled to 100 K. A single symmetric C 1s peak was observed on the (100) surface centered at 284.9±0.1 eV (FWHM = 1.8). This C 1s feature did not shift
Figure 3.1: Thermal desorption traces for propene following adsorption on the Cu$_2$O(100) surface at 100 K. The left panel shows the low dose range (0.015 to 0.06 L) while the right panel shows the higher dose range (0.06 L to 1.5 L). Although not shown, all TDS experiments were run to final temperatures over 700 K.
with annealing temperature. No reduction of the (100) surface was observed as determined by examination of the Cu L\textsubscript{3}VV signal \cite{43}. XPS measurements should show a C 1s peak broadened to higher binding energy for oxygenated surface intermediates \cite{26}, in contrast to the single symmetric C 1s peak observed for the alkene. The symmetric C 1s peak confirms that no oxygen insertion occurs under these conditions.

**Propene-Deuterium Coadsorption, 100 K**

To confirm that propene did not dissociate upon adsorption and then recombine, deuterium-propene coadsorption experiments were carried out. Propene coadsorbed with deuterium should show deuterated propene (C\textsubscript{3}D\textsubscript{5}, m/e\textsuperscript{-} = 43) as a thermal desorption product if propene dissociation occurs. A small m/e\textsuperscript{-} = 43 signal was observed from normal propene due to the natural isotopic abundance of C\textsubscript{13}. Deuterium-labeled propene can be detected by an increase in the m/e\textsuperscript{-} = 43 signal above that due to normal propene. Predissociated deuterium (200 L equivalent dose) was coadsorbed with 0.06 L of propene at 100 K. No deuterated propene or deuterated propane (m/e\textsuperscript{-} = 45,46,47) was detected, and no shift in the desorption temperature of the propene was observed due to coadsorbed deuterium. Thus, there was no detectable hydrogenation activity for propene coadsorbed with deuterium at 100 K, and no detectable C\textsubscript{3}D\textsubscript{5} which would be indicative of dissociation to an allylic species on the (100) surface.

**Propene-Oxygen Coadsorption, 100 K**

Since no dissociation or reaction of propene was observed on the Cu\textsuperscript{+}-terminated (100) surface, coadsorption experiments with oxygen were undertaken in an effort to activate adsorbed propene. Previous photoemission experiments have shown that oxygen dissociatively adsorbs on the (100) surface at 300 K, with photoemission features characteristic of both adsorbed atomic oxygen and incorporated (i.e., lattice) oxygen \cite{19}. Thermal desorption of O\textsubscript{2} from atomic oxygen shows a sharp peak at 310 K and a broad feature centered at 405 K \cite{67}. In contrast, oxygen adsorbed at 100 K shows one desorption feature with a peak
maximum at about 250 K. The lower oxygen desorption temperature after adsorption at 100 K suggests that O₂ adsorbs molecularly at 100 K. Thus, molecular oxygen is obtained after dosing at 100 K, while atomic oxygen is obtained after adsorption at 300 K.

Exposures of propene were varied from 0.06 L to 0.3 L, while oxygen exposures were varied from 0.2 L to 1000 L. All dosing was done with the sample at 100 K. On the (100) surface, no reaction products were detected after coadsorption, only O₂ and propene. No variations in the amount or desorption temperatures of propene were observed due to the presence of molecular oxygen on the (100) surface. The lack of any reaction products demonstrates that adsorbed molecular oxygen does not activate propene on the (100) surface under these conditions of low temperature and pressure.

The absence of any desorption product besides propene from either the clean or deuterium-dosed (100) surface demonstrates that no detectable amounts of dissociated propene are formed on the (100) surface under these conditions. The lack of deuterated propane shows that no hydrogenation occurs. No evidence for an oxygen containing σ-allyl intermediate was observed in either thermal desorption or photoemission experiments. Thus, the lack of products shows clearly that propene adsorbs molecularly on the Cu₂O(100) surface at 100 K, and the desorption can therefore be modeled using first-order kinetics.

Propene Adsorption, 300 K

Since no dissociation of propene was observed after adsorption at 100 K, propene adsorption at 300 K was investigated. Propene exposures of up to 3000 L were studied. As with adsorption at 100 K, no reaction products were detected. Figure 3.2(a) shows the thermal desorption spectrum of C₃H₆ after a 3000 L propene dose. The resulting coverage was very low, and was only about 5% of the coverage obtained for a 9 L dose at 100 K. The sticking coefficient of propene at 300 K was estimated to be less than 10⁻⁵. One propene desorption feature was observed extending from 300 to 425 K with a peak maximum near 315 K. Because propene desorbs immediately upon heating, the order of the desorption process cannot be reasonably determined. However, assuming a first-order process and applying the
Redhead equation [66] gives an activation energy for desorption of 21.1 kcal/mol. It should be noted that propene desorbs at 315 K after adsorption at 300 K, while all propene desorbs by 255 K after adsorption at 100 K. The higher propene desorption temperature suggests that propene is adsorbed in a different (possibly dissociated) form following adsorption at 300 K than it is at 100 K.

**Propene-Deuterium Coadsorption, 300 K**

In an effort to determine the form of the adsorbed propene following a 300 K exposure, deuterium-propene coadsorption experiments were performed. Figure 3.2(b) shows thermal desorption spectra from deuterium (200 L equivalent dose) coadsorbed with 3000 L of propene at 300 K. An increase in the 43 signal after propene-deuterium coadsorption showed that about 6% (±2%) of the propene desorbed as C3H5D. Both the deuterated propene (C3H5D) and the normal propene (C3H6) desorbed in the same temperature range as shown in Figure 3.2(b). Thus, in contrast to propene adsorption at 100 K, a small amount of deuterated propene was detected after propene-deuterium coadsorption. No propane was detected showing that no hydrogenation occurred. The presence of deuterated propene after adsorption at 300 K is clear evidence that propene dissociates under these conditions.

**Propene-Oxygen Coadsorption, 300 K**

Propene-oxygen coadsorption experiments were carried out in an attempt to activate propene with doubly-coordinate, surface atomic oxygen at 300 K. For these experiments oxygen was dosed first, and then propene. Exposures of up to 3000 L of propene and 10^4 L of oxygen were studied. An exposure of 10^4 L of oxygen gives an oxygen coverage of about 0.3 monolayers where one monolayer is defined as the amount of oxygen equivalent to an oxygen-terminated (100) surface [19]. On the (100) surface, propene desorbed in one peak at 315 K and oxygen desorbed in two peaks at 310 and 405 K. No reaction products were detected, only O2 and propene. Additionally, for a given dose, no difference in the amount of desorbing propene was detected due to coadsorption with oxygen. Thus, no evidence for
Figure 3.2: Thermal desorption traces for a 3000 L propene dose on the Cu$_2$O(100) surface following adsorption at 300 K on (a) the clean Cu$_2$O(100) surface and (b) the deuterium-predosed surface.
oxygen insertion to form an oxygen-containing σ-allyl was observed under these conditions.

C 1s XPS was attempted after a 3000 L propene dose at 300 K, however, due to the low coverages of propene obtained at 300 K, there was not enough signal above the background for analysis.

3.3.2 Propene Adsorption on Cu₂O(111)

Propene Adsorption, 120 K

In addition to examining the effects of molecular and doubly-coordinate atomic oxygen on propene adsorption, the experiments described above were repeated for adsorption at 120 K on the Cu₂O(111) surface which contains triply-coordinate surface lattice oxygen. Figure 3.3 shows the propene desorption from the oxygen-deficient Cu₂O(111)-(√3 x √3)R30° surface as a function of dose. At the lowest dose investigated (< 0.02 L) a single desorption feature at 325 K was observed which did not shift with coverage. Larger doses resulted in the appearance of a second desorption feature at 260 K for doses as low as 0.04 L. This second feature also did not shift with coverage. A third feature appeared at 245 K by 0.09 L, and shifted to 220 K by 0.15 L. A fourth feature became apparent at 0.30 L, with a peak temperature of 185 K, and shifted to 175 K with increasing coverage. Continued dosing resulted in the growth of a fifth feature at 150 K by 1.5 L.

The 325 K, 260 K, and 150 K desorption states do not shift with coverage, implying first order desorption processes with corresponding activation energies of 21.8 kcal/mol (325 K), 17.3 kcal/mol (260 K), and 9.8 kcal/mol (150 K). Assuming first-order kinetics (vide infra) for the coverage dependent states gives activation energies of 16.3-14.6 kcal/mol (245 - 220 K) and 12.2-11.5 kcal/mol (185-175 K). CO was the only reaction product detected besides propene.

The CO detected as a reaction product was desorption limited [14] and evolved in three peaks at 130 K, 155 K, and 215 K, with corresponding activation energies for desorption of 8.5, 10.1, and 14.2 kcal/mol. A representative thermal desorption trace showing product
Figure 3.3: Thermal desorption traces for propene following adsorption on the Cu$_2$O(111) surface at 120 K. The left panel shows the low dose range (0.015 to 0.11 L) while the right panel shows the higher dose range (0.11 L to 0.6 L). Although not shown, all TDS experiments were run to final temperatures over 700 K.
CO following a 0.3 L propene dose is shown in Figure 3.4. The conversion of propene to CO was 20±2% for small doses (0.02 L) and decreased to 3±1% by 0.3 L as shown in the inset of Figure 3.4. The absolute amount of CO produced increased with increasing propene dose up to 18 L of propene, after which no additional increase in the amount of desorbing CO was observed. The presence of CO as a desorption limited product demonstrates that some propene is dissociatively adsorbed at 120 K.

An adsorbed propene layer was annealed to successively higher temperatures to determine if lattice oxygen insertion takes place to form an oxygen containing σ-allyl on the (111) surface. Only a single symmetric C 1s peak at 285.1±0.1 eV BE (FWHM =1.8 eV) was observed following a 30 L dose, and no binding energy change was observed in the C 1s peak position as a function of annealing temperature. These XPS results demonstrate that no significant amounts of an oxygen containing σ-allyl were formed under these conditions. It should be pointed out that no oxygen containing surface species associated with the CO production were detected in XPS because of the small amount of propene converted to CO. As on the (100) surface, no reduction to metallic copper on the (111) surface was observed in XPS.

The intensities of the 260 K and 325 K propene desorption signals were found to be strongly dependent on the sample history. Consecutive propene thermal desorption in which CO was detected as a reaction product resulted in a change in the (111) surface structure from a nearly-stoichiometric (1×1) surface to an oxygen deficient ($\sqrt{3} \times \sqrt{3}$)R30° surface. This phenomena is illustrated in Figure 3.5, which shows desorption spectra for 0.06 L propene doses from a freshly prepared (1×1) surface (dashed line), and an oxygen-deficient, ($\sqrt{3} \times \sqrt{3}$)R30° surface (dotted line) obtained after four consecutive 0.06 L propene doses. For the (1×1) surface, the 325 K desorption state is small, but gradually increases in size with each dose (not shown) as the ($\sqrt{3} \times \sqrt{3}$)R30° periodicity appears. Figure 7 shows photographs of a (1×1) LEED pattern from a nearly stoichiometric surface and a ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern from an oxygen deficient (111) surface.

The data discussed above was mentioned earlier as a justification for the proposed
Figure 3.4: Thermal desorption spectrum showing product CO after a 0.3 L propene dose at 120 K on a Cu$_2$O(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ surface. The inset shows the propene conversion to CO as a function of dose.
Figure 3.5: Thermal desorption spectra of 0.06 L propene doses from a nearly stoichiometric Cu$_2$O(111)-(1x1) surface (dashed line) and two different oxygen-deficient Cu$_2$O(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ surfaces (solid and dotted lines). The two desorption spectra from (\sqrt{3} \times \sqrt{3})R30^\circ surfaces are representative of different sample histories. See text for details.
Figure 3.6: (a) (1x1) hexagonal LEED pattern ($E_b = 40\, \text{eV}$) for the nearly stoichiometric $\text{Cu}_2\text{O}(111)$ surface. (b) ($\sqrt{3} \times \sqrt{3}$)R$30^\circ$ LEED pattern ($E_b = 40\, \text{eV}$) for the oxygen deficient $\text{Cu}_2\text{O}(111)$ surface.
compositions of Cu$_2$O(111) surfaces [19]. A ($\sqrt{3} \times \sqrt{3}$)R30° periodicity is typically associated with either 1/3 or 2/3 of a monolayer of adsorbed species on hexagonal substrates [48]. Since the ($\sqrt{3} \times \sqrt{3}$)R30° periodicity can be generated by propene thermal desorption experiments in which CO is observed as a product, the formation of the ($\sqrt{3} \times \sqrt{3}$)R30° pattern can be associated with the removal of surface oxygen. For the Cu$_2$O(111) surface that exhibits a loss of oxygen, domains of ($\sqrt{3} \times \sqrt{3}$)R30° periodicity could be indicative of the ordered loss of 1/3 or 2/3 of the terminating layer of oxygen anions from a stoichiometric surface. The change in LEED pattern from a (1×1) to a ($\sqrt{3} \times \sqrt{3}$)R30° surface occurs gradually, with fractional-order spots appearing over the course of several propene TDS runs. The slow rate of change to the new periodicity, coupled with the observation of low propene conversions to CO per run, suggests that 1/3 (rather than 2/3) of the terminating oxygen layer is removed to form the ($\sqrt{3} \times \sqrt{3}$)R30° periodicity. No significant change was observed in the XPS Cu/O ratio (the ratio changed by less than experimental error) for the (1×1) and ($\sqrt{3} \times \sqrt{3}$)R30° surfaces in spite of the oxygen deficiency. The insensitivity of normal emission XPS to variations in the oxygen concentration in the top atomic layer is supported by calculations of the expected Cu/O ratios for these surfaces [49]. Since the ($\sqrt{3} \times \sqrt{3}$)R30° surface is associated with an ordered array of oxygen vacancies and because the 325 K desorption state is greatest for the oxygen deficient surface, the 325 K state can be assigned to a propene desorption channel associated with the oxygen vacancies available on the Cu$_2$O(111)-($\sqrt{3} \times \sqrt{3}$)R30° surface. An estimate of the oxygen vacancy density in the top atomic layer of the nearly stoichiometric (1×1) surface can be made using the variation in the 325 K desorption state between the (1×1) and ($\sqrt{3} \times \sqrt{3}$)R30° surfaces. Assuming the ($\sqrt{3} \times \sqrt{3}$)R30° periodicity is indicative of 1/3 of a layer of oxygen vacancies, the (1×1) surface prepared by ion bombardment and 1000 K-annealing is estimated to contain about 4% (±1%) oxygen vacancies in the top atomic layer. Thus, the change in the 325 K desorption state as lattice oxygen is removed shows that propene is an excellent probe of surface lattice oxygen vacancies on the Cu$_2$O(111) surface.

If the number of propene thermal desorption cycles (and hence total exposures) was
small, a (1×1) LEED pattern could be regained from the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) surface by annealing to 1000 K in vacuum. This observation implies that mobile lattice oxygen diffuses from the bulk to the surface at higher temperatures, as reported previously for the (100) surface [19]. In cases where many repeated exposures were made, the (1×1) pattern could not be regained simply by annealing the surface to 1000 K. Extended ion bombardment was required to restore the surface to its original condition, such that annealing at 1000 K would again result in a (1×1) LEED pattern. Thus, the bulk oxygen which reoxidizes the surface appears to originate from some “near surface” region of unknown thickness and composition which can eventually be depleted.

The size of the 260 K peak was also found to be dependent on sample history. Changes in the 260 K desorption feature are illustrated in Figure 3.5 for desorption from two different \( (\sqrt{3} \times \sqrt{3})R30^\circ \) surfaces with different sample histories. The solid line in Figure 3.5 is the same 0.06 L propene desorption trace from the TDS series shown in Figure 3.3. This trace shows a clear 325 K and 260 K feature. The sample history is such that annealing at 1000 K could not restore the surface condition to a nearly-stoichiometric (1×1) condition. The dotted line is for a 0.06 L propene desorption trace obtained from a \( (\sqrt{3} \times \sqrt{3})R30^\circ \) surface which was prepared by successive propene exposures to the nearly-stoichiometric (1×1) surface shown as a dashed line in Figure 3.5. While the 325 K feature is clearly apparent, there is (similar to the stoichiometric surface) little intensity due to the 260 K feature. For this surface, it was possible to regain the nearly-stoichiometric (1×1) surface simply by annealing to 1000 K. These observations suggest that while the 325 K propene desorption signal is clearly associated with the oxygen vacancies that give rise to the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) surface, the 260 K desorption is due to some unidentified surface feature, possibly some type of defect, associated with the depletion of “near surface” oxygen.

**Propene-Deuterium Coadsorption, 120 K**

The presence of CO as a desorption product demonstrates that a small amount of the propene is dissociatively adsorbed on the (111) surface. In an effort to character-
ize the type of dissociated propene further, deuterium-propene coadsorption experiments were performed on an oxygen-deficient (111)-(\sqrt{3} \times \sqrt{3})R30^\circ surface. Deuterium (200 L equivalent D_2 dose) was coadsorbed with 0.3 L of propene at 120 K. Figure 3.7 shows the propene desorption spectra from clean and deuterium-predosed (111)-(\sqrt{3} \times \sqrt{3})R30^\circ surfaces. Figure 3.7(a) shows the C_3H_6 desorption from a clean (111) surface, while Figure 3.7(b) shows the desorption of normal propene (C_3H_6) and deuterated propene (C_3H_5D) from a deuterium-predosed (111) surface. No deuterated propane was detected in these experiments, illustrating that no hydrogenation occurred.

Several changes in the propene desorption behavior are observed when comparing the clean and deuterium-predosed surfaces. First, a decrease of 19±3% in the propene uptake for a 0.3 L dose was observed for the deuterium-predosed surface. Second, the 325 K propylene desorption state is greatly reduced on a deuterium-predosed surface, suggesting that atomic deuterium either blocks the propene adsorption at the sites associated with oxygen vacancies or significantly alters the activation energy for desorption. Third, coincident with the disappearance of the 325 K desorption state on a deuterium-predosed surface is an increase of an equal sized area in a desorption peak at 245 K, suggesting that propene lost from the 325 K desorption channel populates sites with a lower activation energy for desorption. Finally, a clear decrease in the desorption peak at 220 K is observed when comparing the deuterium-predosed surface to the clean surface. The overall reduction in the area of the desorbing propene signal on the deuterium-predosed surface is equal to the decrease in area of the 220 K desorption peak. This final observation suggests that the change observed in the area of the 220 K peak is due to site blocking.

In addition to the changes in the shapes of the desorption spectra, deuterium-labeled propene (C_3H_5D) was detected. Figure 3.7(c) shows the desorption behavior of C_3H_5D which desorbed in a broad feature centered at 300 K, and demonstrates that a small amount of propene dissociates then recombines with surface deuterium. The C_3H_5D feature appears to overlap the temperature range where the 260 K and 325 K TDS features (i.e., those features associated with oxygen vacancies and unidentified defects) are observed for propene.
Figure 3.7: Thermal desorption traces following 0.3 L propene doses on the Cu$_2$O(111)-(\sqrt{3} \times \sqrt{3})R30^\circ surface at 120 K on (a) the clean surface and (b) a deuterium-predosed surface.
adsorption on the clean surface. This observation suggests that the 260 K and 325 K features are due to recombination of dissociatively adsorbed propene. The lack of C_2H_5D desorption at lower temperatures suggests the remaining TDS features for propene adsorbed on the clean or hydrogen-predosed (111) surface are associated with a molecular adsorbate, supporting the previous assumption of a first-order desorption process for the 245-220 K and 185-175 K states. Hence, it appears that atomic hydrogen prevents the dissociation of propene at oxygen vacancy and defect sites, giving rise to a molecularly adsorbed species with a lower activation energy for desorption which appears at around 245 K. This conclusion is consistent with the equivalence in amount of the 245 K species gained from the hydrogen-predosed surface coincident with the loss of higher temperature features from the clean surface. In this regard, note that the C_2H_5D species formed by recombination in Figure 3.7(b) represents a very small portion of the total amount of propene detected; similar quantities of C_2H_6 formed by recombination in this temperature range would be unobservable in Figure 3.7(b).

**Propene Adsorption, 300 K**

Adsorption experiments on the Cu_2O(111)-(\sqrt{3} \times \sqrt{3})R30° surface were also carried out at 300 K in an attempt to selectively populate the 325 K adsorption site for further study. Propene doses up to 3000 L were examined. The sticking coefficient under these conditions was estimated to be less than 10^-5, hence the coverages were very low. Figure 3.8(a) shows propene TDS traces after a 3000 L dose on the clean surface. Propene desorbed as one broad feature extending from 300 K to 425 K, with a peak maximum near 360 K. Assuming first order desorption kinetics gives an activation energy of desorption of 24.2 kcal/mol. No reaction products were detected during the TDS experiments besides propene.

**Propene-Deuterium Coadsorption, 300 K**

As on the (100) surface, deuterium-propene coadsorption experiments were performed in order to check for dissociated propene at 300 K. Figure 3.8(b) shows TDS traces for
Figure 3.8: Thermal desorption traces for a 3000 L propene dose on the Cu$_2$O(111)-(\sqrt{3} \times \sqrt{3})R30^\circ$ surface following adsorption at 300 K on (a) a clean Cu$_2$O(100) surface, and (b) a deuterium-predosed surface.
deuterium (200 L equivalent dose) coadsorbed with 3000 L of propene at 300 K. An increase in the m/e⁻ 43 signal after propene-deuterium coadsorption showed that about 12±1% of the desorbing propene was deuterated. The deuterated propene desorbed in the same temperature range as propene (C₃H₆) as shown in Figure 3.8(b). No deuterated propane was detected, showing that no hydrogenation occurred. Thus, the presence of deuterated propene after adsorption at 300 K gives clear evidence that propene is dissociated under these conditions.

C 1s XPS was measured after a 3000 L propene dose at 300 K. However, because of the low coverage of propene at 300 K, there was not enough signal above the background for analysis.

3.3.3 UPS of Adsorbed Propene

In an attempt to gain insight into the bonding and interaction of molecular propene with Cu₂O surfaces, propene adsorption at low temperature was studied with UPS on the (100) and (111) surfaces. Figure 3.9 shows HeI/II UPS of a 3000 L propene dose on the Cu₂O(100) surface at 100 K. No significant differences in the UPS spectra of adsorbed propene were observed dependent on the excitation source (He I or He II), and only small differences were observed between the (100) and (111) surface [67]. Additionally, no significant changes were detected in the UPS spectrum upon annealing to higher temperature. Figure 3.9(b) shows a difference spectrum of adsorbed propene on the (100) surface, which matches well with the gas phase spectrum of molecular propene shown as Figure 3.9(c). The peak at 3.7 eV is assigned to emission from the πC=C bond by comparison with the He I gas phase spectrum of propene [68].
Figure 3.9: (a) He II UPS of a clean (solid line) and 3000 L propene dosed (dashed line) Cu$_2$O(100) surface at 100 K. (b) UPS difference curve between the spectra in (a). (c) Gas-phase C$_3$H$_6$ UPS spectrum reprinted from Ref. [68] by permission of John Wiley & Sons, Ltd. All spectra are referenced to the valence-band maximum, and N(E) spectra have been normalized on the Cu$_2$O valence band feature below 1 eV.
3.4 Discussion

3.4.1 Molecular Propene on Cu$_2$O

The results described above show clear structure sensitivity for propene adsorption on the Cu$_2$O(100) and (111) surfaces. Structure sensitivity for propene adsorption at low temperature was demonstrated by differences in the temperatures and numbers of propene desorption channels on the (100) and (111) surfaces. On the (100) surface, two desorption states were observed, while on the (111) surface, five distinct desorption states were detected. Additionally, a high temperature propene (325 K) desorption state was observed on the (111) surface which was sensitive to the concentration of surface lattice oxygen vacancies.

Molecular propene was observed on both the (111) and (100) surfaces at low temperature. Some insight into the type of bonding of molecular propene to the Cu$_2$O surfaces may be gained by consideration of ethene adsorption on Cu(110) and (111) surfaces. UPS studies have shown that ethene is $\pi$-bonded to the Cu(111) surface, and is oriented parallel to the surface upon adsorption [69]. Electron energy loss studies of ethene on the Cu(110) surface show that it is also adsorbed in a $\pi$-bonded form [70]. Studies of ethene adsorption on ordered Sn/Pt(111) alloys found that di-$\sigma$ bonded ethene did not show a significant $\pi_{C=O}$ bond in either He I or He II UPS [71]. As described in the previous section, a $\pi_{C=O}$ contribution was detected clearly in UPS for propene on Cu$_2$O surfaces. Thus, by analogy with ethene, the observed $\pi_{C=O}$ contribution on Cu$_2$O surfaces is evidence of a $\pi$-bonded rather than a di-$\sigma$ bonded molecular adsorbate.

3.4.2 Dissociated Propene on Cu$_2$O

Form of Dissociated Propene

Although no definitive experimental evidence reported here shows the form of the dissociated propene on the (100) and (111) surfaces, some insights may be gained by consideration of the previously reported chemistry for propene oxidation. For acid-base reactions
involving propene, the allylic (methyl) hydrogen is the most acidic proton [72]. Thus, assuming the propene-surface interaction can be viewed as acid-base chemistry, the dissociated propene molecule most likely dissociates to form an allylic C₃H₅ specie. The formation of an allylic specie from propene on Cu₂O is consistent with previous reports which show that the formation of an allylic species precedes the formation of selective oxidation products [1]-[7],[73]. Dissociation of propene to an allyl species (C₃H₅) is consistent with the C₃H₅D observed as a desorption product in propene-deuterium thermal desorption.

An allylic species from dissociated propene could exist either as a σ-allyl or as a π-allyl bound to a metal center [73]-[76] or as an oxygen containing σ-allyl [1]-[3]. Stable organometallic compounds are known which possess σ-allyl ligands bound to a Cu(I) metal center [74]. On Cu₂O powder catalysts, a π-allyl species has been identified using infrared spectroscopy [73]. Additionally, some organometallic complexes include allyl ligands which can be thought of as resonance structures with attributes of both the π- and σ-allyl forms [75, 76]. From our data, it is not possible to identify the form(s) of the allylic specie(s) (i.e. π or σ) bound to our Cu₂O surfaces. However, the lack of any C₃ oxygen containing products in detectable quantities suggests that no oxygen containing σ-allyl species are formed. Vibrational spectroscopy would be necessary to distinguish between the different forms of adsorbed allyl species. However, the apparently low coverages of allyl vs. molecular propene could make such a characterization difficult.

An alkylidyne (i.e., propylidyne) C₃H₃ species has been proposed for propene adsorption on Rh(111) and Pt(111) surfaces instead of an allyl species [62]-[65]. Studies have shown that propene adsorption is very similar to ethene adsorption over Pt and Rh single crystals [65], thus studies of ethene adsorption may be indicative of the type of bonding expected for propene. For the formation of an alkylidyne (R-CH₂-C≡) species to occur, the adsorbed molecule di-σ bonds to the surface [62]-[65]. Upon heating, an alkylidyne species forms that is bound to three metal atoms. Studies of ethene adsorption on Cu single crystals have shown that ethene does not di-σ bond to either the Cu(110) [70] or Cu(111) surfaces [69]. We would expect the results for alkene adsorption on Cu₂O to more closely resemble Cu.
surfaces than Rh or Pt [77]. Additionally, the UPS results for propene adsorption on Cu$_2$O suggest that molecular propene $\pi$-bonds at low temperature. Since alkylidyne formation typically proceeds through a di-$\sigma$ bonded molecular species, the $\pi$-bonded molecular species on Cu$_2$O is more likely to yield an allyl species upon dissociation rather than an alkylidyne species.

It is not understood why propene recombination appears to be a first order process for the 260 K and 325 K desorption channels associated with defects on the (111) surface. The first order recombination at 325 K and 260 K may involve a rate-limiting step for breaking surface-hydrogen bonds or surface-allyl bonds. In this regard, thermal desorption studies for predissociated hydrogen and deuteronium on the (100) surface have shown that atomic hydrogen recombines in a broad desorption feature at about 300 K [16]. Though far from conclusive, the hydrogen TDS study demonstrates that surface-hydrogen bond breaking and recombination occurs in a temperature range consistent with that observed for propene recombination.

Propene dissociation to an allyl appears to occur at defect sites on the (111) surface at low temperature. In Section 3.3.2, the 325 K and 260 K propene desorption states were assigned to allyl-hydrogen recombination on the (111) surface. In addition, the changes observed in the desorption behavior of the 325 and 260 K propene desorption states as a function of sample history and preparation conditions suggested that the 325 and 260 K adsorption sites were at some type of surface defects. Thus, all the propene recombination peaks observed on the (111) surface after low temperature adsorption appear to be associated with either lattice oxygen vacancies (325 K) or an unidentified type of defect (260 K).

From studies of propene oxidation on low surface area Cu$_2$O crystals, Wood et al. suggested that an oxygen-deficient (i.e., copper-rich) surface favors selective oxidation to acrolein whereas an oxygen-rich surface favors CO$_2$ production [78]. They also found that only a thin surface layer participates in propene oxidation on Cu$_2$O similar to our observation that the oxygen availability of some "near surface" region can be reduced by repeated
exposure to propene. In addition, much previous work on propene oxidation has shown that the formation of allylic species (C₃H₅) is a necessary step for the subsequent formation of selective oxidation products [1-7,73]. The data presented here provides direct evidence that the dissociation of propene to allyl is enhanced under our experimental conditions, at least on the (111) surface by the presence of surface oxygen vacancies and defects, consistent with the conclusions of Wood et al. that a copper-rich surface favors propene selective oxidation. However, since no selective oxidation products are observed under our experimental conditions, there is no direct evidence that the type of allyl formed at these defects sites actually proceeds to selective oxidation products. Nevertheless, the potential importance of oxygen vacancies and defect sites as low activation energy sites for the initial dissociation of propene should not be overlooked.

**Energetics of Propene Dissociation**

A lower limit for the activation energy of propene dissociation to an allylic species can be estimated from the thermal desorption experiments described. The lack of dissociated propene from the (100) surface after adsorption at 100 K suggests that propene did not remain on the surface to a high enough temperature to overcome the activation barrier to dissociation. The highest temperature desorption state on the (100) surface was 255 K, with a corresponding activation energy of 16.9 kcal/mol. Thus, a lower limit on the activation barrier for propene dissociation to an allyl on the Cu₂O(100) surface can be set at 16.9 kcal/mol.

Using similar arguments, the lower limit for propene dissociation on the (111) surface can also be estimated. The presence of CO as a reaction product demonstrates that some propene is converted to CO at or below 130 K. The corresponding activation energy for desorption is 8.5 kcal/mol or less. This activation energy therefore represents the minimum activation barrier to the non-selective oxidation of propene on the (111) surface.

Evidence for propene dissociation to allyl (C₃H₅) was seen for both the (100) and (111) surfaces after adsorption at 300 K. Assuming that the dissociative adsorption of propene
is exothermic, an upper limit of 21.1 and 24.2 kcal/mol can be estimated for propene dissociation to an allyl on the (100) and (111) surfaces, respectively, based on first-order activation energies for recombinative desorption. Our data does not, however, provide any independent confirmation on the sign of the enthalpy change for dissociative adsorption. Within the limits of these assumptions, the activation energy for propene dissociation to an allyl species on the (100) surface is estimated to be between 16.9 and 21.1 kcal/mol. Similarly, an upper limit of 24.2 kcal/mol can be estimated for propene dissociation to an allyl on the (111) surface.

Effects of Oxygen on Propene Dissociation

The effects of three different types of oxygen on propene adsorption were tested by using the differences in adsorbed or lattice oxygen on the Cu₂O(100) and (111) surfaces. On the (100) surface, no activation of propene was caused by either adsorbed molecular or doubly-coordinate atomic oxygen. However, CO was detected as a product during propene thermal desorption on the (111) surface which contains triply-coordinate lattice oxygen in the topmost atomic layer. The reason for propene conversion to CO in the presence of triply-coordinate lattice oxygen and not doubly-coordinate atomic oxygen is not understood. It is not clear whether the CO production is due to differences in local site geometries and compositions between the (111) and (100) surfaces, or because of differences in the coordination numbers of the atomic oxygen species, to the extent that these features may be distinguished.

3.5 Conclusions

Propene adsorption was studied on both the (111) and (100) surfaces using thermal desorption and photoemission. Differences in the number and temperatures of the propene desorption states on the (100) and (111) surfaces demonstrate that propene adsorption is structure sensitive on Cu₂O single crystal surfaces. Propene adsorption at low temperature
is primarily molecular on both the (100) and (111) surfaces. However, a small amount of
dissociated propene was detected after low temperature adsorption on the (111) surface. It
appears that all the propene dissociation to allyl and recombination after low temperature
adsorption on the (111) surface occurs at surface defects. Dissociative adsorption of propene
was observed on the (100) and (111) surfaces at 300 K. However, the sticking coefficients
for propene adsorption are very low at 300 K. No C₃ reaction products of any type were
detected during propene TDS on either the Cu₂O(111) or (100) surface under the conditions
studied.

Propene adsorption was also studied on deuterium-predosed Cu₂O surfaces. No hydro-
genation of the C=O bond by adsorbed atomic deuterium was observed for either surface
under the conditions studied here. No change in the desorption temperature or the amount
of propene adsorbed was observed for propene on a deuterium-predosed Cu₂O(100) surface.
However, preadsorbed deuterium blocked propene adsorption sites on the (111) surface, de-
creasing the amount of propene adsorbed, and significantly reducing propene dissociation
and hence the recombination pathway at surface defect sites.

A distinct change in the high temperature (325 K) propene desorption state on the (111)
surface was observed as a function of surface condition. Because of the increase in size of the
325 K desorption state as the surface progresses from a (1×1) to a (√3 x √3)R30° surface,
this desorption state can be assigned to propene adsorption at or around the threefold
Cu⁺ sites associated with the lattice oxygen vacancies on the (111)-(√3 x √3)R30° surface.
Thus, propene is a sensitive probe of lattice oxygen vacancies on the Cu₂O(111) surface.
Chapter 4

Acrylic and Propionic Acid Decomposition on Cu₂O(100): Reaction Pathways of C₃ Carboxylates

4.1 Introduction

Surface carboxylates (RCOO⁻) have been observed as reaction intermediates in the decomposition of oxygenates on several metal oxide single-crystal surfaces [79]-[90]. In studies of allyl alcohol and 1-propanol decomposition on the Cu₂O(100) surface, carboxylate species were detected in photoemission experiments [10]. In order to better understand the role of carboxylate species in the alcohol decomposition pathways, a study of acrylic and propionic acids on the Cu₂O(100) surface was undertaken.

There are only two reported studies of propionic or acrylic acid decomposition on single-crystal metal oxide surfaces [87, 89]. Formic, acetic and propionic acids were studied on TiO₂(001) faceted surfaces [89]. A unimolecular dehydration pathway was detected for each of the acids studied, yielding CO, ketene, and acrolein from formic, acetic, and propionic acids, respectively. Additionally, a bimolecular ketonization product (methyl ketene) was detected during acetic acid decomposition on the TiO₂(001)-{114} surface. Propionic acid decomposes on ZnO(0001)-Zn through two competing pathways. A net unimolecular dehydration pathway which yields acrolein was observed, as well as a dehydrogenation pathway leading to CO, CO₂ and H₂O [87].
4.2 Experimental

Aldrich propionic acid (99+%) and acrylic acid (99%) were used in these studies, and were purified by repeated freeze-pump-thaw cycles prior to dosing. Matheson Research grade \( \text{H}_2 \) (99.9995%) was used as received. Since \( \text{H}_2 \) does not dissociatively adsorb on the \( \text{Cu}_2\text{O}(100) \) surface under UHV conditions [16], hydrogen was predissociated using a white hot platinum filament located 15 mm from the sample surface. All hydrogen doses are reported as the equivalent \( \text{H}_2 \) dose.

4.3 Results

4.3.1 Thermal Desorption

Propionic Acid

Figure 4.1 shows the thermal desorption spectra following a 0.85 L (1 ML) dose (ML \( \equiv \) Monolayer) of propionic acid at 100 K. For the propionic acid, the operational definition of a one monolayer coverage was taken as the coverage where a propionic acid multilayer first appeared in TDS. This dose also corresponds to the coverage where saturation of the product peaks occurred. No bimolecular products or \( \text{C}_2 \) products were detected.

Propionic acid desorbed in three temperature ranges. For doses greater than 0.85 L, a propionic acid desorption peak at 200 K was observed. This feature did not saturate with coverage, demonstrating that it was due to multilayer formation. A broad propionic acid desorption feature was also observed at 230 K, in addition to a high temperature desorption peak at 580 K. No shifts were observed in the 230 K and 580 K propionic acid TDS peaks as a function of coverage, indicating that the rate-limiting steps obey first-order kinetics. Assuming a preexponential of \( 10^{13} \text{ sec}^{-1} \), and applying the Redhead equation [66] gives activation energies for desorption of 15.2 and 39.5 kcal/mol for the 230 and 580 K propionic acid desorption channels, respectively.

No changes were observed in the temperatures of the desorption products with coverage,
Figure 4.1: Thermal desorption spectra following a 0.85 L dose of propionic acid at 100 K on the Cu$_2$O(100) surface.
implying first-order reaction processes. CO, CO$_2$, and H$_2$O all desorbed at 620 K, with an activation energy of desorption of 42.3 kcal/mol. Higher temperature CO and CO$_2$ peaks were also observed at 705 K and 685 K, respectively, with activation energies of 48.3 and 46.9 kcal/mol. All the CO and CO$_2$ peaks observed are reaction-limited [14, 91].

Water TDS studies have shown that recombination of dissociated water occurs at 465 K on this surface [15], and TDS studies of predissociated hydrogen have shown that atomic hydrogen extracts lattice oxygen to form water at about 500 K [16]. Thus, the rate-limiting step for the water formed at 620 K is dehydrogenation of surface hydrocarbons. H$_2$ was not detected as a desorption product; however, the background of hydrogen was high enough in the vacuum system that small amounts of desorbing H$_2$ might have gone undetected.

A first-order desorption product with a m/e$^-$ of 56 was detected at 580 K which could be either acrolein (CH$_2$=CCH=O) or methyl ketene (CH$_3$C$\equiv$C=O). Studies of propionic acid decomposition over TiO$_2$(001)-(011) and ZnO(0001)-Zn surfaces identified the 56 m/e$^-$ signal as methyl ketene (CH$_3$C$\equiv$C=O) and acrolein (CH$_2$=CCH=O), respectively [87, 89]. No standard mass spectral data for methyl ketene is available; however, previous identification of this product has relied on the relative intensity of the 29 m/e$^-$ signal compared to the 56 m/e$^-$ signal [87, 89]. A significant 29 m/e$^-$ signal is found as a cracking fragment for acrolein [92], but not for methyl ketene. Analysis of our thermal desorption data shows that a 29 m/e$^-$ signal is detected in correct proportion to the 56 m/e$^-$ signal for acrolein. Thus, the 56 m/e$^-$ signal is assigned to acrolein rather than to methyl ketene. Previous studies of acrolein adsorption on the Cu$_2$O(100) surface show that the product acrolein which desorbs at 580 K is reaction-limited [9]. The rate-limiting step for acrolein formation at 580 K has an activation energy of 39.5 kcal/mol.

The conversion of propionic acid was 98% for coverages up to 1 monolayer. The selectivities to products were calculated on a C$_3$-basis. The selectivity to CO was 36%, to CO$_2$ was 50%, and to acrolein was 14%. The relative yields of the desorption products from a 0.85 L dose (1 ML) of propionic acid are shown in Table 4.1. The amounts of oxygen-containing products clearly indicates the extraction of lattice oxygen during propionic acid TDS.
Table 4.1: Relative Yields of a 0.85 L dose (1 ML) of propionic acid on Cu$_2$O(100).

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$C(=O)CH$_2$COOH TDS</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>0.13</td>
</tr>
<tr>
<td>CO</td>
<td>1.00</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.40</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.95</td>
</tr>
</tbody>
</table>
Acrylic Acid

Figure 4.2 shows thermal desorption spectra following a 0.9 L dose (1 ML) of acrylic acid at 100 K. As with propionic acid, a monolayer of acrylic acid was defined as the coverage where a multilayer peak first appeared, and saturation of the reaction products occurred. The only products detected from acrylic acid were CO, CO$_2$, and H$_2$O. No bimolecular, C$_3$, or C$_2$ products were detected. Desorption of acrylic acid was observed in three temperature ranges. For doses greater than 0.9 L, an acrylic acid desorption peak at 200 K was observed. This feature did not saturate with increasing coverage, demonstrating that it was due to multilayer formation. A second desorption feature was observed at 225 K, with an additional higher temperature desorption feature at 595 K.

Similar to the results for propionic acid, no change in the acrylic acid TDS peaks or desorption product peak positions was observed as a function of coverage, suggesting that all the rate-limiting kinetic steps are first-order. Assuming a preexponential factor of 10$^{13}$ sec$^{-1}$ and applying the Redhead [66] equation gives activation energies of desorption of 14.9 and 40.5 kcal/mol for the 225 and 595 K acrylic acid peaks, respectively. Product CO desorbed as a reaction-limited product [14] at 600 K with a very small lower temperature shoulder at 630 K. The activation energies of the rate-limiting steps correspond to 47.2 and 43.0 kcal/mol. CO$_2$ desorbed in a reaction-limited peak [91] at 670 K with a lower temperature shoulder at 630 K, with corresponding activation energies of 45.8 and 43.0 kcal/mol. H$_2$O desorbed at 630 K with a shoulder at 670 K, both from the dehydrogenation of surface hydrocarbons. The H$_2$O desorption peaks have corresponding activation energies of 43.0 (630 K) and 45.8 kcal/mol (670 K).

No coverage dependence was observed for the conversion of acrylic acid up to a monolayer coverage. The conversion was 95% with a selectivity to CO of 31% and to CO$_2$ of 69% (on a C$_3$ basis). A summary of the relative yields of the acrylic acid desorption products is given in Table 4.2. The amounts of oxygen-containing products clearly indicate the extraction of lattice oxygen during propionic acid TDS.
Figure 4.2: Thermal desorption spectra following a 0.9 L dose of acrylic acid at 100 K on the Cu$_2$O(100) surface.
Hydrogen Coadsorption

Propionic and acrylic acid thermal desorption was also studied on a hydrogen-predosed (100) surface. Hydrogen (200 L equivalent dose) was coadsorbed with monolayer coverages of either acrylic or propionic acid at 100 K. No effects on either the conversion or selectivity of the adsorbed acids were observed due to the presence of coadsorbed hydrogen. Additionally, no change in the desorption temperature of the acids was observed due to the presence of hydrogen.

4.3.2 XPS

Propionic Acid

In an effort to characterize the surface species leading to the desorption products from propionic acid, C 1s XPS spectra were taken as an adsorbed layer was successively heated to higher temperatures. For these experiments, 17 L of propionic acid was dosed at 100 K, heated to the desired temperature, cooled back to 100 K, and the XPS spectrum was taken.

The XPS spectrum of multilayer propionic acid is shown in Figure 4.3(a). Two distinct peaks are observed at binding energies of 289.9 and 285.7 eV. By comparison to gas phase spectra of carboxylic acids, the peak at higher binding energy (289.9 eV) is assigned to the carboxyl group of molecular propionic acid, while the lower binding energy peak (285.7 eV) is assigned to the alkyl carbons in the ethyl group of molecular propionic acid [93]. The separation between high and low binding energy peaks is 4.2 eV, in good agreement with a separation of 4.0 eV for the C 1s signals for gas phase acetic acid [93]. The ratio of the alkyl (ethyl) carbons to the carboxyl carbons was 2:2 for the propionic acid multilayer, slightly higher than the expected stoichiometric value of 2.0. In general, the calculated ratio for a given spectrum can vary by ±0.2 for small changes in the peakfitting parameters.

Heating the propionic acid multilayer to 210 K resulted in the desorption of the multilayer, leaving chemisorbed propionic acid on the surface. A decrease of about 50% in the total C 1s signal was observed after heating to 210 K. The resulting C 1s spectrum is shown
Figure 4.3: C 1s XPS of propionic acid on the Cu₂O(100) surface at 100 K. (a). Spectrum of propionic acid multilayer. (b) Surface in (a) heated to 210 K. (c) Surface in (b) heated to 500 K.
in Figure 4.3(b). Three peaks were fit to this spectrum at binding energies of 289.4, 287.9 and 285.2 eV. The separation between the high binding energy peak (289.4 eV) and the low binding energy peak (285.2 eV) remained at 4.2, suggesting that these peaks can be assigned to the carboxyl group and alkyl carbons of molecular propionic acid, respectively. However, the 289.4 and 285.2 eV peaks due to molecular propionic acid are both 0.5 eV lower than in the multilayer. This decrease in binding energy is thought to occur because the binding energy of the physisorbed multilayer tracks the work function instead of the Fermi level [94]. The major contribution to the C 1s spectrum was the peak at 285.2 eV. The peak at 289.4 eV for the carboxyl group of molecular propionic acid represented only about 10% of the C 1s signal.

The assignment of the peak at 287.9 eV is not straightforward. Peaks in a similar binding energy range have been observed for allyl alcohol and 1-propanol decomposition on Cu$_2$O(100) [12]. However, the peak at 287.9 eV is not due to the oxygenated carbon of an alkoxide (286.4 eV) [12] or an aldehydeic surface species (287.2 eV) [9]. The presence of this 287.9 eV peak at a higher binding energy than for the formyl group of an aldehyde suggests that it is due to a C-O bond order greater than two, and it is thus assigned to a surface carboxylate. The peak at 287.9 eV is associated with propionic acid dissociation by loss of the acidic proton of the carboxyl group. Thus, XPS suggests the formation of a surface propionate by dissociative adsorption of propionic acid.

In summary, the peak at 289.4 eV is assigned to the carboxyl group of molecular propionic acid, the peak at 287.9 eV is assigned as adsorbed propionate species, and the peak at 285.2 eV is assigned to the alkyl carbons for both molecular and dissociated propionic acid. A useful measure of the stoichiometry of the adsorbed surface species is to compare the intensities of the C 1s signals of all the oxygenated carbons of carboxyl and carboxylate species (designated CO$_2$) to the intensity of the non-oxygenated carbons due to ethyl groups, vinyl groups or hydrocarbon fragments (designated C$_x$H$_y$). The C$_x$H$_y$/CO$_2$ ratio for the spectrum shown in Figure 4.2(b) is 3.1. The change in the C$_x$H$_y$/CO$_2$ ratio from 2.2 for the multilayer to 3.4 after heating to 210 K indicates that some reduction of surface
oxygenates occurred, and that contributions from hydrocarbon fragments also contribute to the C 1s signal at 285.2 eV.

Further heating of the chemisorbed layer to 500 K leaves surface species which form CO, CO₂, H₂O, and acrolein. The C 1s intensity decreases to about 80% of the intensity observed after heating to 210 K. The resulting C 1s spectrum is shown in Figure 4.3(c). Peaks were fit to this spectrum at binding energies of 288.0 and 284.9 eV. The peak assignments are as given previously. The peak at 284.9 eV is the dominant peak, with the propionate species accounting for only about 15% of the C 1s signal. The C₂H₆/CO₂ ratio for the spectrum shown in Figure 4.3(c) is 5.6. The continued increase in the C₂H₆/CO₂ ratio indicates further reduction of the surface oxygenates has taken place and suggests that the 284.9 eV feature is due to the ethyl carbons of surface propionate and hydrocarbon fragments. The absence of a peak due to carboxyl carbons (289.5 eV) demonstrates that no molecular propionic acid remains on the surface.

Further heating of the surface to 1000 K resulted in a carbon free surface. No reduction of the surface to Cu⁰ was observed in XPS, as determined by examination of the position of the Cu L₃VV Auger feature [43]. The oxygen extracted during the propionic acid TDS is replenished by oxygen diffusion from the bulk to reoxidize the surface near 900 K [19].

Acrylic Acid

Acrylic acid was also studied with XPS as a function of annealing temperature. Variations in the pressure of the liquid nitrogen source used to cool the sample sometimes affected the lowest attainable sample temperature. During the acrylic acid XPS experiments, the lowest substrate temperature was 120 K. As shown below, a thick multilayer was not obtained, demonstrating that the sticking coefficient for multilayer formation was significantly reduced by the 20 K increase in the substrate temperature.

Figure 4.4(a) shows the XPS spectrum following a 7.2 L dose of acrylic acid. Three peaks were fit to this spectrum at binding energies of 289.6, 288.0, and 285.4 eV. These peaks are in similar binding energies as described for propionic acid C 1s XPS, and are assigned
in a similar fashion. The highest binding energy peak (289.6 eV) is due to the carboxyl group of molecular acrylic acid, and the low binding energy peak (285.4 eV) is assigned to the vinyl group of both dissociated and molecular acrylic acid. The peak at 288.0 eV is in the same binding energy range as that previously assigned to surface propionate. Thus, by analogy with propionic acid, the 288.0 eV feature is attributed to a surface acrylate. The \( C_2H_4/CO_2 \) ratio for the spectrum shown in Figure 4.4(a) is 2.1, similar to the expected stoichiometric value to 2.0.

The chemisorbed acrylic acid layer was heated to 210 K to desorb any multilayer acrylic acid. The resulting C 1s spectrum is shown in Figure 4.4(b). Three peaks were fit to this spectrum with binding energies of 289.5, 288.0, and 285.2 eV. The positions of these peaks are essentially the same as for acrylic acid at 100 K, and are assigned in an identical fashion. The peak at 289.5 eV is due to the carboxyl carbon of molecular acrylic acid, and the peak at 288.0 eV is due to an acrylate. The \( C_2H_4/CO_2 \) ratio for the spectrum shown in Figure 4.4(b) is 2.8, and illustrates the further reduction of surface oxygenate species. Thus, the peak at 285.2 eV is due not only to the vinyl group of surface acrylate and molecular acrylic acid, but also to some hydrocarbon fragments.

No significant change in the overall area of the C 1s carbon signal was observed upon heating from 120 to 210 K. However, several changes were observed in the relative intensities of the three contributions. The area of the peak at 285.2 eV showed a very small \( (\approx 10\%) \) increase, while the peak due to the carboxyl group decreased by 70%. The peak due to acrylate doubled in size. These changes in relative intensities are consistent with either the conversion of molecular acrylic acid to surface acrylate species or the desorption of a molecular acrylic acid multilayer to uncover dissociatively adsorbed acrylic acid.

Heating the adsorbed layer to 580 K results in the desorption of all surface species except those eventually producing CO, CO\(_2\), and H\(_2\)O. No significant change in the overall area of the C 1s signal was observed. The resulting C 1s spectrum is shown in Figure 4.4(c). Peaks were fit to this spectrum at binding energies of 288.0 and 284.9 eV. No molecular acrylic acid features were detected under these conditions. The \( C_2H_4/CO_2 \) ratio for the
this spectrum is 5.1, which demonstrates further reduction of the surface oxygenates. The peak at 284.9 eV is the dominant feature in the C 1s XPS, with the characteristic acrylate feature (288.0 eV) accounting for only about 20% of the C 1s signal at 580 K. Thus, the only oxygen-containing surface species detected with XPS after heating to 580 K is a surface acrylate, but the majority species on the surface are hydrocarbon fragments produced by the reduction of the acrylates.

Further heating of the surface to 1000 K results in a carbon free surface. Similarly to the propionic acid C 1s XPS, no evidence of Cu⁰ was detected during the XPS experiments after heating to any temperature.

4.4 Discussion

4.4.1 Adsorption and Bonding of C₃ Acids to Cu₂O(100)

Similar desorption temperatures were observed for both propionic and acrylic acid desorption from the (100) surface. Multilayer peaks for both acids were observed at 200 K, in addition to high-temperature peaks at 580-595 K. Additionally, a desorption feature was observed at 230 K for propionic acid and 225 K for acrylic acid. The similarity in desorption temperatures for both acrylic and propionic acid suggest that their bonding modes to the (100) surface are similar. Additionally, the difference in the activation energies for the formation of CO, CO₂, and H₂O from propionic and acrylic acid differ by less than 1 kcal/mol, suggesting similar non-selective oxidation pathways on Cu₂O(100).

Molecular acid features were observed for both acids in the C 1s signals after heating to 200-210 K. These observations suggest that the TDS peaks in 225-230 K range are due to the desorption of molecular surface species.

The acrylic and propionic acid desorption features at 580-595 K are at a much higher temperature than expected for molecular acids. The XPS results show no features due to molecular acids above 500 K, in agreement with this expectation. Additionally, coincident with the high-temperature acid desorption peaks is the start of H₂O desorption, suggesting
the initial dehydrogenation of surface species. Thus, the acid desorption peaks at 580-595 K are attributed to the recombination of dissociated acids (i.e., propionate or acrylate recombination with surface hydrogen). The first-order kinetics and coincident desorption of water indicate that the rate-limiting step is the unimolecular decomposition of surface carboxylates.

4.4.2 Propionic Acid Dehydration Pathway

For propionic acid on Cu$_2$O, a pathway which produced small amounts of an unsaturated carbonyl compound (i.e., acrolein) was observed at 580 K. The coincident desorption of acrolein with the first-order propionic acid recombination peak suggests that the rate-limiting step in acrolein formation is the unimolecular decomposition of the propionate intermediate. The temperature at which acrolein is formed from a propionate species (580 K) agrees well with acrolein production from propionate species on TiO$_2$ (595 K) and ZnO(0001)-Zn (620 K) [84, 87].

Studies of the surface chemistry of acrolein on Cu$_2$O(100) detected propionaldehyde as a product during thermal desorption from a hydrogen-predosed surface [9]. Thus, one might expect the coincident appearance of propionaldehyde with acrolein. However, the propionaldehyde formed by hydrogen-acrolein coadsorption is thought to be produced via the hydrogenation of a surface enolate intermediate at temperatures below 500 K. In contrast, the proposed production of acrolein from propionate occurs 80 K higher than the maximum temperature where a surface enolate is stable, suggesting that acrolein is not produced via an enolate intermediate in the present case.

The ketonization of carboxylic acids has been observed over supported oxide, mixed oxide, and single-crystal catalysts [87,89,95,96,97]. Swaminathan and Kuriacose studied the ketonization of acetic acid over supported chromia [95,96]. They suggested that two acetic acid molecules react on different adsorption sites to form acetone, with the requirement of both dehydration and dehydrogenation sites on a catalyst for bimolecular ketonization to occur. Thus, the ketonization reaction over chromia was suggested to involve two surface
species on separate sites combining to form a bimolecular reaction product.

A bimolecular ketonization pathway was also observed on TiO$_2$(001)-(114) faceted surfaces [89]. Kim and Barteau suggested that the sight requirements for bimolecular ketonization reactions are surface cations with more than one vacant coordination site. On the Cu$_2$O(100) surface, only singly-coordinated Cu$^+$ cations are found on the surface, suggesting that the Cu$^+$ cations lack the necessary vacant coordination sites to form bimolecular reaction products. This view is supported by carboxylic acid decomposition over single crystal ZnO(0001)-Zn and MgO(100), where no bimolecular ketonization products are observed, and where the surface cations have only a single vacant coordination site [87, 98]. Kim and Barteau also suggest that for the dissociative adsorption of carboxylic acids and net dehydration to occur, surface cations with only a single vacant coordination site are required [89]. This is also consistent with our results for carboxylic acid decomposition over Cu$_2$O, where only Cu$^+$ cations with one vacant coordination site are available, and where dissociative adsorption and dehydration of propionic acid to acrolein is observed.

Results from MgO(100), ZnO(0001)-Zn, and TiO$_2$(001) surfaces also suggest that a cation-anion (acid-base) pair is required for the net dehydration of acids to occur [87, 89, 98]. The requirement of an anion is to serve as a base site which extracts an acidic proton from the carboxylic acid and forms a surface OH group. However, no large amounts of OH groups were formed from acids upon adsorption on Cu$_2$O(100) as no water was detected below 500 K. Indeed, hydrogen adsorption studies on Cu$_2$O(100) have shown that atomic hydrogen adsorbs on Cu$^+$ sites to form surface hydrides [16]. The acidities of transition-metal hydrides are known to increase on moving from left to right across a transition series [75], suggesting that a surface Cu$^+$ hydride should be acidic. Thus, on Cu$_2$O (100), Cu$^+$ cations may scavenge and release acidic protons, suggesting that anion sites may not be required for the net dehydration pathway. We note also that the hydrogen-covered (100) surface has been shown to hydrogenate $\alpha,\beta$ unsaturated aldehydes (acrolein specifically) via a process similar to (1,4) addition [9], a reaction for which Cu$^+$ hydride organometallics are known to be quite specific [75]. Hence, some similarities between surface hydrogen and Cu$^+$ hydrides
have already been established [9].

4.4.3 Non-selective Oxidation Pathway

The similarity in the desorption temperatures of the CO, CO₂, and H₂O from both propionic and acrylic acid suggests that both molecules break-up and form the non-selective oxidation products in a similar fashion. Studies of H adsortion on the (100) surface show that atomic hydrogen produces H₂O near 500 K by extraction of lattice oxygen [16]. Thus, the lack of water desorption at 500 K from either propionic or acrylic acid demonstrates that little dehydrogenation of the surface species occurs below temperatures of 550 K. The increase to over two in the CₓHᵧ/CO₂ ratio measured by XPS for both acids demonstrates that reduction of surface species occurs by the break-up of the adsorbed acrylate and propionate species into unidentified hydrocarbon fragments. The chemical nature of these fragments (C₁, C₂, C₃, alkyl, vinyl, etc.) cannot be determined from our data, but the acid recombination features near 600 K demonstrate that at least some oxygenates are present as C₃’s up to these temperatures.

The major reaction pathway to produce CO and CO₂ from acrylic and propionic acids involves the reduction of the surface oxygenate species via the breakup of the C₃ molecules into hydrocarbon fragments. Dehydrogenation of the hydrocarbon fragments and burn-off (reoxidation) of surface carbon occurs between 600 and 700 K. Reoxidation of the surface then occurs via the diffusion of oxygen from the bulk to the surface at 900 K. This process is much different than observed for CO and CO₂ production from carboxylic acids on ZnO(0001)-Zn [83, 85, 86]. On ZnO(0001)-Zn, CO and CO₂ are formed from carboxylates without first being reduced to surface carbon.

4.5 Conclusions

Propionic acid and acrylic acid reactivity was studied on the Cu₂O(100) surface with TDS and XPS. The thermal desorption and XPS data suggest that the acids dissociatively
adsorb to form propionate (from propionic acid) or acrylate (from acrylic acid) species. Acrylic acid decomposition gave only CO, CO₂, and H₂O as products. However, propionic acid decomposition gave acrolein as a product in addition to non-selective oxidation products. Acrolein formation occurs via the first-order, unimolecular decomposition of surface propionate.
Table 4.2: Relative Yields of a 0.9 L dose (1 ML) of acrylic acid on Cu$_2$O(100).

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CHCOOH TDS</td>
<td>1.00</td>
</tr>
<tr>
<td>CO</td>
<td>1.00</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.20</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Chapter 5

Enolate-Mediated Reactions of Acrolein and Propionaldehyde on Cu$_2$O(100)

5.1 Introduction

The partial oxidation of propene (CH$_2$=CHCH$_3$) to acrolein (CH$_2$=CHCHO) is a useful model for the class of allylic oxidation reactions of olefins. The basic steps in the propene oxidation pathway have been widely studied, but the form of the oxygen-containing $\sigma$-allyl surface species in the propene oxidation pathway is not well understood [1]-[4],[7]. Adsorbed acrolein has been used to study the postulated $\sigma$-allyl species obtained by hydrogen abstraction from a $\pi$-allyl prior to oxygen insertion [1]. A study of acrolein reactivity also gives information on any additional products formed from subsequent reactions of adsorbed acrolein. Since propionaldehyde (CH$_3$CH$_2$CHO) has also been detected as a minor product in studies of propene oxidation to acrolein on Cu$_2$O catalysts [8] and single crystal surfaces [13], the chemistry of both acrolein and propionaldehyde have been investigated on Cu$_2$O(100).

There is one study of the adsorption of acrolein and propionaldehyde on metal oxide single crystal surfaces under ultrahigh vacuum (UHV) conditions [85]. Voks and Barteau studied propionaldehyde and acrolein decomposition on ZnO(0001) polar surfaces [85], and demonstrated that the oxidation of aldehydes occurs by the nucleophilic attack of lattice oxygen at the carbonyl carbon. The resulting C$_3$ surface specie decomposes through parallel pathways by either alkyl elimination to formate or hydride elimination to the corresponding carboxylate species. Acrolein, CO, CO$_2$, and H$_2$O were all detected as reaction products from propionaldehyde, while CO, CO$_2$ and H$_2$O were detected as reaction products from
acrolein. Acrolein formation from propionaldehyde occurred via the unimolecular decomposition of propionate species by comparison with propionic acid results on the same surface.

5.2 Experimental

Aldrich propionaldehyde (99+%) and acrolein (97%) were used in these studies, and were purified by repeated freeze-pump-thaw cycles prior to dosing. MSD Isotopes propionaldehyde-2,2-d2 (CH₃CD₂CHO, 98% Isotopic Purity) was used after repeated freeze-pump-thaw cycles. Matheson Research grade H₂ (99.9995%) was used as received. Since hydrogen does not dissociatively adsorb on the Cu₂O(100) surface under UHV conditions [16], hydrogen was dissociated using a white hot platinum filament located 15 mm from the sample surface. All hydrogen doses are reported as the equivalent H₂ dose.

5.3 Results

5.3.1 Thermal Desorption

Figure 5.1 compares the thermal desorption spectra of acrolein and propionaldehyde following 0.2 L doses on the Cu₂O(100) surface at 100 K. The primary desorption channel for both propionaldehyde and acrolein appears at 240 K, and the similarity in desorption behavior in this temperature range suggests similar bonding modes on the Cu₂O(100) surface. However, clear differences in the desorption behavior of propionaldehyde (Figure 5.1(a&b)) and acrolein (Figure 5.1(c)) were observed. No acrolein desorption is observed above 325 K, while propionaldehyde desorption is clearly observed between 325 and 400 K in Figure 5.1(b) and out to 500 K in Figure 5.1(a).

Differences in the number of propionaldehyde thermal desorption features were observed dependent on sample history. Figure 5.1(a) and 5.1(b) show propionaldehyde doses from Cu₂O(100) surfaces with the same XPS Cu/O ratio (1.6) and the same (3\sqrt{2} \times \sqrt{2})RA45° LEED pattern but which were done several months apart. During the several month lapse, the decomposition of other C₃ oxygenates was studied on the Cu₂O(100) surface. In ad-
Figure 5.1: Thermal desorption of 0.2 L doses of acrolein and propionaldehyde on the Cu(100) surface at 100 K.
dition to the primary desorption peak at 240 K, the propionaldehyde thermal desorption trace in Figure 5.1(a) shows a distinct shoulder at 335 K as well as a second peak at 450 K. In contrast, the propionaldehyde desorption trace in Figure 5.1(b) shows only a small desorption feature between 300 and 400 K in addition to the primary desorption peak at 240 K. No difference in conversion or selectivity to products was observed for propionaldehyde as a function of sample history. This difference in desorption behavior may be due to the presence of surface defects. All further propionaldehyde results reported here are for a surface corresponding to that of Figure 5.1(a). Differences in the behavior due to surface defects have been observed previously for propene thermal desorption from the Cu2O(111) surface [12]. All acrolein doses reported here were done on the non-defective surface.

Propionaldehyde Thermal Desorption

Propionaldehyde reactivity was studied as a function of coverage after adsorption at 100 K. At low surface coverages (doses less than 0.05 L) the primary propionaldehyde desorption channel appeared as a single peak at 260 K, and shifted to 205 K by 0.4 L (not shown). Additional desorption features were observed at 335 K and 450 K as noted above. Further dosing resulted in the growth of a peak at 145 K by 1.1 L which did not saturate with increasing coverage, indicating that this peak is due to a propionaldehyde multilayer. No bimolecular or C2 products were observed during propionaldehyde TDS. For propionaldehyde, the operational definition of a monolayer coverage was taken as the coverage where a propionaldehyde multilayer first appeared in TDS and where saturation of the product peaks occurred. The dose corresponding to a monolayer coverage at 100 K was 1.1 L.

Propene, acrolein, CO2, CO, and H2O were all detected as reaction products during propionaldehyde thermal desorption. Thermal desorption traces of the reaction products detected after a 0.4 L (0.40 ML) dose of propionaldehyde are shown in Figure 5.2. The data from a 0.40 ML propionaldehyde coverage are shown because the desorption feature at 335 K is obscured by the main desorption channel at higher coverages. Propene desorbs
in a broad feature from 200 to 500 K, with maxima at 205 K and between 300 and 400 K. Acrolein desorbs over a wide temperature range extending from 200 to 550 K, with a clear desorption feature at 205 K. The width of the acrolein, propionaldehyde, and propene peaks was such that no definitive assignment of the reaction order of the rate-limiting step could be estimated from the TDS data.

No temperature shift in the H₂O, CO, or CO₂ desorption signals was observed as a function of coverage, implying first-order kinetic processes [66]. Water desorbed in a peak at 575 K, with a lower temperature shoulder at 500 K. Water TDS studies have shown that recombination of dissociated water occurs at 465 K [15], and predissociated hydrogen adsorption studies have shown that atomic hydrogen extracts lattice oxygen to form water at about 500 K [16]. Thus, the rate-limiting step for the water at produced at 575 K is dehydrogenation of surface hydrocarbon species. The water desorption peaks at 500 and 575 K have activation energies of 33.9 and 39.1 kcal/mol, respectively.

Reaction-limited CO₂ [91] desorbed in a broad feature with a peak maximum at 625 K and a lower-temperature shoulder at 575 K, with corresponding activation energies of 42.6 and 39.1 kcal/mol. CO desorbed in one reaction-limited peak [14] at 650 K, corresponding to an activation energy of 44.4 kcal/mol. H₂ was not detected as a desorption product, however, the background of hydrogen in the vacuum system was high enough that some H₂ might have gone undetected.

A change in the conversion of propionaldehyde was observed as a function of coverage and varied from 65% at low coverage (0.06 ML) to 10% at monolayer coverage. The selectivity to reaction products remained constant at the coverages studied. The selectivity (on a C₃-basis) to CO was 37±5%, to CO₂ was 52±5%, to propene was 5±3%, and to acrolein was 6±3%. The relative yields of the products from a 0.4 L propionaldehyde dose are summarized in Table 5.1. From the amounts of oxygen-containing products formed it is clear that lattice oxygen is extracted during the TDS experiments.

No products were observed above 450 K from propionaldehyde decomposition on the non-defective surface shown in Figure 5.1(b). Thus, the desorption of all species above 450
Figure 5.2: Thermal desorption spectra of 0.4 L dose of propionaldehyde on the Cu2O(100) surface at 100 K.
K is attributed to unidentified surface defects. This suggests that the different temperatures for product formation are due to differences in surface condition, and not different reaction intermediates.

H-Propionaldehyde Thermal Desorption

Figure 5.3 shows thermal desorption spectra of 0.4 L of propionaldehyde from a hydrogen-predosed (200 L equivalent H₂ dose) surface. No new products were detected besides those reported previously for propionaldehyde adsorption on the clean (100) surface. Propionaldehyde desorbed at 190 K, 15 K lower than observed for a 0.4 L dose on the clean (100) surface. Acrolein and propene both desorbed in a temperature range extending from 160 to 500 K, with clear desorption features at 195, 300, and 450 K. The range of desorption temperatures for propene and acrolein is similar to that observed for the clean (100) surface with two exceptions. The desorption of propene and acrolein at 190 K is 15 K lower than on the clean (100) surface, and the high-temperature desorption of acrolein has decreased by 50 K.

CO₂ desorbs in two peaks at 480 and 585 K which are both reaction-limited [91]. The CO₂ desorption peak at 480 K was not observed on the clean (100) surface, and the 585 K peak is 40 K lower than from the clean surface. Significant amounts of background water and CO were generated by the procedure used to predissociate hydrogen, thus preventing quantification of the CO and H₂O formed as surface reaction products.

Since the CO could not be quantitated, no calculation of conversion or selectivity for hydrogen-propionaldehyde coadsorption could be made. However, about three times more propene and acrolein was detected from the hydrogen-predosed surface than from the clean surface. The increase in the propene signal due to the presence of adsorbed hydrogen demonstrates the importance of surface hydrogen in the formation of propene via the hydrogenation of surface intermediates. The relative yields of the products from propionaldehyde co-adsorption with hydrogen are shown in Table 5.1.
Table 5.1: Relative yields for propionaldehyde TDS on Cu$_2$O(100).

<table>
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<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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</tr>
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<td>CH$_2$=CHCHO</td>
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</tr>
<tr>
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</tr>
<tr>
<td>CO</td>
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<td>CO$_2$</td>
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<tr>
<td>H$_2$O</td>
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</tr>
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<td>H/CH$_3$CH$_2$CHO TDS (0.4 ML)</td>
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<td>CH$_2$=CHCHO</td>
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</tr>
<tr>
<td>CH$_2$=CHCH$_3$</td>
<td>0.12</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 5.3: Thermal desorption of 200 L H₂ coadsorbed with 0.4 L of propionaldehyde on the Cu₂O(100) surface at 100 K.
CH$_3$CD$_2$CHO Thermal Desorption

The adsorption of deuterium-labeled propionaldehyde (CH$_3$CD$_2$CHO) was studied to help elucidate the reaction pathways. The deuterium content of product propene and acrolein was specifically examined, but it should be noted that no assignment of the position of the deuterium label in the C$_3$ products could be made. The assignment of desorption products from CH$_3$CD$_2$CHO was made using the parent mass numbers of the expected products. Thus, singly-deuterated acrolein (C$_3$H$_3$DO) was identified using an m/e$^-$ of 57, and labeled propionaldehyde (CH$_3$CD$_2$CHO) was identified using an m/e$^-$ of 60. Different types of propene (C$_3$H$_5$D, C$_3$H$_4$D$_2$) were identified by examination of cracking fragments using several mass numbers from 40 to 44.

The thermal desorption behavior of the CH$_3$CD$_2$CHO was the same as for the non-labeled propionaldehyde discussed previously. Similar trends in selectivity and conversion to acrolein, propene, and the non-selective oxidation products were observed for both CH$_3$CD$_2$CHO and for the non-labeled propionaldehyde. Singly-labeled acrolein (C$_3$H$_3$DO), doubly-labeled propene (C$_3$H$_4$D$_2$), and CH$_3$CD$_2$CHO were the only C$_3$ compounds detected during thermal desorption, and desorbed in the same temperature ranges observed with unlabeled propionaldehyde.

The possibility of intramolecular hydrogen transfer to form the doubly-deuterated propene was checked by repeating CH$_3$CD$_2$CHO thermal desorption on a hydrogen-predosed surface. For these experiments, doubly-labeled propene (C$_3$H$_4$D$_2$), singly-labeled propene (C$_3$H$_5$D), and singly-labeled acrolein (C$_3$H$_3$DO) were detected as products. The singly-labeled (C$_3$H$_5$D) and doubly-labeled (C$_3$H$_4$D$_2$) propene were detected in a ratio of 5/4. The presence of the singly-labeled propene demonstrates that propene formation occurs via the hydrogenation of a surface species by surface hydrogen. No singly-labeled propionaldehyde (C$_3$H$_5$DO) was detected, however, separation of the m/e$^-$ 59 signal for this product from the cracking fragments of the other desorbing molecules was difficult. Thus, some singly-labeled propionaldehyde may have been produced but not detected in the TDS.
experiments.

Acrolein Thermal Desorption

Acrolein reactivity was studied on the Cu$_2$O(100) surface as a function of coverage after adsorption at 100 K. Acrolein desorbed at low coverages (< 0.02 L) in one peak at 260 K, which shifted to 220 K by 1.2 L (not shown). For doses of 1.2 L and higher, a peak was observed at 145 K which did not saturate with increasing coverage, demonstrating that the 145 K desorption state was due to multilayer formation. No C$_3$ or C$_2$ products were detected. Some of the C$_3$ products checked for and not detected include propene, allyl alcohol, propanol, propionaldehyde, acrylic acid, and propionic acid. Additionally, no bimolecular reaction products were detected. As with the propionaldehyde, the operational definition of a monolayer coverage was taken as the coverage where a acrolein multilayer first appeared in TDS. This dose of 1.2 L also corresponds to the coverage where saturation of the product peaks occurred. The dose corresponding to a multilayer coverage at 100 K was 1.2 L. The only reaction products detected were non-selective oxidation products: CO, CO$_2$, H$_2$O.

Figure 5.4 shows the thermal desorption spectra for a 0.25 L dose (0.2 ML) of acrolein following adsorption at 100 K. CO, CO$_2$, and H$_2$O were all detected as reaction products. No shift in the desorption temperatures of CO and CO$_2$ was observed as a function of coverage, implying that the desorption behavior of the products can be modeled using first-order kinetics [66]. CO and CO$_2$ evolved in three reaction-limited peaks [14, 91] at 325 K, 480 K, and 665 K, which correspond to activation energies of 21.7, 32.5, and 45.4 kcal/mol for the rate-limiting steps. H$_2$O desorbed in three peaks at 300, 480, and 500-650 K. The 300 and 480 K peaks are in a range for the recombination of dissociated water [10], while the water desorbing between 500 and 650 K is due to dehydrogenation of adsorbed species. Because of the broadness of the H$_2$O desorption feature, no assignment of a reaction order is possible.

The conversion of acrolein to non-selective oxidation products varied from 65% at low
Figure 5.4: Thermal desorption spectra for 0.5 L of acrolein on the Cu$_2$O(100) surface at 100 K.
coverages (.07 ML) to 30% at monolayer coverage. No change in the selectivity of acrolein to products was observed as a function of coverage. The selectivity to CO was 45% and to CO$_2$ was 55%. Table 5.2 gives the relative amounts of the desorption products following a 0.25 L acrolein dose. As with propionaldehyde, the amounts of oxygen-containing products formed demonstrate that removal of lattice oxygen occurs during acrolein TDS.

**H-Acrolein Thermal Desorption**

The observation of acrolein as a product from propionaldehyde suggested the possibility of producing propionaldehyde from acrolein if the coverage of surface hydrogen were high enough. Therefore, hydrogen-acrolein coadsorption experiments were done in an effort to hydrogenate the C=C bond. Acrolein coadsorption with hydrogen did not affect the uptake of acrolein under the experimental conditions described. A large background of CO and H$_2$O generated by the predissociation of hydrogen made quantification of these signals difficult.

Figure 5.5 shows the thermal desorption spectra following predissociated hydrogen (200 L equivalent H$_2$ dose) coadsorption with 0.5 L of acrolein at 100 K. In contrast to acrolein thermal desorption on the clean (100) surface, propene and propionaldehyde were detected as reaction products. Propene desorbed in a broad feature with two desorption-limited [12] peaks at 160 and 235 K in addition to a small, broad, reaction-limited feature between 400 and 500 K. Propionaldehyde desorbed in a broad feature with two peaks at 335 K and 450 K. CO$_2$ evolved in a broad reaction-limited [91] feature extending from 520 to 710 K. The presence of adsorbed hydrogen lowered the temperature of the main acrolein desorption channel by 25 K compared to the clean (100) surface.

Since the CO signal could not be quantitated, no calculation of conversion or selectivity could be made from the hydrogen-acrolein TDS experiments. However, the presence of propene and propionaldehyde as reaction products on the hydrogen-predosed surface demonstrates that these products are formed via the hydrogenation of adsorbed acrolein. The relative yields of the products from acrolein-hydrogen coadsorption are given in Table 5.2.
Table 5.2: Relative yields for acrolein TDS on Cu$_2$O(100).

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CHCHO TDS (0.2 ML)</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>0.60</td>
</tr>
<tr>
<td>CO</td>
<td>0.80</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.90</td>
</tr>
<tr>
<td>H/CH$_3$=CHCHO TDS (0.4 ML)</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>1.31</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CHO</td>
<td>0.08</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_3$</td>
<td>0.09</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 5.5: Thermal desorption spectra following 200 L H₂ coadsorbed with 0.5 L of acrolein on the Cu₂O(100) surface at 100 K.
The desorption of propionaldehyde and propene above 450 K is in the same temperature range as was attributed to surface defects for the propionaldehyde TDS. However, a comparison of the absolute intensities of the propionaldehyde TDS spectrum shown in Figure 5.1(b) with the propene and propionaldehyde from hydrogen-acrolein TDS suggests that the production of these products via defect sites is small enough so that the amount of product propionaldehyde would not be observable in a propionaldehyde TDS trace like 5.1(b).

Comparison of C₃ Products from Propionaldehyde and H-Acrolein Coadsorption

Figure 5.6 shows the C₃ reaction products from hydrogen-acrolein and propionaldehyde TDS. The desorption of propionaldehyde and propene from hydrogen-acrolein coadsorption occurs in the same temperature range as propionaldehyde, acrolein, and propene from propionaldehyde TDS. The similarity in the desorption temperatures of these three molecules (propene, propionaldehyde, acrolein) suggest their formation via a common surface intermediate. However, the formation of propene at 160 K from hydrogen-acrolein coadsorption suggests that this propene is formed via an alternative, facile reaction pathway.

5.3.2 XPS Experiments

Variations in the pressure of the liquid nitrogen source used to cool the sample sometimes affected the lowest attainable sample temperature. These variations in sample temperature primarily affected multilayer formation. As observed in the TDS experiments, multilayer formation was observed for both acrolein and propionaldehyde at 100 K. For the XPS studies reported below, the minimum sample temperature was 100 K for acrolein adsorption and 120 K for propionaldehyde adsorption. As shown below, a thick multilayer of acrolein was formed at 100 K but not for propionaldehyde at 120 K. The sticking coefficient for propionaldehyde multilayer formation was significantly reduced by the 20 K increase in the substrate temperature.
Figure 5.6: $C_3$ Products from hydrogen-acrolein coadsorption and propionaldehyde on the Cu$_2$O(100) surface.
Acrolein

In an effort to identify the surface species leading to the non-selective oxidation products, C 1s XPS spectra were taken of adsorbed acrolein annealed to successively higher temperatures. For these experiments, 24 L of acrolein was dosed at 100 K, heated to the desired temperature, cooled to 100 K, and then the XPS spectrum was taken.

The C 1s XPS spectrum of an acrolein multilayer is shown in Figure 5.7(a). Two distinct peaks are observed at binding energies of 288.4 and 285.8 eV. The separation between these peaks is 2.6 eV, in good agreement with the separation of 2.7 eV observed in the C 1s spectrum of gas phase acetaldehyde [93]. By comparison to the spectra of gas phase aldehydes [93], the high binding energy peak is due to the formyl group in multilayer acrolein (288.4 eV), and the low binding energy peak is due to the vinyl carbons of multilayer acrolein (285.8 eV). The ratio of the vinyl carbons to the carbonyl carbon was 2.3, which is slightly higher than the expected stoichiometric value to 2.0. In general, the calculated ratio for a given spectrum can vary by ±0.2 for small changes in the peakfitting parameters.

Heating of the (100) surface to 145 K desorbs the multilayer, and the resulting C 1s XPS spectrum is shown in Figure 5.7(b). A decrease in the C 1s intensity of about 10% occurs by desorption of the multilayer. Peakfitting of this spectrum gives contributions at binding energies of 288.6, 287.2, and 285.7 eV (shown as dashed lines). The peak at 288.6 eV is assigned to the carbonyl group of a multilayer-like (i.e., weakly-bound) molecular acrolein, and the peak at 285.7 eV is assigned to the vinyl carbons of molecular acrolein. About 20% of the C 1s peak is due to weakly-bound molecular acrolein.

The assignment of the peak at 287.2 eV is not straightforward. Alcohol adsorption studies on Cu$_2$O have shown that surface alkoxide species have binding energies of 286.5 eV [10], thus, a peak at 287.2 eV is at too high a binding energy to be due to an adsorbed alkoxide, and too low to be due to a weakly-bound molecular specie (288.6 eV). However, the peak at 287.2 eV is clearly due to an oxygenated carbon, and suggests that acrolein is bound to the surface through the formyl group. Thus, the peak at 287.2 eV is assigned to
Figure 5.7: C 1s XPS spectra of 24 L of acrolein on the Cu2O(100) surface as a function of annealing temperature. (a) Surface at 100 K. (b) Surface in (a) heated to 145 K. (c) Surface in (b) heated to 215 K.
an aldehyde bound through the formyl group, and will be referred to as a "chemisorbed" aldehyde.

A useful measure of the stoichiometry of adsorbed surface species is to compare the intensity of the C 1s intensities for the oxygenated carbons of the carbonyl and "strongly adsorbed" aldehyde species (designated CO₂) to the intensity of the non-oxygenated carbons of alkyl carbons, vinyl carbons, and hydrocarbon fragments (designated C₂H₇). The C₂H₇/CO₂ ratio for the spectrum shown in Figure 5.7(b) is 2.0.

Further heating of the adsorbed acrolein to 215 K desorbs most of the molecular acrolein and leaves surface species leading to the non-selective oxidation products. A 75% decrease in the C 1s intensity was observed after heating to 215 K. The resulting C 1s XPS spectrum is shown in Figure 5.7(c). Peakfitting gives four contributions with binding energies of 288.5, 287.2, 285.6, and 284.2 eV. The peak assignments for the 288.5, 287.2, and 285.6 eV peaks are as described above. The presence of a peak at 288.5 eV demonstrates some weakly-bound molecular acrolein is still on the surface; however, it accounts for less than 5% of the C 1s signal. The new peak at 284.2 eV is in the same binding energy range expected for graphitic carbon [26] and is assigned to completely dehydrogenated surface species. The vinyl group and hydrocarbon species account for about 75% of the C 1s signal. The C₂H₇/CO₂ for the spectrum in Figure 5.7(c) is 3.3, demonstrating that reduction of surface oxygenates has occurred. Thus, some contribution to the 285.6 eV signal is from hydrocarbon fragments. Further heating of the adsorbed acrolein layer to 1000 K removes all the remaining surface carbon. Reduction of the surface to Cu⁰ is observed similar to that described below for propionaldehyde. Reoxidation of the surface occurs by diffusion of oxygen from the bulk to the surface above 800 K [19].

Propionaldehyde

Propionaldehyde adsorption was studied with XPS in an attempt to gain insight into the surface intermediates leading to the different reaction products. For these experiments, 22 L of propionaldehyde was dosed onto the surface at 120 K, and successively annealed to
higher temperatures prior to taking an XPS spectrum.

The C 1s XPS spectrum for adsorbed propionaldehyde at 120 K is shown in Figure 5.8(a). Three peaks were fit to this spectrum at binding energies of 289.0, 287.2, and 285.7 eV. The assignment of these peaks is analogous to the assignments made for acrolein. The high binding energy peak at 289.0 eV is assigned to the carbonyl carbon of molecular propionaldehyde, while the peak at 285.7 eV is assigned to the alkyl carbons of molecular propionaldehyde. The peak at 287.2 eV is assigned as a “chemisorbed” propionaldehyde species. The \( \text{C}_x\text{H}_y/\text{CO}_2 \) ratio is 1.8 for the spectrum shown as Figure 5.8(a), which is slightly lower than the expected stoichiometric value of 2.0.

Heating the surface to 150 K should result in desorption of multilayer propionaldehyde. The C 1s XPS spectrum for chemisorbed propionaldehyde is shown in Figure 5.8(b). No significant change in the C 1s intensity was observed compared with propionaldehyde at 120 K. Three peaks were fit to the C 1s spectrum (shown as dashed lines) with binding energies of 289.2, 287.2, and 285.4 eV. The peak assignments are analogous to the assignments for Figure 5.8(a). The peak at 289.2 eV decreased by about 50% compared with the signal at 120 K, while the peak at 285.4 eV increased by about 20%. The \( \text{C}_x\text{H}_y/\text{CO}_2 \) ratio for the spectrum shown as Figure 5.8(b) is 2.3.

Heating the surface to 275 K removes most of the surface species which desorb molecular propionaldehyde, and results in a decrease of 20% in the C 1s intensity compared with 150 K. The resulting C 1s spectrum is shown in Figure 5.8(c). Three peaks were fit to this spectrum at binding energies of 289.2, 287.4, and 285.2 eV, and are assigned as given previously. The \( \text{C}_x\text{H}_y/\text{CO}_2 \) for the spectrum shown as Figure 5.8(c) is 3.6. The increase in this ratio when heating from 150 K to 275 K shows that reduction of surface oxygenates has occurred, suggesting that hydrocarbon fragments contribute to the peak at 285.2 eV. The peak at 285.2 eV represents the largest contribution to the C 1s spectrum, with less than 5% of the C 1s signal due to molecular propionaldehyde species. The small size of the peak at 289.2 eV suggests that this peak may be due to Readsorption of molecular propionaldehyde during the XPS experiments.
Figure 5.8: C 1s XPS of 24 L of propionaldehyde on the Cu$_2$O(100) surface successively heated to higher temperature. (a) Surface at 120 K. (b) Surface in (a) heated to 150 K. (c) Surface in (b) heated to 275 K. (d) Surface in (c) heated to 500 K. (e) Surface in (d) heated to 600 K.
Further heating of the adsorbed propionaldehyde to 500 K left species on the surface that lead to CO, CO$_2$, and H$_2$O, and resulted in a 60% reduction in the intensity of the C 1s spectrum. The resulting C 1s XPS spectrum is shown in Figure 5.8(d). Four peaks were fit to this spectrum at binding energies of 289.0, 287.2, 285.0, and 284.0 eV. The first three peaks (289.0, 287.2, and 285.0 eV) are assigned as described above. The lowest binding energy peak (284.0 eV) is in the same binding energy range as expected for graphitic carbon [26], and is assigned to dehydrogenated surface carbon. The C$_{x}$H$_{y}$/CO$_{2}$ ratio for the spectrum shown in Figure 5.8(d) is 5.3, illustrating the further reduction of surface oxygenate species. The peak due to molecular propionaldehyde at 289.0 V represents less than 5% of the total C 1s signal, and may be due to readsoption of molecular species during the XPS experiment.

Continued heating of the adsorbed propionaldehyde layer to 600 K results in a decrease in the C 1s intensity of 90% compared to the 500 K spectrum. The resulting C 1s spectrum is shown in Figure 5.8(e). Three peaks were fit to this spectrum at binding energies of 287.2, 285.0, and 283.6 eV. The peak assignments are as given above. Over 90% of the C 1s signal is due to contributions from adsorbed carbon, alkyl carbons and hydrocarbon fragments. The spectrum shown as Figure 5.8(e) had a C$_{x}$H$_{y}$/CO$_{2}$ ratio of 9.6, illustrating the continued reduction of surface species as the surface is heated. Further annealing of the surface to 1000 K removed all remaining carbon species and gave a carbon free surface.

In addition to examining the C 1s feature as a function of heating, the Cu L$_3$VV Auger feature was examined. Previous studies on copper oxides have shown that a clear differentiation between Cu$^0$, Cu$^+$, and Cu$^{2+}$ can be made by shifts in the binding energy of the Cu L$_3$VV feature [43]. Several Cu L$_3$VV XPS spectra are shown in Figure 5.9 which correspond to the C 1s XPS spectra described above. Figure 5.9(a) shows the Cu L$_3$VV feature after heating 22 L of propionaldehyde on the (100) surface to 275 K. The only features in the spectrum are due to Cu$^+$. Heating of the surface to 500 K results in the appearance of features at 335.1 and 332.3 eV indicative of Cu$^0$, as shown in Figure 5.9(b). Continued heating of the surface to 600 K results in a more pronounced Cu$^0$ feature, shown in Fig-
ure 5.9(c). Final heating of the surface to 1000 K (Figure 5.9d) results in the reoxidation of the surface, leaving a spectrum showing evidence of only Cu⁺. Reoxidation of the surface occurs by diffusion of oxygen from the bulk to the surface above 800 K [19].

5.4 Discussion

5.4.1 Bonding of Aldehydes to Cu₂O(100)

The C 1s XPS results (i.e., peak at 287.2 eV) suggest that the “chemisorbed” aldehydes interact with the Cu₂O(100) surface through the carbonyl group. The peak at a binding energy of 287.2 eV is intermediate between the binding energy expected for an alkoxide (286.4 eV) and a carbonyl group (289.0 eV), and thus may be a surface species with an intermediate carbon-oxygen bond order (i.e., 2 > carbon-oxygen bond order > 1). Vohs and Barateau have suggested that both acrolein and propionaldehyde adsorb on the ZnO(0001)-Zn surface through the carbonyl oxygen [85]. Additionally, Miyata et al. proposed that propionaldehyde adsorption occurs through the carbonyl oxygen on ZnO powder catalysts [99]. The bonding of acrolein and propionaldehyde to the Cu₂O(100) surface through the carbonyl oxygen is consistent with the XPS results on Cu₂O and previous studies of aldehyde adsorption on oxides. This initial adsorption may be thought of as an acid-base interaction, where the weakly-basic lone pair electrons on the carbonyl oxygen interact with acidic Cu⁺ cations at the surface. Thus, the adsorbed aldehydes could be viewed as Lewis-acid/base adducts.

Some general observations about the molecular orientation of the adsorbates can also be made. The presence of both unsaturated products from propionaldehyde and saturated products from acrolein suggest that the C₃ backbone of both molecules interacts with the surface. Thus, it is likely that the adsorbed aldehydes which undergo some surface reactions are bonded in a configuration which is more parallel than perpendicular.

The decrease in desorption temperatures of both propionaldehyde and acrolein during hydrogen coadsorption is consistent with the proposed bonding mode. Studies of atomic hy-
Figure 5.9: Cu L$_3$VV of Cu$_2$O(100) surface as a function of temperature for the propionaldehyde XPS experiments. All spectra taken at 120 K. (a) Surface heated to 275 K. (b) Surface heated to 500 K. (c) Surface heated to 600 K. (d) Surface heated to 1000 K.
drogen adsorption on Cu$_2$O(100) are consistent with the formation of a surface hydride [16]. Hydride formation is thought to cap the vacant coordination sites on some of the cations and block the acid-base interaction resulting in a lower activation energy for desorption, consistent with that observed for weakly bound molecular species at high coverages.

5.4.2 C$_3$ Reaction Pathways

Enolate-Mediated Reactions

The presence of propene, propionaldehyde, and acrolein following propionaldehyde adsorption in the same temperature range as propionaldehyde, propene, and acrolein following hydrogen-acrolein coadsorption suggests that the formation of these three molecules is via a common surface intermediate. An intermediate that is consistent with the propionaldehyde, CH$_3$CD$_2$CHO, and H-acrolein thermal desorption data is a surface enolate anion.

Keto-enol tautomerization is common for aldehydes and ketones in solution [72], and has been observed for acetylacetone ($\beta$-diketone) interaction with metal centers [100]. The applicability of solution phase acid-base chemistry to describe surface reactions on metal and metal-oxide surfaces has been suggested previously [101, 102], and provides some chemical insight into reasonable surface reaction pathways. A surface enolate anion (CH$_3$CH=CHO$^-$) can be formed from propionaldehyde via a Lewis acid catalyzed process similar to Brönsted-acid catalyzed keto-enol tautomerization in solution. The analogous surface process would be Lewis acid attack at the carbonyl oxygen (initial adsorption) followed by loss of an acidic proton $\alpha$ to the carbonyl group. The proposed route is illustrated in Figure 5.10(a).

Since the C$_3$ reaction products (propene, propionaldehyde) from adsorbed acrolein were only detected on the hydrogen-predosed surface, surface hydrogen is clearly required for the hydrogenation reactions. An enolate intermediate can be formed by hydrogenation of adsorbed acrolein via pathways similar to known solution phase chemistry. Acrolein is an $\alpha,\beta$ unsaturated aldehyde, which undergo either simple (1,2) or conjugate (1,4) addition [72]. The initial adsorption and interaction between the carbonyl oxygen and the Cu$^+$ cation can
Figure 5.10: Surface Enolate Formation
be thought of as Lewis acid attack at position ‘1’. Addition of a surface hydride, H−, at position ‘4’ would form the proposed surface enolate intermediate. The addition of a surface hydride at position ‘4’ is consistent with the proposed formation of Cu+ hydrides on the (100) surface by adsorption of atomic hydrogen [16], and the known chemistry of Cu+ hydrides, which are effective in the (1,4) reduction of conjugated ketones [75]. The process is illustrated in Figure 5.10(b). Figure 5.11 summarizes surface enolate formation from acrolein and propionaldehyde on Cu2O(100).

If the proposed routes from the two C3 aldehydes to enolate are assumed to be reversible, the pathway is capable of explaining the observed chemistry. The formation of singly-labeled acrolein (C3H5DO, thought to be CH2=CDCHO) from labeled propionaldehyde (CH3CD2CHO) is completely consistent with this pathway. Loss of an acidic proton α to the carbonyl group would give the proposed enolate intermediate, and hydride elimination via a process the reverse of (1,4) addition would give the expected product. This process is illustrated in Figure 5.11.

The desorption of propionaldehyde over a wide temperature range suggests that in addition to the higher temperature propionaldehyde production at defect sites, recombination of an enolate intermediate with hydrogen to form propionaldehyde might occur in several different ways. Propionaldehyde could be formed from the enolate anion by a reverse pathway of the initial dehydrogenation. An alternative pathway is protonation of the enolate anion at the oxygen atom to form an unstable enol (CH3CH=CHOH), which would be expected to rearrange to form propionaldehyde. Some propionaldehyde desorption from H-acrolein coadsorption is observed near 525 K in a similar temperature range similar to that for alcohol recombination [10]. Propionaldehyde formation via an enol would only be expected in the temperature range for alcohol recombination (i.e. 400-525 K), suggesting that hydrogenation of the enolate via the pathway the reverse of the initial of propionaldehyde deprotonation occurs below 400 K. Thus, propionaldehyde may be formed not only at different adsorption sites, but also by different enolate-hydrogen recombination pathways.

Propene was observed as a reaction product during both propionaldehyde and hydrogen-
Figure 5.11: Summary of Surface Enolate Formation from Acrolein and Propionaldehyde
acrolein thermal desorption. Since enolate anions are ambidentate, protonation can occur at either the carbon or oxygen atom of the carbonyl group. Propene could be formed from the proposed surface enolate between 200 and 550 K by hydrogenation of the carbon atom coupled with C-O bond scission. The formation of propene by the hydrogenation of a surface enolate is consistent with the formation of the singly-labeled propene (C3H5D) from the hydrogen-CH3CD2CHO coadsorption experiments. The singly-labeled propene is thought to be CH3CD=CH2, the expected product for propene production from an enolate via proton addition from surface hydrogen accompanied by C-O bond scission. The addition of protons from surface hydrides is consistent with the known chemistry of transition-metal hydrides. The acidities of transition-metal hydrides are known to increase on moving from left to right across a transition series [75], suggesting that a surface Cu⁺ hydride should be acidic. Thus, on Cu2O(100), Cu⁺ cations may scavenge and release acidic protons.

Surface enolate species have been detected on several oxide catalysts. A surface enolate complex was proposed as an intermediate in the decomposition of 2-methyl-oxirane on ZnO powder catalysts [99], for acetone decomposition on MgO and NiO powder catalysts [103], and for acetone and 2-propanol decomposition on ZnO(0001)-Zn [104]. The enolate species were identified by a C-O stretch at 1550 cm⁻¹ using IR which were attributed to an enolic species from dissociatively adsorbed acetone [99, 103], or by XPS [104].

The binding energy of the oxygenated carbon in a surface enolate would be expected to be intermediate between the oxygenated carbons of an alkoxide species and a “bound” carbonyl group. The peak at 287.2 eV identified as a Lewis acid adduct with the carbonyl oxygen bound to the surface is in a binding energy range consistent with that expected for an enolate intermediate. The presence of the 287.2 eV peak in XPS from 150 K to 500 K for propionaldehyde suggests that the Lewis acid adduct may transform into an enolate without an observable change in binding energy. The binding energy of 287.2 eV for the enolate species on Cu2O(100) is about 0.5 eV higher then the binding energy reported for an enolate on ZnO(0001)-Zn [104]. However, differences of up to 1 eV in the binding energies of other oxygenated surface species (ex., carboxyates) have been observed between ZnO(0001)-Zn
and Cu$_2$O [11].

**Low Temperature Propene Pathway**

Propene was observed at 160 K in the hydrogen-acrolein TDS experiments. There are several possible pathways which could form propene from acrolein. If simple (1,2) addition to adsorbed acrolein were to occur, hydrogen would be added at position ‘2’ to the formyl carbon to form an allyloxy (CH$_2$=CHCH$_2$O-) species. However, studies of allyl alcohol adsorption on the Cu$_2$O(100) surface [10] have shown that allyloxy species recombine with surface hydrogen to produce allyl alcohol as a product. Since allyl alcohol was not detected as a reaction product during acrolein thermal desorption, addition of hydrogen at position ‘2’ to the adsorbed acrolein to form allyloxy does not take place in detectable amounts. However, if hydrogen addition at position ‘2’ occurs with C-O bond scission, an allylic (C$_3$H$_5$) species would be formed, and no allyl alcohol produced. The allylic species could then undergo further hydrogenation to form propene.

Propene production at similar temperatures has been observed during allyl alcohol decomposition on Cu$_2$O(100) [10]. Because of the low temperature of the propene formation, the allylic species is thought to be a π-allyl. The formation of a π-allyl species which hydrogenates to propene is consistent with the proposed pathway for propene oxidation to acrolein over Cu$_2$O [1]–[5]. No low temperature (160 K) propene has been observed during propionaldehyde or 1-propanol decomposition [10]. These results suggest that the unusual stability of an allyl greatly reduces the activation energy for deoxygenation reactions compared to those involving propyl radicals or cations. Note that no hydrogenation of the carbonyl carbon to give surface alkoxides and alcohols is observed for either aldehyde.

**Summary of C$_3$ Reaction Pathway for Acrolein and Propionaldehyde**

A summary of the proposed C$_3$ reaction pathway for propionaldehyde and acrolein is shown in Figure 5.12. A surface enolate species is proposed as the common intermediate from which acrolein, propionaldehyde, and propene can all be formed. The initial steps in
Figure 5.12: Summary of C₃ reaction pathway on the Cu₂O(100) surface.
the pathway are the adsorption of propionaldehyde and acrolein to form a Lewis acid/base adduct. Adsorbed propionaldehyde loses an acidic proton α to the carbonyl group to form an enolate species, while adsorbed acrolein undergoes H⁻ addition at position ‘4’ to form an enolate intermediate. Both acrolein and propionaldehyde can be formed via the reverse pathways. An additional pathway to form propionaldehyde above 400 K is by hydrogenation of the enolate to form an enol, which rearranges to form propionaldehyde.

Two different pathways to propene were proposed. At 160 K, propene is believed to be formed by the addition of hydrogen to acrolein at position ‘2’ coupled with C-O bond scission to form a π-allyl. The subsequent hydrogenation of the allylic species gives propene. Propene formation from the surface enolate is thought to occur above 200 K, where protonation of the oxygenated carbon coupled with C-O bond scission forms propene.

Although no definitive experimental evidence for the enolate intermediate is given here, the proposed pathway is consistent with the thermal desorption and XPS data, as well as known solution phase processes. It might be possible to obtain direct experimental evidence for a surface enolate using a vibrational spectroscopy.

5.4.3 Acrolein and Propionaldehyde Non-selective Oxidation Pathways

It is not clear from the thermal desorption and photoemission experiments what types of surface intermediates from acrolein and propionaldehyde give rise to form CO, CO₂, and H₂O. However, some possible intermediates can be eliminated by comparison of the desorption temperatures of the non-selective oxidation products from acrolein and propionaldehyde to those from other molecules studied on the (100) surface.

C₃ acid decomposition studies on the Cu₂O(100) surface [11] have shown that surface acrylate and propionate species decompose to CO, CO₂, and H₂O near 690, 670, and 630 K, respectively, much higher than for the non-selective oxidation products from acrolein and propionaldehyde. Thus, the non-selective oxidation products from acrolein and propionaldehyde do not proceed through acrylate or propionate species.

The multiple CO, CO₂, and H₂O peaks observed from acrolein suggest that several
different surface species may be responsible for the formation of the non-selective oxidation products. A possible pathway to CO, CO₂, and H₂O which deserves consideration was proposed by Vohs and Barteau for acrolein decomposition on ZnO(0001)-Zn [85]. They reported that the lower temperature CO and CO₂ peaks observed during acrolein decomposition on ZnO(0001)-Zn occurred by vinyl elimination of the adsorbed acrolein to form vinyl and formate surface species. The formate species subsequently decomposed to CO, CO₂, and H₂O. Studies of formic acid (CHOOH) adsorption on the Cu₂O(100) surface [105] show that surface formates (HCOO⁻) decompose to CO, CO₂, and H₂O at 510, 525, and 535 K, respectively, all of which are about 2-3 kcal/mol different than the CO, CO₂, and H₂O desorption features at 480 K from acrolein. Thus, although some temperature differences exist between CO, CO₂, and H₂O desorption from acrolein (at 480 K) and from formate decomposition (510 to 525 K), the possibility of the formation of non-selective oxidation products near 500 K via vinyl elimination from adsorbed acrolein cannot be completely dismissed.

Hydrogen TDS experiments have shown that atomic hydrogen extracts lattice oxygen to form water at about 500 K [16]. Thus, the relatively small amount of water which desorbs near 500 K in the propionaldehyde TDS experiments, coupled with the increase in the C₃H₄/CO₂ ratio upon heating from 275 to 500 K suggests that break-up of propionaldehyde forms hydrocarbon (C₃H₄) fragments below 500 K. An increase in the C₃H₄/CO₂ ratio in the propionaldehyde XPS experiments when heating from 500 K to 600 K demonstrates that an overall reduction of surface oxygenates occurs. Heating the (100) surface to 600 K also results in the formation of completely dehydrogenated carbon surface species as seen in the propionaldehyde XPS, and the desorption of H₂O above 500 K which is rate-limited by the dehydrogenation reactions. This suggests that the hydrocarbon fragments breakup and dehydrogenation occurs mainly between 500 K and 600 K. The remaining surface carbon then extracts lattice oxygen for the burnoff reaction to form CO and CO₂ above 600 K. Reoxidation of the surface occurs by diffusion of oxygen from the bulk to the surface above 800 K [19].

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The presence of water over a broad temperature range for the acrolein TDS suggests that a much different decomposition pathway is operable. The presence of H$_2$O coincident with the desorption of CO and CO$_2$ suggests that several different types of hydrocarbon fragments may break up to give the observed non-selective oxidation products. The H$_2$O near 300 K is characteristic of OH disproportionation [16], and suggests that some dehydrogenation occurs at a much lower temperature for acrolein than for propionaldehyde. However, it is not possible to make a more definitive assignment of surface species leading to the CO, CO$_2$ and H$_2$O from the thermal desorption and photoemission data presented here.

5.5 Conclusions

The reactions of propionaldehyde and acrolein were studied on the Cu$_2$O(100) surface using TDS and XPS. The coincident desorption of propene, propionaldehyde, and acrolein from either acrolein-hydrogen coadsorption or from propionaldehyde adsorption suggests that a common surface intermediate is involved. A surface enolate anion was suggested as the common intermediate. The surface enolate anion is formed by hydride addition to acrolein, and by the dehydrogenation of propionaldehyde. Propene was found to desorb via both a low temperature and high temperature pathway. The high temperature pathway was proposed to occur through the enolate intermediate, while the low temperature pathway was thought to occur through an allylic species.
Chapter 6

Oxidation and Reduction of Allyl Alcohol and 1-Propanol on Cu₂O(100)

6.1 Introduction

The partial oxidation of propene (CH₂=CHCH₃) to acrolein (CH₂=CHCHO) is a useful model for the class of allylic oxidation reactions of olefins. The basic steps in the propene oxidation pathway have been widely studied, but the form of the oxygen-containing σ-allyl intermediate in the propene oxidation pathway has been the subject of debate [1]-[4],[7]. The dissociative adsorption of allyl alcohol (CH₂=CHCH₂OH) to give a surface allyloxy (CH₂=CHCH₂O-) has been used previously to model the σ-allyl intermediate obtained if oxygen insertion occurs prior to the final hydrogen abstraction [3]. In this study we have investigated the reactivity of allyl alcohol with Cu₂O(100) for comparison with studies of propene oxidation [13]. In conjunction with the allyl alcohol studies, the reactivity of 1-propanol was also studied on Cu₂O for insight into the effects of the C=C functionality on the reaction pathway.

Alcohol decomposition has been studied extensively on metal single-crystal surfaces, however, there are few studies of higher alcohols on metal oxide single-crystal surfaces. 1-Propanol decomposition has been studied on ZnO and TiO₂ single-crystal surfaces [88, 106]. 1-Propanol dissociatively adsorbs on the polar ZnO(0001)-Zn surface to form surface propoxy [88]. The adsorbed propoxy then undergoes either oxidation to a carboxylate (propionate) or dehydrogenation to propionaldehyde. 1-Propanol decomposes on the TiO₂(001)-(001) faceted surface to give propene, propionaldehyde, water, and H₂ as reaction products [106]. This pathway also proceeds through a propoxy intermediate, with
propionaldehyde produced via hydride elimination, and propene by deoxygenation of the propoxy accompanied by hydride elimination.

6.2 Experimental

Aldrich allyl alcohol (99+%) and HPLC grade 1-propanol (99.9%) were purified by repeated freeze-pump-thaw cycles prior to use. Matheson Research grade H₂ (99.9995%) was used as received. Since H₂ does not dissociatively adsorb on the Cu₂O(100) surface under UHV conditions [16], H₂ was dissociated using a white hot platinum filament located 15 mm from the sample face. All hydrogen doses are reported as the equivalent H₂ dose.

6.3 Results

6.3.1 Thermal Desorption

Allyl Alcohol

Figure 6.1 shows the TDS traces obtained following a 0.22 L (.33 ML) dose of allyl alcohol at 120 K. A 0.22 L dose was chosen for this illustration because at higher coverages a large, low-temperature allyl alcohol desorption feature obscures the higher-temperature features near 500 K. A coverage of 1 monolayer was defined as the coverage where an allyl alcohol multilayer feature first appears, and where the signal from reaction products saturated. A 0.65 L dose corresponds to a coverage of 1 ML. Allyl alcohol, CO, CO₂, H₂O, propene, propionaldehyde (CH₃CH₂CHO), and acrolein were all detected as reaction products. No bimolecular or C₂ products were detected.

Allyl alcohol desorbs in three temperature ranges. An allyl alcohol peak appeared at 170 K (not shown in Figure 6.1) for doses greater than 0.65 L. This feature did not saturate with coverage, demonstrating that it was due to multilayer formation. A coverage-dependent allyl alcohol desorption state was also observed, which shifted in temperature from 250 K at 0.33 ML to 210 K at 1.0 ML. An allyl alcohol desorption feature was also observed at 525 K.
Figure 6.1: Thermal desorption spectra of 0.2 L dose of allyl alcohol on the Cu₂O(100) surface at 120 K.
The temperatures of the 525 K allyl alcohol desorption feature and the majority of the reaction products did not shift as a function of coverage, implying first-order reaction processes for the rate-limiting step. Assuming a preexponential of $10^{13}$ sec$^{-1}$, and using the Redhead equation [66] gives an activation energy of 35.6 kcal/mol for the allyl alcohol feature at 525 K. Acrolein and propionaldehyde also desorb in reaction-limited [9] peaks at 525 K, with an activation energy of 35.6 kcal/mol. Acrolein desorbs in an additional lower temperature peak at 310 K, with a first-order activation energy of 20.7 kcal/mol. The coincident desorption of acrolein and allyl alcohol at 525 K is characteristic of a rate-limiting step involving the first-order, unimolecular, decomposition of a surface alkoxide species, in this case an allyloxy (CH$_2$=CHCH$_2$O-). The acrolein is formed in this process at 525 K by hydride elimination from the carbon $\alpha$ to oxygen, while the allyl alcohol is due to the recombination of allyloxy with surface hydrogen. Propionaldehyde desorption is also observed in this temperature range.

Propene evolves over a broad temperature range with three clear desorption features. Two desorption-limited peaks are visible at 170 and 215 K [12], with corresponding activation energies for desorption of 11.2 and 14.2 kcal/mol, respectively. A broad propene peak is also observed between 400 and 600 K, in the same temperature range as the first-order allyloxy decomposition. However, this feature is broad enough so that assignment of a reaction order is not possible.

CO desorbs in a reaction-limited peak at 685 K [14], with a corresponding activation energy of 46.9 kcal/mol. CO$_2$ desorbs in a broad reaction-limited peak [108] at 675 K with a lower-temperature shoulder near 590 K. The corresponding activation energies for the rate-limiting steps are 46.2 and about 40 kcal/mol, respectively.

H$_2$O desorbs in a broad feature at 545 K with a higher temperature shoulder at 675 K, with activation energies of 37.0 kcal/mol and 46.2 kcal/mol, respectively. H$_2$O thermal desorption studies have shown that dissociated water recombination occurs at 465 K [15], and hydrogen adsorption studies have shown that atomic hydrogen extracts lattice oxygen to form water at 500 K [16]. Thus, the rate-limiting step for the H$_2$O observed above 500 K
is the dehydrogenation of surface hydrocarbons. No H₂ was detected as a reaction product, however, the background of H₂ in the system was high enough that some H₂ may have gone undetected.

The conversion of allyl alcohol to products was coverage dependent, and varied from about 40% at low coverages (.33 ML) to about 20% at higher coverages (1 ML). The selectivity (on a C₃ basis) did not change significantly with coverage, and was 15% to CO, 20% to CO₂, 25% to propene, 6% to propionaldehyde, and 34% to acrolein. The relative yields of the desorption products from a 0.22 L dose of allyl alcohol are shown in Table 6.1. From the amounts of oxygen-containing products, it is clear that lattice oxygen is extracted during allyl alcohol thermal desorption.

1-Propanol

Figure 6.2 shows the thermal desorption traces following a 0.20 L (.33 ML) dose of 1-propanol at 120 K. As with allyl alcohol, 1 monolayer of 1-propanol was defined as the dose (0.61 L) where the 1-propanol multilayer first appeared, and the signals from the reaction products saturated. 1-Propanol, acrolein, propionaldehyde, propene, CO, CO₂, and H₂O were all detected as reaction products. No C₂ or bimolecular reaction products were detected.

1-Propanol desorbed in three temperature ranges. A 1-propanol peak was observed at 170 K (not shown in Figure 6.2) for doses greater than 0.61 L. This feature did not saturate with coverage, demonstrating that it was due to multilayer formation. A coverage-dependent 1-propanol peak was observed which shifted from 350 K at 0.08 ML to 200 K by 1 ML, in addition to a high-temperature desorption state at 525 K.

No coverage dependence was observed in the desorption temperatures of the 525 K 1-propanol peak or the products, implying a first-order process for the rate-limiting step. Assuming a pre-exponential of 10¹³ sec⁻¹ and applying the Redhead equation [66] gives an activation energy of 35.6 kcal/mol for the 525 K 1-propanol feature. Propionaldehyde [9], acrolein [9], and propene [12] also desorbed as reaction-limited products at 525 K. The
Table 6.1: Allyl Alcohol (CH₂=CHCH₂OH) TDS

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CHCH₂OH (0.33 ML) TDS</td>
<td></td>
</tr>
<tr>
<td>CH₂=CHCH₂OH</td>
<td>2.27</td>
</tr>
<tr>
<td>CH₂=CHCHO</td>
<td>0.58</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>0.11</td>
</tr>
<tr>
<td>CH₂=CHCH₃</td>
<td>0.42</td>
</tr>
<tr>
<td>CO</td>
<td>0.76</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.00</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.90</td>
</tr>
<tr>
<td>H/CH₂=CHCH₂OH (1 ML)</td>
<td></td>
</tr>
<tr>
<td>CH₂=CHCH₂OH</td>
<td>12.2</td>
</tr>
<tr>
<td>CH₂=CHCHO</td>
<td>0.44</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>0.46</td>
</tr>
<tr>
<td>CH₂=CHCH₃</td>
<td>1.40</td>
</tr>
<tr>
<td>CO</td>
<td>0.66</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Figure 6.2: Thermal desorption spectra of 0.2 L dose of 1-propanol on the Cu$_2$O(100) surface at 120 K.
coincident desorption of propionaldehyde with 1-propanol is characteristic of the first-order, unimolecular decomposition of a surface alkoxide, in this case propoxy (CH$_3$CH$_2$CH$_2$O-). The propionaldehyde is formed in this process by hydride elimination from the carbon α to oxygen, while the 1-propanol is due to the recombination of propoxy with surface hydrogen.

Propionaldehyde and acrolein also desorb with a reaction-limited, lower-temperature shoulder near 400 K, with an associated activation energy of about 27 kcal/mol. Propene desorbs in a broad temperature range, with peak maxima at 310 K and 525 K. The 310 K propene desorption feature is reaction-limited [12], with a corresponding first-order activation energy of 20.7 kcal/mol.

CO and CO$_2$ desorb in reaction-limited [14, 108] peaks at 580 and 720 K, with activation energies of 39.5 and 50.7 kcal/mol, respectively. Water desorbs in a broad feature at 600 K, corresponding to an activation energy of desorption of 40.9 kcal/mol. The high desorption temperature of water is again due to the dehydrogenation of surface hydrocarbons. As with allyl alcohol, no H$_2$ was detected as a reaction product. However, some H$_2$ might have gone undetected due to the high background of H$_2$ in the vacuum system.

The conversion of 1-propanol varied from 65% at lower coverages (0.33 ML) to 20% at higher coverages (1 ML). The selectivity (calculated on a C$_3$ basis) did not vary as a function of coverage. The selectivity to propionaldehyde was 57%, to acrolein was 3%, to CO was 18%, to CO$_2$ was 10%, and to propene was 12%. The relative yields of the products from a 0.2 L dose of 1-propanol are shown in Table 6.2. From the amounts of oxygen-containing products, it is clear that lattice oxygen is extracted during 1-propanol thermal desorption.

**Allyl Alcohol and 1-Propanol TDS from the H-Predosed Surface.**

The allyl alcohol TDS experiments were repeated on a hydrogen predosed surface at 120 K to study the effectiveness of surface hydrogen in hydrogenating the C=C double bond. Hydrogen (200 L equivalent H$_2$ dose) was coadsorbed with 0.65 L (1 ML) of allyl alcohol at 120 K. The same desorption products were observed during the coadsorption experiments as were observed following allyl alcohol adsorption on the clean surface. No changes in the
Table 6.2: 1-Propanol (CH$_3$CH$_2$CH$_2$OH) TDS

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$CH$_2$OH (0.33 ML) TDS</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$OH</td>
<td>1.61</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CHO</td>
<td>1.87</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_3$</td>
<td>0.41</td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>0.10</td>
</tr>
<tr>
<td>CO</td>
<td>1.81</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/CH$_3$CH$_2$CH$_2$OH (1 ML)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$OH</td>
<td>31.0</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CHO</td>
<td>2.92</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_3$</td>
<td>1.28</td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>0.23</td>
</tr>
<tr>
<td>CO</td>
<td>1.40</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
</tbody>
</table>
desorption temperatures of allyl alcohol or the reaction products were observed due to the presence of preadsorbed hydrogen. However, no allyl alcohol recombination feature was visible at 525 K, but peaks due to reaction products were still observed at 525 K.

No difference in conversion of allyl alcohol to products was observed for a 0.65 L allyl alcohol dose on the H-predosed (100) surface. The selectivity was 15%(±3%) to acrolein, 16%(±3%) to propionaldehyde, 49%(±3%) to propene, 8%(±3%) to CO, and 12%(±3%) to CO$_2$. An increase in the selectivity to propene and propionaldehyde was observed on the hydrogen-predosed surface, thus demonstrating the importance of surface hydrogen in the formation of these products via the hydrogenation of surface intermediates. Quantification of the H$_2$O signal was not possible because of a high background pressure of H$_2$O generated by the predissociation of hydrogen. The relative yields of the desorption products from allyl alcohol TDS on a hydrogen-predosed surface are given in Table 6.1.

1-Propanol TDS was also repeated on a hydrogen-predosed surface. Hydrogen (200 L equivalent H$_2$ dose) was coadsorbed with 0.61 L (1 ML) of 1-propanol at 120 K. The same desorption products were observed during the coadsorption experiments as were observed following 1-propanol adsorption on the clean surface. The 1-propanol recombination feature at 525 K was no longer visible on the hydrogen-predosed surface. No significant shift in the low-temperature desorption of 1-propanol was observed due to predosed hydrogen. Propionaldehyde, acrolein, CO, and CO$_2$ all evolved in the same temperature range as for the clean surface. However, propene desorbed in a single peak at 350 K, with no propene features detected in the 400 to 600 K temperature range as observed for propene following 1-propanol adsorption on the clean surface.

No difference in the conversion of 1-propanol to products was observed for a 0.61 L dose of 1-propanol on the H-predosed (100) surface. The selectivity was 4%(±3%) to acrolein, 56%(±3%) to propionaldehyde, 24%(±3%) to propene, 9%(±3%) to CO, and 6%(±3%) to CO$_2$. An increase in the selectivity to propene was observed on the hydrogen-predosed surface, demonstrating the importance of surface hydrogen in the formation of propene via the hydrogenation of surface intermediates. Quantification of the H$_2$O signal was not
possible because of a high background pressure of H₂O generated by the predissociation of hydrogen. The relative yields of the products from 1-propanol TDS on a hydrogen-predosed surface are given in Table 6.2.

### 6.3.2 XPS

**Allyl Alcohol**

Allyl alcohol adsorption was also studied with XPS in order to gain some insight into the surface intermediates involved in the allyl alcohol reaction pathways. For these experiments, 8.7 L of allyl alcohol was dosed on the surface at 120 K, the sample was heated to the desired temperature, and then cooled back down to 120 K before collecting the C 1s XPS spectrum.

The C 1s spectrum of an allyl alcohol multilayer is shown as Figure 6.3(a). Two peaks were fit to this spectrum (shown as dashed lines) at binding energies of 286.9 and 285.2 eV. The separation between these peaks is 1.7 eV, a little higher than a separation of 1.4 eV observed in the C 1s spectrum of gas phase ethanol [93]. By comparison to the spectra of gas phase alcohols [93], the higher binding energy peak at 286.9 eV is assigned to the carbon bound to the hydroxyl group of molecular allyl alcohol (hereafter referred to as a "hydroxyl carbon"), while the lower binding energy peak is assigned to the vinyl carbons of molecular allyl alcohol. The ratio of the intensities of the C 1s signals of the vinyl carbons to the "hydroxyl carbons" is 2.2, slightly higher than the stoichiometric value of 2.0. In general, the calculated ratio for a given spectrum can vary by ±0.2 for small changes in the peakfitting parameters.

Heating the surface to 170 K resulted in the desorption of the multilayer, leaving chemisorbed species on the surface. The resulting C 1s spectrum is shown in Figure 6.3(b). A 10% decrease in the total C 1s signal was observed after heating to 170 K. Three peaks were fit to this spectrum at binding energies of 288.0, 286.4, and 285.1 eV. The peak at 285.1 eV is assigned to the vinyl carbons. The peak at 288.0 eV is assigned to the oxygenated carbon of a surface carboxylate (i.e., acrylate) by comparison to results for acrylic
Figure 6.3: Allyl alcohol C 1s XPS on Cu$_2$O(100) surface. (a) Multilayer allyl alcohol. (b) Sample in (a) heated to 170 K. (c) Sample in (b) heated to 400 K. (d) Sample in (c) heated to 580 K.
acid adsorption on Cu$_2$O(100) [21].

The peak at 286.4 eV is 0.5 eV lower in binding energy that observed for the "hydroxyl carbon" in the allyl alcohol multilayer. However, the binding energy of this feature (286.4 eV) is lower than expected for either a carboxylate species (288.0 eV) [11] or the formyl group of a chemisorbed aldehyde (287.2 eV) [9], suggesting a surface species with only a single C-O bond. A similar decrease in the C 1s binding energy has been reported for the formation of surface alkoxides by alcohol dissociation on ZnO(0001)-Zn and Cu$_2$O [83, 88, 109]. The thermal desorption and XPS results are consistent with a 286.4 eV peak due to the oxygenated carbons of surface allyloxy species.

In summary, the peak at 286.4 eV is characteristic of a surface alkoxide and assigned to allyloxy species. The peak at 288.0 eV is characteristic of an acrylate species, and the peak at 285.1 eV is assigned to the vinyl carbons of either acrylate or allyloxy species. The largest signal was due to the vinyl carbon peak at 285.1 eV, with the ratio of areas of the peaks approximately 1:2.5:8 for the 285.1, 286.4, and 288.0 eV peaks, respectively.

A useful measure of the stoichiometry of the adsorbed species is made by comparing the intensity of the C 1s signals of all the nonoxygenated carbons due to vinyl groups, alkyl carbons, or hydrocarbon fragments (designated C$_x$H$_y$) to the intensity of all the oxygenated carbons of carboxylates and alkoxide species (designated CO$_z$). This C$_x$H$_y$/CO$_z$ ratio gives a measure of the extent of oxidation or reduction of the adsorbate. The spectrum shown as Figure 6.2(b) has a corresponding C$_x$H$_y$/CO$_z$ ratio of 2.3, slightly higher than the expected stoichiometric value of 2.0.

Further heating to 400 K removes the 210-250 K allyl alcohol desorption feature and low-temperature propene and acrolein. A decrease of about 40% in the overall intensity of the C 1s signal was observed compared to that at 170 K. The resulting C 1s XPS spectrum is shown in Figure 6.3(c). Three peaks were fit to this spectrum at binding energies of 287.8, 286.2, and 284.9 eV. The peak assignments are as given above. The C$_x$H$_y$/CO$_z$ ratio for the spectrum shown as Figure 6.3(c) is 2.9. The increase in the C$_x$H$_y$/CO$_z$ ratio demonstrates that some reduction of surface oxygenates occurred, suggesting that the peak at 284.9 eV
contains contributions from surface hydrocarbon fragments as well as the vinyl carbons of acrylate and allyloxy species. Despite an overall decrease in the C 1s signal, no change was noted in the relative sizes of the oxygenate peaks. The intensities appear in the ratio of 1:2.5:10 for the 284.9, 286.2, and 288.0 eV peaks, respectively.

Further heating to 580 K left only those surface species eventually leading to CO, CO₂, and H₂O. A decrease of about 80% in the C 1s signal was observed compared to that for 400 K. The resulting C 1s spectrum is shown in Figure 6.3(d). Four peaks were fit to this spectrum at binding energies of 287.8, 286.2, 285.0, and 284.0 eV. The peak at 284.0 eV is in the same binding energy range as reported for graphitic carbon [26], and is assigned to completely dehydrogenated surface carbon. In addition to the observed decrease in the C 1s intensity, changes in the relative sizes of the different contributions were observed. The features characteristic of allyloxy (286.2 eV) and acrylate (287.8 eV) were of similar intensities, and accounted for about 10% of the C 1s signal. The peak at 286.2 eV characteristic of alkoxide species is thought to be due to the readsoption of molecular allyl alcohol during the XPS measurements, since allyloxy decomposition is observed at 525 K in TDS. The major contributions to the C 1s signal were from equal sized peaks at 285.0 eV (due to vinyl carbons and hydrocarbon fragments) and 284.0 eV (due to dehydrogenated surface carbon). The CₓHᵧ/CO₂ ratio was 2.5, slightly lower than the 400 K value. Further heating to 1000 K results in a carbon free surface.

In addition to examining the C 1s features, the Cu L₃VV feature was also examined. Previous studies on copper oxides have shown that a clear differentiation between Cu⁰, Cu⁺, and Cu²⁺ can be made by shifts in the binding energy of the Cu L₃VV Auger feature [43]. Several Cu L₃VV spectra are shown in Figure 6.4 which correspond to the C 1s spectra described above. Figure 6.4(a) shows the Cu L₃VV feature after heating 8.7 L of allyl alcohol to 400 K. The only features in the spectrum are due to Cu⁺. Heating of the surface to 580 K results in the growth of features with binding energies of 334.9 and 332.3 eV indicative of Cu⁰, as shown in Figure 6.4(b). Continued heating of the surface to 1000 K results in the diffusion of oxygen from the bulk to reoxidize the surface [19]. The presence
Figure 6.4: Cu L\textsubscript{3}VV of Cu\textsubscript{2}O(100) surface as a function of temperature for the allyl alcohol XPS experiments. All spectra were taken at 120 K. (a) Surface heated to 400 K. (b) Surface heated to 580 K. (c) Surface heated to 1000 K.
of Cu⁰ at the surface is consistent with the thermal desorption results which showed that lattice oxygen is removed during the TDS experiments.

1-Propanol

Adsorbed 1-propanol was also studied with XPS in order to identify the surface intermediates in the reaction pathway. For these experiments, 8.1 L of 1-propanol was dosed on the surface at 120 K. The XPS experiments were done as described for the allyl alcohol C 1s XPS.

The C 1s XPS spectrum of a 1-propanol multilayer is shown in Figure 6.5(a). Two peaks were fit to this spectrum (shown as dashed lines) at binding energies of 286.9 and 285.4 eV. The separation between the high and low binding energy peaks is 1.5 eV, in good agreement with the separations observed for molecular allyl alcohol (1.7 eV) and gas phase ethanol (1.4 eV) [93]. The assignment of these peaks is similar to the assignments for the allyl alcohol multilayer. The peak at higher binding energy (286.9 eV) is assigned to the oxygenated (“hydroxy carbon”) carbon of molecular 1-propanol, while the lower binding energy peak (285.4 eV) is assigned to the alkyl carbons in the ethyl group of molecular 1-propanol. The C₂H₆/O₂ ratio for the multilayer is 2.0, the expected stoichiometric value.

Heating to 170 K results in the desorption of the multilayer. A 40% decrease in the overall C 1s intensity was observed. The resulting C 1s spectrum is shown in Figure 6.4(b). Three peaks were fit to this spectrum at binding energies of 287.8, 286.4, and 285.0 eV in an area ratio of 1:3:5:10, respectively. The assignment of these peaks is similar to the assignments for allyl alcohol. The highest binding energy peak (287.8 eV) is assigned to the oxygenated carbon of surface propionate (CH₃CH₂COO⁻) by comparison to propionic acid decomposition studies [11]. The intermediate binding energy feature (286.4 eV) is in a range similar to the allyloxy peak from allyl alcohol, and is assigned to the oxygenated carbon of surface propoxy (CH₃CH₂CH₂O⁻). The lowest binding energy peak (285.0 eV) is assigned to the alkyl carbons from surface propionates and propoxy species. The C₂H₆/O₂ ratio for the spectrum shown as Figure 6.4(b) is 2.2.
Figure 6.5: 1-Propanol C 1s XPS on Cu$_2$O(100) surface. (a) Multilayer 1-propanol. (b) Sample in (a) heated to 170 K. (c) Sample in (b) heated to 430 K. (d) Sample in (c) heated to 600 K.
Heating to 430 K removes the 200-350 K 1-propanol desorption feature as well as the low temperature propene, acrolein, and propionaldehyde. A 50% decrease in the C 1s signal is observed. The resulting spectrum is shown in Figure 6.4(c). Three peaks were fit to this spectrum at binding energies of 287.8, 286.3, and 284.8 eV, in an intensity ratio of 1:3.5:12. The $C_2H_5/CO_2$ ratio is 2.7 for the spectrum shown as Figure 6.4(c). The increase in the $C_2H_5/CO_2$ ratio demonstrates that some reduction of surface oxygenates occurred, suggesting that a contribution to the 284.8 eV peak is from hydrocarbon fragments.

Further heating to 600 K desorbs all the C$_3$ products, and leaves only those surface species eventually leading to CO, CO$_2$, and H$_2$O. A decrease in the C 1s signal of about 50% is observed compared with the 430 K spectrum. The resulting C 1s spectrum is shown in Figure 6.4(d). Three peaks were fit to this spectrum at binding energies of 286.3, 285.0, and 284.0 eV. The peak at 286.3 eV characteristic of an alkoxide species is thought to be due to readesorption of 1-propanol during the XPS experiment. No peak at 287.8 eV due to surface propionate species was observed. As observed with allyl alcohol, the 284.0 eV contribution is assigned to completely dehydrogenated surface carbon. The 285.0 eV peak is responsible for about 50% of the overall carbon signal. The $C_2H_5/CO_2$ ratio for this spectrum is 2.5, in the same range as the $C_2H_5/CO_2$ ratio at 430 K. Further heating to 1000 K resulted in a carbon-free surface.

As with allyl alcohol, examination of the Cu L$_3$VV Auger feature (not shown) shows that some Cu$^0$ is detected at the surface after heating to 600 K, illustrating removal of lattice oxygen. The presence of Cu$^0$ in XPS is consistent with the thermal desorption results which demonstrated that lattice oxygen is removed during 1-propanol TDS experiments. Heating to 1000 K results in the diffusion of oxygen from the bulk to reoxidize the surface.
6.4 Discussion

6.4.1 Molecular Alcohol Adsorption

Desorption of both 1-propanol and allyl alcohol was observed between 200 K and 400 K, and is thought to be due to the desorption of molecular surface alcohol. The assignment of molecular alcohol desorption in this range is consistent with 1-propanol TDS results on TiO\textsubscript{2}(001)-{001}, where a desorption state due to molecular 1-propanol was observed between 300 and 400 K [106], and on Cu(110), where molecular 1-propanol was observed between 200 and 300 K [110].

Molecular alcohol species on the surface should show intermediate C 1s binding energies (286.9 eV) between those expected for carboxylate species (288.0 eV) and alkoxide species (286.4 eV), but were not reported in this temperature range in the XPS results described above. We note that it is possible to peakfit the C 1s spectra for 1-propanol and allyl alcohol after heating to 170 and 400 K with four peaks characteristic of molecular, alkoxide, and carboxylate contributions. However, the variation in BE's for intermediate peaks of \pm 0.2 eV made a 3-peak fit equally reasonable. Thus, the XPS data is consistent with the presence of both molecular and dissociated alcohols on the surface between 225 and 400 K. We wish to emphasize, however, that peakfitting with a higher binding energy contribution due to carboxylate species was required to give an adequate fit.

6.4.2 C\textsubscript{3} Reaction Pathways

Alkoxide Decomposition

For both alcohols, the desorption of the parent molecule in TDS at 525 K was assigned above to alkoxide (i.e., allyloxy or propoxy) recombination with surface hydrogen. The allyloxy and propoxy species both form propene, propionaldehyde, and acrolein as reaction products.

No recombination feature at 525 K was observed for either allyl alcohol or 1-propanol
during the hydrogen coadsorption experiments. The presence of reaction products at 525 K from both allyl alcohol and 1-propanol coadsorbed with hydrogen demonstrates that some allyloxy and preoxy species are still present at 525 K. Thus, the addition of adsorbed hydrogen may have resulted in some recombination of alkoxides at lower temperature. Since the hydrogen-coadsorption studies were done for 1 ML alcohol coverages where the alkoxide-hydrogen recombination peak was obscured by low temperature alcohol desorption features, a small change in the amount of alkoxide species at 525 K could make this feature indistinguishable from the background.

**Allyloxy Decomposition, 525 K**  Three different products were produced via an allyloxy species: acrolein, propionaldehyde, and propene. The desorption of acrolein with the allyl alcohol is characteristic of the first-order unimolecular decomposition of surface alkoxide species. The formation of acrolein from the allyloxy occurs via hydride elimination on the carbon α to the oxygen, a pathway also observed for the formation of acrolein from allyl alcohol on Cu(110) [60]. The C-H bonds on the oxygenated carbon are activated, with lower bond dissociation energies than in the absence of the oxygen heteroatom [110]. The hydride elimination step releases hydrogen onto the surface, as evidenced by water desorption near 525 K [15] in the allyl alcohol TDS results. This surface hydrogen also recombines with the surface allyloxy to give allyl alcohol.

Formation of a saturated product (propionaldehyde) from allyloxy demonstrates that the C=C bond can be hydrogenated. Since propionaldehyde desorption is coincident with acrolein desorption and allyl alcohol recombination, it could be interpreted as either (1) hydrogenation of the double bond at or below 525 K to a propoxy, or (2) that the allyloxy decomposition is rate-limiting. Since no propanol is observed as a desorption product, it is clear that propionaldehyde is not formed via hydrogenation of an allyloxy to propoxy. A likely route to propionaldehyde from allyloxy is by hydrogenation of the acrolein product formed by decomposition of the allyloxy. The formation of propionaldehyde and propene from acrolein has been observed in this same temperature range (≈ 525 K) during thermal
desorption studies of hydrogen-acrolein coadsorption on Cu$_2$O(100) [9]. This pathway has been attributed to hydrogenation of a surface enolate intermediate, which is described in the next section. The formation of propionaldehyde and acrolein from propoxy and allyloxy species is summarized in Figure 6.6.

Brainard et al. studied allyl alcohol decomposition over Cu(110) [60]. Their experimental data was consistent with the presence of alkoxide and oxametallacycles as reaction intermediates. The oxametallacycles were proposed as reaction intermediates because acrolein and propionaldehyde were evolved at temperatures higher than those where alkoxide species are stable on Cu. However, for allyl alcohol on Cu$_2$O(100), the desorption of the reaction products coincident with allyloxy decomposition suggests that no oxametallacycles are required to explain the observed products.

Propoxy Decomposition, 525 K Three products were observed from propoxy decomposition at 525 K: propionaldehyde, acrolein, and propene. Similar to acrolein production from an allyloxy, the formation of propionaldehyde from propoxy occurs via hydride elimination on the carbon α to the oxygen. A similar pathway to propionaldehyde from propoxy has been observed on ZnO(0001)-Zn, TiO$_2$(001)-{001}, and Cu(110) surfaces [88, 106]. The decomposition temperature of propoxy to propionaldehyde on Cu$_2$O (525 K) is intermediate between propoxy decomposition at 400 K on ZnO(0001)-Zn [88] and 580 K on TiO$_2$(001)-{001} [106]. The propoxy decomposition temperature to give propionaldehyde on Cu(110) is at 340 K [110], considerably lower than on Cu$_2$O(100).

The formation of unsaturated products (acrolein and propene) from 1-propanol was also observed in this temperature range during propionaldehyde decomposition studies over Cu$_2$O(100) [9]. These products are believed to be formed by dehydrogenation of product propionaldehyde from propoxy decomposition through an enolate intermediate. Hence the production of all C$_3$ products in this temperature range from 1-propanol can be explained by the subsequent hydrogenation/dehydrogenation of propionaldehyde to a surface enolate. The enolate-mediated chemistry for all temperature ranges is described in the next section.
Figure 6.6: Formation of propionaldehyde from 1-propanol and acrolein from allyl alcohol.
Propene has been observed as a reaction product from 1-propanol decomposition over TiO$_2$(001)-(001) surfaces [106]. The propene was produced coincident with propoxy decomposition at 580 K by deoxygenation of the alkoxide species accompanied by $\beta$-hydride elimination [106]. Although propene production from 1-propanol on Cu$_2$O by this pathway cannot be discounted, the formation of propene between 400 and 550 K via an enolate intermediate is consistent with previously observed surface chemistry of propionaldehyde decomposition on Cu$_2$O [9].

**Enolate Decomposition Pathway**

Propene, acrolein, and propionaldehyde have been observed as desorption products between 250 and 500 K during studies of C$_3$ aldehyde (acrolein and propionaldehyde) reactions over Cu$_2$O(100) [9]. The formation of these products between 250 and 500 K is thought to proceed through a common enolate intermediate [9]. The desorption of propene, acrolein, and propionaldehyde between 250 and 400 K on the (100) surface from the C$_3$ alcohols is consistent with the previously observed chemistry for surface enolate species. The enolate species are formed by the initial dehydrogenation of the alkoxides to form the corresponding aldehyde. The formation of the enolate occurs either through adsorbed acrolein (from allyl alcohol) or propionaldehyde (from 1-propanol). The formation of these products (acrolein, propene, propionaldehyde) from a surface enolate has been reported previously [9]. However, it should be noted that the formation of aldehydes from alkoxide species is irreversible on Cu$_2$O. A summary of the formation of an enolate species from adsorbed acrolein or adsorbed propionaldehyde is shown in Figure 6.7.

The amount of propionaldehyde produced during the allyl alcohol thermal desorption studies is more than would be expected via a surface enolate pathway. Thus, an additional pathway exists to produce propionaldehyde through an allyloxy species. Although the details of this pathway are not completely understood, it is clear that the propionaldehyde is not produced by hydrogenation of allyloxy to propoxy, as no 1-propanol was observed in the allyl alcohol TDS. However, the amounts of C$_3$ reaction products produced during the
Figure 6.7: Surface enolate formation from adsorbed acrolein and propionaldehyde.
1-propanol TDS is consistent with their formation through an enolate species. The observation that no propionaldehyde was observed from allyl alcohol from 225 to 400 K is in apparent contradiction with an enolate-mediated reaction pathway at this temperature. However, the propionaldehyde (m/e = 58) signal shown in Figure 6.1 has had the maximum possible contribution due to allyl alcohol subtracted. Thus, the desorption trace shown in Figure 6.1 represents the absolute minimum amount of propionaldehyde formed. However, the cracking patterns of alcohols in our skimmer-equipped mass spectrometer vary with pressure. A variation of only 5% in the cracking pattern correction due to the alcohols would give the appearance of propionaldehyde between 225 and 400 K. Thus, the absence of propionaldehyde between 225 K to 400 K may be due to the way in which the data was processed, and not because propionaldehyde was not formed.

The formation of propene, propionaldehyde, and acrolein from a surface enolate between 225 and 400 K is reasonable based on previously observed chemistry on Cu$_2$O(100) [9]. However, the reason for the apparent hydride abstraction from allyloxy and propoxy in this temperature range is not well understood. It is not clear as to why the aldehydes which initiate the enolate-mediated chemistry are formed from the alcohols in two different temperature ranges. However, two sets of reaction products in different temperature ranges have also been observed for methanol decomposition over both Cu$_2$O(100) and (111) surfaces [109].

Low Temperature Propene Pathway

Only allyl alcohol yields reaction products below 225 K. The presence of desorption-limited propene at 170 and 215 K demonstrates that some propene is formed by a facile reaction at or below 170 K. Further, the formation of propene below 170 K demonstrates that C-O bond scission occurs upon adsorption. A similar reaction pathway to propene below 215 K has been observed for H-acrolein coadsorption [9]. No low temperature propene (< 225 K) was observed during 1-propanol TDS or during the decomposition of propionaldehyde [9]. It is believed that this low energy pathway for the olefinic species is attributable to a decrease
in the C-O bond dissociation energy since an allyl species would be formed from allyl alcohol or acrolein hydrogenated via a (1,2) addition [9]. The lower stability of the propyl radical which would be formed by C-O bond dissociation of 1-propanol appears to be the reason no low temperature deoxygenation products are formed. The low temperature at which propene is formed suggests that the formation of propene via a facile reaction for allyl alcohol goes through a π-allylic species. However, it is not possible from our experimental data to make a clear distinction between deoxygenation of allyloxy or dehydroxylation of molecular allyl alcohol to give the π-allylic species.

6.4.3 Non-Selective Oxidation Pathway

Carboxylate species are observed during both 1-propanol and allyl alcohol XPS after heating to 170 K and are thought to be formed from both alcohols by a similar process. The carboxylate species are most likely formed by the nucleophilic attack of lattice oxygen at the oxygenated carbon of the adsorbed surface alkoxides. Adsorbed surface oxygen from C-O bond scission is not thought to be involved in the formation of surface carboxylates, as no evidence for C-O bond scission below 225 K was observed in the 1-propanol TDS even though a clear carboxylate signal was observed in the C 1s XPS after heating to 170 K. Thus, subsurface lattice oxygen and not adsorbed oxygen is involved in carboxylate formation. Carboxylate formation via incorporation of second layer oxygen has also been observed for 1-propanol adsorption on ZnO(0001)-Zn [88].

The desorption temperatures for CO, CO₂, and H₂O from allyl alcohol and 1-propanol are within 2-4 kcal/mol to those for the non-selective oxidation products formed during the decomposition of acrylate and propionate species during acrylic and propionic acid thermal desorption studies [11]. This similarity suggests that the primary pathway for the formation of CO, CO₂, and H₂O is by decomposition of surface carboxylates. This process has been shown to occur by reduction, dehydrogenation, and reoxidation.

Heating of the surface during the allyl alcohol or 1-propanol XPS experiments from 170 K to 400-430 K results in an increase in the C₂H₅/CO₂ ratio, illustrating an overall reduction of
surface oxygenate species. The reduction of oxygenate species occurs by the initial break-up of adsorbed species into hydrocarbon fragments. Continued heating to 580-600 K results in several changes. The appearance of surface carbon is observed in XPS, which demonstrates that the complete dehydrogenation of some surface species occurs. The presence of $H_2O$ desorption near 600 K gives additional evidence for the break-up of hydrocarbon species and(or) the dehydrogenation of surface oxygenates. The subsequent desorption of CO and $CO_2$ occurs by extraction of lattice oxygen by adsorbed carbon species. Reoxidation of the surface occurs by diffusion of oxygen from the bulk to the surface above 800 K [19].

Thus, a general picture of the non-selective oxidation pathways of 1-propanol and allyl alcohol can be made on Cu$_2$O(100). The initial break up of the surface oxygenates into hydrocarbon fragments occurs between 400-600 K. Further heating to 600 K results in the dehydrogenation of the hydrocarbon fragments to surface carbon. Reoxidation of adsorbed carbon by lattice oxygen to form the non-selective oxidation products occurs above 600 K.

6.5 Conclusions

Allyl alcohol and 1-propanol reactivity on the Cu$_2$O(100) surface was studied with TDS and XPS. Allyl alcohol reacts on the (100) surface to give oxidation products (CO, $CO_2$, $H_2O$, acrolein), an isomerization product (propionaldehyde), and a reduction product (propene). 1-Propanol reacts on the (100) surface to give oxidation products (acrolein, propionaldehyde, CO, $CO_2$, $H_2O$) and a reduction product (propene). Both alcohols disassociatively adsorb to form alkoxides. The alkoxide species undergo hydride elimination on the carbon α to the oxygen to form the corresponding aldehydes. Between 225 and 400 K, the acrolein and propionaldehyde formed from the alkoxides are linked by a common surface enolate intermediate which explains the similarity in C$_3$ products observed from the two alcohols. The propionaldehyde, acrolein, and propene formed between 400 and 600 K are thought to be formed from alkoxide and enolate surface species. A low temperature pathway to produce propene was observed via C-O bond scission of allyl alcohol upon adsorption to
give a π-allyl. Hydrogenation of the resulting π-allyl produced propene at low temperature.
Chapter 7

Propene Activation and Selective Oxidation Over Cu$_2$O Single Crystal Surfaces: A Combined UHV and Atmospheric Pressure Study

7.1 Introduction

The partial oxidation of propene (CH$_2$=CHCH$_3$) to acrolein (CH$_2$=CHCHO) is a useful model for the class of allylic oxidation reactions of olefins. Several mixed oxides catalyze propene partial oxidation to acrolein, but Cu$_2$O is the only reported single component oxide catalyst [1]-[3]. There is evidence that some details of the reaction pathway are similar over the bismuth-molybdate [4], tin-antimony oxide [5], uranium-antimonate [6], and single component Cu$_2$O catalysts [4]. Thus, mechanistic information obtained over Cu$_2$O may be applicable to more complex mixed oxide systems [2]-[7].

The basic steps in the reaction pathway of propene oxidation to acrolein have been widely studied. In the rate-determining step over Cu$_2$O and bismuth-molybdate catalysts, a methyl hydrogen is abstracted from propene producing a symmetric π-allyl intermediate [4, 8]. The order in which the second and third steps occur is not well understood, but involves a second hydrogen abstraction and lattice oxygen insertion into the symmetric π-allyl to form an oxygen-containing σ-allyl species. Grasselli and coworkers [3] advocate the formation of a σ-allyl on bismuth-molybdate catalysts where oxygen insertion occurs prior to a final hydrogen abstraction (i.e., an allyloxy intermediate, CH$_2$=CHCH$_3$O-). However, several groups advocate the formation of a σ-allyl species on bismuth-molybdate [1] and Cu$_2$O [7] catalysts where lattice oxygen insertion occurs after a final hydrogen abstraction (i.e., an intermediate similar to adsorbed acrolein).
Propene adsorption has been studied previously on Cu$_2$O single crystal surfaces under ultrahigh vacuum (UHV) conditions [12]. No C$_3$ partial oxidation products were detected for propene adsorption in UHV at 100 K or 300 K. However, evidence for propene dissociation to an allyl (C$_3$H$_5$) was observed after adsorption at 300 K. No determination could be made from the thermal desorption and photoemission data concerning the nature of the C$_3$H$_5$ allyl species (i.e., $\pi$- or $\sigma$-allyl). A complete description of these results is given elsewhere [12].

Propene oxidation over Cu$_2$O catalysts has been widely studied over the past several decades [4]-[7],[111]. Mikhal'chenko et al. studied propene adsorption and oxidation over Cu$_2$O powders. They proposed two different forms of adsorbed propene on Cu$_2$O: a reversibly adsorbed and an irreversibly adsorbed propene species [112, 113]. The reversibly-adsorbed propene formed partial oxidation products, while the irreversibly adsorbed propene formed CO$_2$ and H$_2$O [113]. A continuation of these studies using IR suggested that acrolein was formed from propene through allyl complexes on Cu$_2$O [112].

Wood et al. studied propene oxidation over low-surface-area, unoriented, Cu$_2$O crystals as a function of surface condition [78]. They found that copper-rich Cu$_2$O tends to favor acrolein production, while oxygen-rich Cu$_2$O favors CO$_2$ and H$_2$O production. Results over supported Cu$_2$O catalysts have found that Cu$_2$O favors partial oxidation products, while CuO favors non-selective oxidation products [115].

Several recent studies have focused on the form and stability of the intermediates in the propene oxidation pathway on Cu$_2$O [73, 111, 116]. Davydov et al. used IR to study propene adsorption on Cu$_2$O and copper oxide-magnesium oxide mixed catalysts [73]. They observed both $\pi$- and $\sigma$-allyl species on Cu$_2$O following propene adsorption, and suggest that the $\pi$-allyl species is stable to about 573 K, whereas the $\sigma$-allyl is stable to about 473 K. The assignment of a $\pi$-allyl species was made via C-C bond stretches at 1440 and 1510 cm$^{-1}$ by comparison with the IR spectra of allyl bromide. Davydov and co-workers also suggested that propene forms acrolein through an allyloxy species (CH$_2$=CH-CH$_2$O-).

Imachi and co-workers studied the reactions of deuterium-labeled propene over Cu$_2$O with microwave spectroscopy [111]. They observed a discrimination isotope effect for the
production of two different forms of acrolein from CH3CH=CHD. This observation lead
them to suggest that conversion from a π-allyl to a σ-allyl from adsorbed propene is not
reversible, and that once the σ-allyl species is formed it does not readily convert to a σ-allyl
isomer or a π-allyl.

Choi et al. examined the reaction of 18O-labeled allyl alcohol over supported Cu2O in
an effort to model the σ-allyl intermediate formed when oxygen insertion occurs prior to
hydrogen abstraction in the propene oxidation pathway [111]. From the 18O-allyl alcohol
reaction over Cu2O, they found partial loss of the 18O in the product acrolein, illustrating
that some scission of the C-O bond and reoxidation by surface oxygen had occurred. Choi
and coworkers also suggest that the σ-allyl intermediate formed from allyl alcohol is similar
to the σ-allyl formed during acrolein production from propene. Further, their results sug-
gest that the oxygen-containing σ-allyl is not in equilibrium with a π-allyl under reaction
conditions.

7.2 Experimental

All experiments were performed in a dual-chamber, stainless steel, ultrahigh vacuum
system equipped for XPS, LEED, and TDS. Dosing was accomplished by exposure of the
sample to propene or oxygen at atmospheric pressure in a high pressure cell attached to
the vacuum system. The sample rod manipulator passes through sliding seals that separate
the UHV system from the high pressure cell. Thus, it was possible to dose at atmospheric
pressure without exposing the sample to air. The background pressure was less than 1.0 ×
10−8 Torr throughout the thermal desorption experiments.

For all thermal desorption experiments the samples were heated linearly at a rate of
2K/sec. An Inficon Quadrex 200 was used to monitor up to 6 masses simultaneously
during the thermal desorption experiments. The mass spectrometer was equipped with a
quartz skimmer to minimize the sampling of desorption products from the sample support
hardware.
Significant variations in the amounts of desorbing propene were observed during the TDS experiments due to variations in the total propene dose from run to run. The exposures were done in flowing propene in the high-pressure cell. The sample was moved from UHV into the high-pressure cell (in approximately 5 seconds), exposed to flowing propene at atmospheric pressure for about 2 seconds, then moved back into UHV (in approximately 5 seconds). These exposures are nominally referred to as $10^9$ L doses. The background pressure was allowed to decrease below $1 \times 10^{-8}$ Torr prior to the start of a thermal desorption run. The data shown in this paper are representative of the most reproducibly obtained desorption traces. All TDS traces have been corrected for mass spectrometer sensitivity.

Matheson polymer-grade propene (99.5%) containing 0.4% propane as the major contaminant was used. Matheson research grade O$_2$ (99.997%) was passed through a coiled tube immersed in liquid nitrogen in an attempt to minimize the water content before use.

7.3 Results

7.3.1 Thermal Desorption: 300 K, 1 atm. Exposures

Cu-terminated Cu$_2$O(100)

Figure 7.1 shows the TDS spectra obtained after a $10^9$ L dose of propene on the Cu-terminated Cu$_2$O(100) surface at 300 K. Propene, acrolein, allyl alcohol (CH$_2$=CHCH$_2$OH), propane (CH$_3$CH$_2$CH$_3$), CO, CO$_2$, and H$_2$O were all detected as desorption products. No bimolecular products were detected, and no C$_1$ or C$_2$ products were detected besides non-selective oxidation products (CO and CO$_2$). Propene desorbed as a broad feature with two peaks at 335 and 400 K. This desorption temperature range for propene from the Cu-terminated (100) surface is similar to the desorption temperature range of 383 to 403 K reported by Mikhal’chenko et al. for “reversibly adsorbed” propene on Cu$_2$O powders [113]. The coverage of propene under these conditions was very low, with an estimated sticking coefficient on the order of $10^{-10}$.

Acrolein and allyl alcohol both desorb with a peak maximum at 335 K. The coincident
Figure 7.1: Thermal desorption traces following a $10^9$ L dose of propene at 300 K on the Cu$_2$O(100) surface.
desorption of allyl alcohol and acrolein suggests that their evolution involves the same rate-limiting step from a common surface intermediate. The production of CO [14] and CO$_2$ [91] at 750 K is reaction-limited. CO and CO$_2$ peaks in this temperature range have been attributed to the burn-off of adsorbed carbon and hydrocarbon species during studies of C$_3$ oxygenate decomposition on Cu$_2$O(100) [9]-[11]. Propane desorbed in a single peak with a desorption maximum at 325 K. No H$_2$ was detected, however, the background pressure of hydrogen was high enough in the vacuum system that some H$_2$ desorption might have gone undetected.

H$_2$O desorbs in a broad desorption feature extending from 325 K to 800 K, with small peaks above the background at 335, 420, and 750 K. H$_2$O thermal desorption studies have shown that the recombination of dissociated water occurs below 460 K [15], while studies of predissociated hydrogen desorption have shown that atomic hydrogen extracts lattice oxygen to form water at 500 K [117]. Water desorption above 500 K is therefore associated with a rate-limiting step(s) for the dehydrogenation of surface hydrocarbons. The broad temperature range for water desorption suggests that the rate-limiting steps for water desorption involve disproportionation of surface hydroxyl groups, lattice oxygen extraction by surface hydrogen, and dehydrogenation of surface hydrocarbons.

Propane and propene represented the majority of the desorbing products. The conversion of propene following a 10$^3$ L propene dose was about 50%. The selectivity (calculated on a C$_3$ basis) was 77% to propene, 14% to CO, 8% to CO$_2$, 0.3% to allyl alcohol, and 0.1% to acrolein. Thus, C$_3$ oxidation products (allyl alcohol, acrolein) were produced in only trace amounts for propene on the Cu-terminated (100) surface following adsorption at atmospheric pressure and 300 K. The relative product yields are given in Table 7.1. Since the propene exposures are done in the absence of oxygen, it is clear that all oxidation products (selective and nonselective) utilize lattice oxygen for their formation.
Table 7.1: Relative yields for $10^9$ L propene on Cu-terminated Cu$_2$O(100)

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>3.09</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_2$OH</td>
<td>0.01</td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>&gt;0.005</td>
</tr>
<tr>
<td>CO</td>
<td>1.68</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.45</td>
</tr>
</tbody>
</table>
Oxygen-Terminated Cu$_2$O(100)

The propene thermal desorption experiments performed on the Cu-terminated (100) surface were repeated on an oxygen-terminated Cu$_2$O(100) surface to examine the effects of doubly-coordinate surface lattice oxygen on the oxidation of propene. The oxygen-terminated surface was prepared by exposure to $10^9$ L of O$_2$ at 300 K. The oxygen terminated surface is stable to less than 500 K in vacuum [19], therefore a fresh oxygen-terminated surface was prepared prior to each propene thermal desorption run.

Figure 7.2 shows the TDS spectra following a $10^9$ L propene dose on an oxygen-terminated Cu$_2$O(100) surface. Propene, acrolein, allyl alcohol, CO, CO$_2$, and H$_2$O were all detected as desorption products. As with the Cu-terminated surface, no bimolecular, C$_2$, or C$_3$ products were detected in addition to the C$_1$ non-selective oxidation products. Propene desorbed in a broad feature with a peak at 495 K, and a lower-temperature shoulder at 390 K. The desorption of propene from the oxygen-terminated (100) surface occurs with nearly a 100 K higher desorption temperature than from the Cu-terminated (100) surface, illustrating structure sensitivity to propene adsorption at 300 K under these conditions. As on the Cu-terminated (100) surface, the amount of propene adsorbed under these conditions was small, with an estimated sticking coefficient estimated of about $10^{-10}$.

Acrolein and allyl alcohol desorbed in a single, broad desorption feature with a peak maximum at 480 K. As on the Cu-terminated (100) surface, the coincident desorption of allyl alcohol and acrolein suggests that their evolution involves the same rate-limiting step from a common surface intermediate. Propane desorbed as a broad feature extending from 375 K to 525 K, with a maximum at 485 K.

CO and CO$_2$ both desorbed in a reaction-limited [14, 91] peak at 485 K. H$_2$O was also observed at 485 K, in the temperature range expected for water desorption via the extraction of lattice oxygen by surface hydrogen [117]. No H$_2$ was detected, however, the background pressure of hydrogen was high enough in the vacuum system that some H$_2$ might have gone undetected.
Figure 7.2: Thermal desorption traces following a $10^9$ L dose of propene at 300 K on the oxygen-terminated Cu$_2$O(100) surface.
Several changes in the conversion and selectivities of propene to products were observed when comparing the Cu-terminated (100) surface with the oxygen-terminated surface. The selectivity (calculated on a C₃ basis) was 43% to propane, 2% to allyl alcohol, 1% to acrolein, 32% to CO, and 22% to CO₂ on the oxygen-terminated surface. The conversion of propene to products decreased from 50% on the Cu-terminated (100) surface to 30% on the oxygen-terminated surface. The selectivity to propane decreased from 77% on the Cu-terminated (100) surface to 43% on the oxygen-terminated (100) surface. However, the selectivity to acrolein and allyl alcohol increased from a total of less than 0.4% on the Cu-terminated (100) surface to 3% on the oxygen-terminated surface. Table 7.2 gives the relative yields for a 10⁹ L propene dose on an oxygen-terminated Cu₂O(100) surface.

Cu₂O(111)

Figure 7.3 shows TDS traces following a 10⁹ L propene dose on the Cu₂O(111) surface at 300 K. All propene TDS experiments were done on an oxygen-deficient Cu₂O(111) surface exhibiting a (√3×√3)R30° LEED pattern [12, 19]. Propene, acrolein, allyl alcohol, propane, CO, CO₂, and H₂O were all detected as desorption products. Trace signals at the detection limits of the mass spectrometer were observed for mass numbers 78 and 67. These signals are attributed to trace amounts of benzene and 1,5 hexadiene, but the signals were small enough that identification based on multiple mass numbers in the cracking patterns was not possible. No C₂ or C₁ products other than non-selective oxidation products were observed. Propene desorbed in one peak at 360 K, with a higher temperature shoulder at 435 K. The coverage of propene was very small, with an estimated sticking coefficient of about 10⁻¹⁰ under these experimental conditions.

Acrolein and allyl alcohol desorbed in two peaks at 350 and 435 K. As on the copper and oxygen-terminated (100) surfaces, the coincident desorption of allyl alcohol and acrolein suggests that their evolution involves the same rate-limiting step from a common surface intermediate. Propane desorbed in a single feature with a peak maximum at 350 K. CO and CO₂ both desorbed in two reaction-limited peaks [14, 91], one coincident with propene
Table 7.2: Relative yields for $10^9$ L propene on O-terminated Cu$_2$O(100)

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>0.66</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_2$OH</td>
<td>0.03</td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>0.02</td>
</tr>
<tr>
<td>CO</td>
<td>1.44</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.54</td>
</tr>
</tbody>
</table>
Figure 7.3: Thermal desorption traces following a $10^9$ L dose of propene at 300 K on the Cu$_2$O(111) surface.
at 360 K, and a second higher temperature peak at 660 K. H₂O desorbs in two peaks at 360 and 435 K, which are both in the temperature range for dissociated water recombination [15].

The conversion of propene was about 40% for a 10⁹ L dose on the (111) surface at 300 K. The selectivity (calculated on a C₃ basis) to propane was 80%, to CO was 7%, to CO₂ was 8%, to acrolein 2%, and to allyl alcohol 3%. The relative yields of the products are summarized in Table 7.3.

Structure Sensitivity in Propene Adsorption and Acrolein Production

Figure 7.4 shows the propene and acrolein TDS traces in a single figure for the three different surfaces described above for comparison. Figures 7.4 (a), (b), and (c) show propene (solid lines) and acrolein (dashed lines) desorption from the (111) surface, the Cu-terminated (100) surface, and the oxygen-terminated (100) surface, respectively. The differences in the temperatures of the propene desorption states from the three different surfaces clearly demonstrate structure sensitivity for propene adsorption. Specifically, propene from the oxygen-terminated (100) surface desorbs at 480 K for its primary desorption channel, 100 K higher than the primary desorption channel from the (111) and Cu-terminated (100) surfaces. The reason for the higher propene desorption temperature on the oxygen-terminated (100) surface is not understood. Structure sensitivity for propene adsorption has also been observed for propene adsorption in UHV at low temperature on the Cu₂O(111) surface and the Cu-terminated Cu₂O(100) surface [12].

Differences in the desorption temperatures and relative amounts of acrolein produced from the different surfaces are also observed in Figure 7.4. The acrolein desorption traces (shown as dotted lines) have been scaled so as to show the relative amounts produced from the different Cu₂O surfaces studied. The largest amount of acrolein was produced from the Cu₂O(111) surface, and is shown in Figure 7.4(a). In contrast, approximately 20 times less acrolein was produced from the Cu-terminated (100) surface (Figure 7.4(b)). Acrolein was also produced on the oxygen-terminated (100) surface, but in a yield about 5 times less
Table 7.3: Relative yields for $10^9$ L propene on Cu$_2$O(111)

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>3.20</td>
</tr>
<tr>
<td>CH$_2$=CHCH$_2$OH</td>
<td>0.11</td>
</tr>
<tr>
<td>CH$_2$=CHCHO</td>
<td>0.07</td>
</tr>
<tr>
<td>CO</td>
<td>0.85</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>6.20</td>
</tr>
</tbody>
</table>
Figure 7.4: TDS traces of propene and acrolein following a $10^8$ L dose of propene. (a) Cu$_2$(111) surface. (b) Cu$_2$O(100)-Cu surface. (c) Oxygen-terminated Cu$_2$O(100) surface.
than from the Cu₂O(111) surface. Thus, the largest acrolein signals were obtained from the Cu₂O surfaces with readily-accessible, coordinately-unsaturated surface lattice oxygen in the top atomic layer.

Comparison of Acrolein Desorption Signals from Different Adsorbates

Figure 7.5 shows acrolein thermal desorption traces from several different adsorbates on Cu₂O single-crystal surfaces. The acrolein traces following a 10⁹ L exposure of propene (300 K, 1 atm.) on the Cu₂O(111) and oxygen-terminated (100) surfaces are shown as Figures 7.5(a) and (b), respectively. The acrolein traces in Figure 7.5(a) and (b) have been arbitrarily scaled for comparison. Acrolein TDS traces from both allyl alcohol (0.22 L at 120 K) [10] and acrolein (0.25 L at 100 K) [9] adsorption studies in UHV on the Cu-terminated (100) surface at low temperature are shown as Figure 7.5(c) and (e), respectively. An acrolein trace from allyl alcohol decomposition on the Cu₂O(111) surface is shown in Figure 7.5(d). By comparison to the desorption signal from molecular acrolein, it is seen that the desorption of acrolein from the allyl alcohol and propene exposures is reaction-limited. The similarity in desorption temperatures of the acrolein peaks from allyl alcohol on the (100) and (111) surfaces and the acrolein peaks from propene TDS suggests that the rate-limiting steps involve the same surface intermediates.

7.3.2 XPS

Cu₂O(100)

XPS was used to study propene adsorption (at 300 K, 1 atm.) on the Cu₂O(100) surface, and to check for the formation of an oxygen-containing η-allyl. A C 1s peak broadened to higher binding energies would be expected for an oxygen-containing surface intermediate because of the electron withdrawing nature of oxygen [9]-[11],[26]. For the XPS experiments, 10⁹ L exposures of propene on both the Cu-terminated and O-terminated (100) surfaces at 300 K were examined. The resulting C 1s XPS spectra are shown in Figure 7.3. Heating
Figure 7.5: TDS traces of product acrolein on Cu$_2$O. (a) Acrolein from $10^9$ L propene on the Cu$_2$(111) surface. (b) Acrolein from $10^9$ L propene on the oxygen-terminated Cu$_2$O(100) surface. (a) and (b) are not shown to scale, but have been shown the same size for clarity. (c) Acrolein from allyl alcohol TDS on Cu$_2$O(100). (d) Acrolein from allyl alcohol TDS on Cu$_2$O(111). (e) Acrolein from acrolein TDS on Cu$_2$O(100).
either surface above 300 K resulted in a carbon signal which was not high enough above the background for analysis.

The C 1s spectrum of the Cu-terminated (100) surface is shown in Figure 7.6(a). One peak was fit to this spectrum at a binding energy of 284.9±0.1 eV. This binding energy (284.9 eV) is characteristic of adsorbed hydrocarbons (i.e., propene, alkyl carbons, vinyl carbons, etc.) on Cu$_2$O [12]. No broadening of the C 1s XPS spectrum to higher binding energy was observed, illustrating that oxygen insertion does not occur to an extent detectable with XPS. This result is consistent with the thermal desorption data which showed that less than 0.2% of the propene was converted to C$_3$ oxidation products.

Figure 7.6(b) shows the C 1s spectrum of $10^9$ L of propene adsorbed on the oxygen-terminated (100) surface. This spectrum is broadened to higher binding energy, characteristic of the formation of an oxygen-containing surface species following propene adsorption. Two contributions are observed at binding energies of 286.6±0.1 and 284.9±0.1 eV. The peak at 286.6 eV is at the same binding energy (within experimental error) expected for the oxygenated carbon of a surface alkoxide species (286.4 eV) [10]. This XPS feature is not characteristic of the bound formyl group of an aldehydic specie (287.2 eV) on this surface [9].

Previous studies of propene oxidation over Cu$_2$O have suggested the formation of an oxygen-containing σ-allyl species in the propene oxidation pathway [1, 2, 3]. The presence of an alkoxide species in XPS and the occurrence of acrolein as a thermal desorption product are consistent with the formation of an oxygen-containing σ-allyl species, thus, the species giving rise to the C 1s XPS peak at 286.6 eV is assigned to the oxygenated carbon of an oxygen-containing σ-allyl.

Cu$_2$O(111)

Figure 7.7 shows the C 1s spectrum following a $10^8$ L propene dose on the (111) surface at 300 K and 1 atm. Two contributions were found to this spectrum at binding energies of 284.9±0.1 eV and 286.4±0.1 eV. As on the oxygen-terminated (100) surface, the peak
Figure 7.6: C 1s XPS spectra of $10^9$ L of propene on Cu$_2$O(100). (a) Propene adsorbed on the propene-terminated (100) surface. (b) Propene adsorbed on the oxygen-terminated (100) surface.
Figure 7.7: C 1s XPS spectra of $10^9$ L of propene on Cu$_2$O(111).
at 286.4 eV is assigned as an oxygen-containing $\sigma$-allyl. Thus, evidence for an oxygen insertion into an adsorbed surface specie(s) was observed in XPS for both the (111) and the oxygen-terminated (100) surfaces.

7.4 Discussion

7.4.1 Comparison of Propene Adsorption in UHV and 1 atm.

Several differences and similarities were observed between propene adsorption in UHV and at atmospheric pressure. The desorption temperatures of propene following either UHV or atmospheric pressure adsorption at 300 K were similar for the (111) and Cu-terminated (100) surfaces. Propene desorbed after a 3000 L dose ($10^{-4}$ Torr) at 315 K on the Cu-terminated (100) surface, and at 360 K from the (111) surface [12]. The primary desorption channel following a $10^9$ L propene dose is 335 K for the Cu-terminated (100) surface, and 360 K for the (111) surface, similar to the values reported for propene adsorption in UHV. Propene adsorption was also studied on a Cu$_2$O(100) surface predosed with 0.3 ML of atomic oxygen [12]. The primary propene desorption channel from this surface was at 315 K, 180 K lower than the primary propene desorption channel (495 K) from the oxygen-terminated (100) surface following a 1 atm. exposure.

Several differences were observed between the propene reactivity for UHV and 1 atm. exposures at 300 K. First, no selective or nonselective oxidation products were observed for propene adsorption in UHV [12]. Thus, no evidence of oxygen insertion was observed under any conditions for propene adsorption at 300 K with exposures up to 3000 L in UHV. The presence of an oxygen-containing $\sigma$-allyl species following a $10^9$ L (1 atm.) propene dose on either the oxygen-terminated (100) or the (111) surfaces gives clear evidence that oxygen insertion takes place at higher pressure. Second, no hydrogenation activity was observed on either the (100) or (111) surfaces for propene adsorption in UHV. Indeed, no propane was formed even for propene adsorption on hydrogen-predosed surfaces in UHV. Thus, clear differences in the reactivity of propene were observed for exposures in UHV
and at atmospheric pressure, suggesting a "pressure gap" exists between the UHV and atmospheric pressure chemistry.

The origin of the "pressure gap" in catalysis has been addressed recently for methane activation on Ni(111) [117]. For methane adsorption on Ni (111), dissociation is observed for pressures above 1 Torr, but no dissociation is observed below $10^{-4}$ Torr [117]. Ceyer and co-workers found that the pressure dependence for CH$_4$ dissociation on Ni is related to the presence of an energy barrier along the dissociative reaction coordinate [117]. Only those molecules with sufficient translational energy overcome the barrier to dissociation. An increase in pressure increases the absolute number of gas-phase molecules whose translational energy is sufficient to overcome this energy barrier.

Similar processes could explain the differences in chemistry between the UHV and 1 atm. exposures for propene over Cu$_2$O surfaces. In the UHV work [12], dissociative adsorption of propene to allyl was observed with a sticking coefficient of less than $10^{-5}$. Since no oxidation products (selective or nonselective) were observed, it is clear that the propene "activation" process involves more than simply dissociation, and that the reaction probability for such events at 300 K are well below $10^{-5}$. The clear observations of oxygen-containing surface species and subsequent selective oxidation following exposures at 300 K and 1 atm. strongly suggests that oxygen insertion to form a $\sigma$-allyl can be accomplished via translational or collisional activation [117].

While translational or collisional activation can explain the pressure effects observed at 300 K, we note that these are clearly not the only activation processes involved in propene oxidation. For exposures at elevated surface temperatures and 1 atm., we have observed that reduction of our Cu$_2$O single-crystal surfaces to metallic copper occurs in flowing propene at temperatures between 500 and 600 K. Clearly, thermal activation at increased surface temperatures is also important in the oxidation of propene.

As mentioned above, propene dissociation to an allylic species was observed for 3000 L propene doses at 300 K in UHV [12]. However, the presence of a hydrogenation product (propane) following a $10^9$L propene exposure which was not observed for propene adsorption
in UHV implies that a different surface intermediate is required for propene hydrogenation. Unfortunately, no definitive identification of the surface intermediate which gives propane can be made from our experimental data.

7.4.2 Allyloxy: Key Intermediate for Acrolein Formation

UHV thermal desorption studies have shown that product acrolein is formed during allyl alcohol decomposition via the first-order, unimolecular, dehydrogenation of surface allyloxy at the carbon α to oxygen [10]. On the (100) surface, this reaction occurs at 525 K and on the (111) surface at 400 K with corresponding activation energies of 35.6 and 26.9 kcal/mol, respectively. The characteristic signature of this reaction is the concurrent desorption of allyl alcohol by recombination of allyloxy with surface hydrogen at the same temperature observed for acrolein formation. A lower-temperature pathway involving the production of an enolate intermediate from allyloxy has also been observed at 310 K on the (100) surface and 300 K on the (111) surface [10].

For atmospheric pressure exposures of propene on the Cu$_2$O(111) and oxygen-terminated (100) surfaces, acrolein is evolved at 435 K (29.4 kcal/mol) and 480 K (32.5 kcal/mol), respectively. Comparison with the desorption trace of adsorbed acrolein in Figure 7.5(d) shows clearly that the acrolein produced from propene is reaction-limited and falls with the range of temperatures and activation energies observed for allyloxy dehydrogenation on the (111) and (100) surfaces. The concurrent desorption of allyl alcohol is also confirmed in Figure 7.2 and 7.3 following atmospheric pressure propene exposures. Hence, the production of acrolein from propene clearly involves an allyloxy intermediate rather than an aldehydic (i.e., acrolein-like) intermediate. Some acrolein production from propene is even observed at 350 K, similar to the enolate-mediated route for allyloxy decomposition [9].

The assignment of acrolein production from an allyloxy is consistent with the C 1s XPS data for adsorbed propene. The binding energy for the oxygen-containing σ-allyl species is consistent with the binding energy observed for allyloxy species on Cu$_2$O(100) [10]. The production of acrolein via an allyloxy demonstrates that oxygen insertion occurs before
the second hydrogen abstraction in the propene oxidation pathway. Additionally, studies of hydrogen-acrolein coadsorption on Cu₂O(100) have shown that hydrogenation of an aldehydic (acrolein-like) species to an allyloxy does not occur [9]. Thus, the coincident desorption of allyl alcohol and acrolein demonstrate that an aldehydic (i.e., acrolein-like) intermediate is not responsible for the observed allyl alcohol or acrolein from propene on Cu₂O.

Adams and Jennings studied the oxidation of various deuterated propenes over Cu₂O [4]. They observed a kinetic isotope effect in the formation of acrolein from deuterated propenes, and concluded that removal of a hydrogen from a π-allyl occurs prior to insertion of an oxygen heteroatom. In their explanation of the kinetic isotope effect, Adams and Jennings assumed that the first step (hydrogen abstraction) in the formation of a σ-allyl from a π-allyl was rate-limiting. However, our results show clearly that the rate-limiting step is the first-order, unimolecular, dehydrogenation at the carbon α to the oxygen in a surface allyloxy species. Thus, we are in agreement with Adams and Jennings that the rate-limiting step is a hydrogen abstraction, however, we believe the rate-limiting hydrogen abstraction occurs on an allyloxy species and not during the initial attack on the π-allyl. This is supported by the formation of a stable allyloxy species at 300 K as detected in XPS and by the observed TDS products.

7.4.3 Role of Surface Oxygen in Propene Oxidation to Acrolein

The dissociative adsorption of propene was observed on the both oxygen and Cu-terminated (100) surfaces and the (111) surface, suggesting that propene dissociation at 300 K may be independent of the available surface sites.

The role of lattice versus adsorbed oxygen in the formation of acrolein on oxide surfaces is not well understood [118, 119]. Akimoto and co-workers studied propene oxidation over Cu₂O catalysts with ¹⁸O and propene and found that adsorbed oxygen was incorporated into acrolein, not lattice oxygen [118]. In contrast, Keulks studied propene oxidation with ¹⁸O over bismuth-molybdate catalysts, and suggested that lattice oxygen, not adsorbed oxygen, was incorporated into acrolein [119]. However, our results clearly demonstrate that lattice
oxygen is incorporated in all the oxidation products (selective and non-selective) observed under the conditions in our study. The presence of C2 oxygen-containing products from both the oxygen-terminated (100) and (111) surfaces demonstrates that oxygen insertion occurs with both two-coordinate and three-coordinate oxygen anions. However, the trace amounts of selective oxidation products from the Cu-terminated (100) surface compared with the (111) and oxygen-terminated (100) surfaces suggests that coordinately unsaturated lattice oxygen is necessary for selective oxidation product formation.

Hence, there is no clear correlation between the oxygen coordination number and the formation of selective oxidation products on Cu2O. However, it should be noted that oxygen coordination did effect the desorption temperatures of the products, indicating differences in the kinetic parameters with variations in the oxygen coordination numbers.

For the non-selective oxidation pathway, CO and CO2 production is via burnoff of surface carbon at high temperature from from the Cu-terminated (100) surface where all the oxygen is fully-coordinate (i.e. four-coordinate), subsurface, second-atomic-layer, lattice oxygen. Additionally, lower-temperature non-selective oxidation pathways are available in the presence of coordinately-unsaturated lattice oxygen on the (111) and oxygen-terminated (100) surfaces.

7.4.4 Reversibility of Oxidation Pathway

Propene production via a facile, low-temperature reaction is observed during allyl alcohol TDS [10], and during hydrogen-acrolein coadsorption experiments [9]. The low-temperature (160 K) pathway observed for this propene formation likely occurs because deoxygenation forms a resonance-stabilized allyl species. The formation of propene via a low temperature facile reaction through a π-allyl is consistent with previous studies of propene oxidation over Cu2O which have demonstrated that propene dissociates to form a symmetric, π-allyl species [4, 8] prior to oxygen insertion. Thus, our results suggest that the pathway from propene to a π-allyl species to an allyloxy species is reversible on Cu2O.

Imachi et al. suggest that no interconversion from a σ-allyl to a π-allyl takes place under
reaction conditions in propene oxidation over Cu$_2$O [116]. They base this conclusion on kinetic isotope results which suggests that the different allylic species are not in equilibrium. The lack of equilibrium between the $\pi$- and $\sigma$-allyls is consistent with our results and interpretation of the chemistry over Cu$_2$O. The stability of the allyloxy to temperatures of over 400 K, and the facile, low-temperature reaction to propene thought to be associated with a $\pi$-allyl suggests recombination of $\pi$-allyl to propene proceeds at a much faster rate under our conditions than the decomposition of allyloxy ($\sigma$-allyl), thus leading to kinetic, rather than equilibrium, control of the concentrations of $\pi$- and $\sigma$-allyls. The observation of propene from allyl alcohol [10] and from acrolein hydrogenation [9] provides evidence that the reaction pathway between $\pi$- and $\sigma$-allyls is reversible, if not at equilibrium. In related work over Cu$_2$O, Choi et al. [111] report unexplained oxygen scrambling from $^{18}$O-labeled allyl alcohol to give labeled and unlabeled acrolein product. We suggest that these observations are evidence for the reduction of $\sigma$-allyl with subsequent reoxidation, consistent with a reversible pathway for the conversion of $\pi$- to $\sigma$-allyl.

### 7.5 Conclusions

Propene oxidation was studied on Cu$_2$O single-crystal surfaces using XPS and TDS with propene exposures at atmospheric pressure and 300 K. Three different Cu$_2$O surfaces were studied: a Cu-terminated (100) surface, an oxygen-terminated (100) surface, and a (111) surface with accessible copper cations and lattice oxygen. Clear structure sensitivity to propene adsorption was observed by differences in the desorption temperatures of propene from each of the three surfaces studied. Propene dissociation appears to be independent of available surface sites on Cu$_2$O. However, the selective oxidation to acrolein requires coordinately-unsaturated surface lattice oxygen. No clear correlation between the formation of partial oxidation products and oxygen coordination was observed. Under the experimental conditions described here, both the selective and non-selective oxidation products were formed from lattice oxygen.
The propene oxidation pathway was shown to proceed through an allyloxy (CH$_2$=CHCH$_2$O-) species where oxygen insertion occurs prior to the second hydrogen abstraction over Cu$_2$O. This conclusion was reached by comparison of propene TDS results from atmospheric pressure exposures with UHV allyl alcohol and acrolein thermal desorption studies. The desorption of propene from either allyl alcohol or acrolein hydrogenation demonstrates that the formation of the oxygen-containing, $\sigma$-allyl (allyloxy) species is reversible on Cu$_2$O. The selective oxidation process over Cu$_2$O is subject to a “pressure gap” at 300 K (with oxygen insertion occurring at higher pressures), but can be effectively modeled by dissociative adsorption of oxygenates under UHV to simulate the oxygenated surface intermediates.
Chapter 8

Summary and Recommendations for Future Work

8.1 Summary

The partial oxidation of propene (CH$_2$=CHCH$_3$) to acrolein (CH$_2$=CHCHO) has been studied over Cu$_2$O(100) and (111) single crystal surfaces. Propene adsorption under ultrahigh vacuum conditions yields no significant oxidation products, but the propene desorption temperatures are sensitive to the structural differences in the surfaces.

Propene adsorption at atmospheric pressure followed by thermal desorption in ultrahigh vacuum demonstrates that propene may be activated at higher pressure. Over the Cu$_2$O(111) and O-terminated(100) surfaces, lattice oxygen insertion occurs at 300 K and 1 atm. with the formation of the $\sigma$-bonded allyl intermediate. Once formed, this specie is stable in ultrahigh vacuum and produces acrolein during TDS via a reaction-limited process. A comparison of these data with studies of allyl alcohol decomposition over Cu$_2$O surfaces indicate that the $\sigma$-bonded intermediate is surface allyloxy (CH$_2$=CHCH$_2$O-) which dehydrogenates to acrolein via hydride elimination on the carbon $\alpha$ to the oxygen. Thus, oxygen insertion precedes the final hydrogen abstraction in the partial oxidation pathway. Propene is also observed during allyl alcohol decomposition indicating that the transformation between the $\pi$-bonded and $\sigma$-bonded allyloxy intermediate during propene oxidation is reversible.

Both allyl alcohol and acrolein were observed as minor reaction products on the (100) and (111) surfaces following propene adsorption at room temperature and atmospheric pressure, thus allyl alcohol and acrolein decomposition was investigated on the (100) surface in order to gain further information on the propene oxidation pathway. Similar decomposition
products were observed between 200 and 550 K in both acrolein-hydrogen and allyl alcohol thermal desorption experiments, suggesting a similar surface intermediate. A surface enolate intermediate (CH$_2$CH=CHO$^-$) is consistent with the observed thermal desorption and photoemission results, and is thought to be a common intermediate species in acrolein, propionaldehyde, allyl alcohol, and 1-propanol decomposition. Thus, the chemistry of an adsorbed surface enolate intermediate explains the similar types of products (acrolein, propionaldehyde, propene) observed in similar temperature ranges (200 to 550 K) from both C$_3$ alcohols and aldehydes.

In addition to similarities in the reaction pathways leading to C$_3$ products, the decomposition of C$_3$ oxygenates (acids, alcohols, aldehydes) to non-selective oxidation products occurred via similar processes. For all molecules studied, an overall reduction of adsorbed surface oxygenate species was observed as the Cu$_2$O(100) surface was heated to higher temperature. Following reduction of surface oxygenates, subsequent dehydrogenation of hydrocarbon fragments to adsorbed carbon was observed. The subsequent reoxidation of the adsorbed carbon then gave the non-selective oxidation products.

8.2 Future Directions

The C$_3$ oxygenate thermal desorption and photoemission experiments should be repeated on the Cu$_2$O(111) surface. These experiments should give additional information on the effect of lattice oxygen on the reaction pathways for the aldehydes (acrolein, propionaldehyde), alcohols (allyl alcohol and 1-propanol), and acids (acrylic and propionic) on Cu$_2$O. Further, the oxygenate reactivity studies should be performed on both the stoichiometric (1x1) and oxygen-deficient ($\sqrt{3} \times \sqrt{3}$)R30° surface. The two different (111) surface conditions (i.e., stoichiometric and oxygen-deficient) may allow for the determination of adsorption sites as observed for propene adsorption on the (111) surface.

The use of IRAS (Infrared Reflection Absorption Spectroscopy) to study several of the proposed intermediates would strengthen their tentative identification. Specifically, the
surface enolate intermediate should be examined because of the central importance of this surface species to the reaction pathways for the C₃ alcohols and aldehydes on Cu₂O(100). It is suggested that acetone be considered as a test molecule for enolate formation because of its previous identification on MgO and NiO using IR [103]. The nature of the allylic species from propene adsorption on Cu₂O(100) and (111) in UHV conditions could also be probed using IR spectroscopy.

Additional study of the acid-base properties of Cu₂O surfaces could give further evidence that many oxide surfaces possess properties which give them both acidic and basic properties. The acid/base properties of oxides can be measured by comparing the relative amounts of dehydration and dehydrogenation products for alcohol decomposition. Other studies on metal oxide single crystal materials have postulated that metal cations act as acid sites and oxygen anions act as basic sites. However, results on the Cu₂O surface suggest that this model may be too simplistic. Thus, further investigation with ethanol, isopropanol, and butanol may give important insight into the acid-base properties of metal oxide surfaces.

Very similar reaction pathways are thought to be involved in propene oxidation to acrolein and propene ammoxidation to acrylonitrile. Acrolein is thought to play some role in the reaction pathway from propene to acrylonitrile, but the role is not well understood. Thus, a natural extension of propene oxidation to acrolein over Cu₂O is to perform similar studies with ammonia and propene over Cu₂O single crystals. The possible nitrogen containing surface intermediates in the ammoxidation pathway could be formed by using nitrogen containing compounds analogous to the oxygenate compounds used in the present study.
REFERENCES


[20] An ion gauge sensitivity of 3.3 was used for propene. This ion gauge sensitivity was calculated using a correlation by S. George for hydrocarbons and alkyl chlorides reported in Ref. [21].

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[22] An ion gauge sensitivity of 5.89 and 5.56 was used for propionic and acrylic acid, respectively. This ion gauge sensitivity was calculated using a correlation by S. George for hydrocarbons and alkyl chlorides reported in Ref. [21].

[23] An ion gauge sensitivity of 4.26 and 4.59 was used for acrolein and propionaldehyde, respectively. This ion gauge sensitivity was calculated using a correlation by S. George for hydrocarbons and alkyl chlorides reported in Ref. [21].

[24] An ion gauge sensitivity of 4.59 and 4.91 was used for allyl alcohol and 1-propanol, respectively. This ion gauge sensitivity was calculated using a correlation by S. George for hydrocarbons and alkyl chlorides reported in Ref. [21].


[46] Sensitivity factors of 5.3 and 0.61 were used for copper and oxygen respectively, and were obtained from Leybold Vacuum Products.


[49] Estimates of the expected XPS Cu/O ratios were calculated assuming (1) an exponential decay of signal intensity with distance for normal emission, (2) no diffraction effects, and (3) inelastic mean-free paths of 7.5 Å and 11.0 Å for copper (KE ≈ 320 eV) and oxygen photoelectrons (KE ≈ 720 eV), respectively (from "universal" curve, Ref. [50]).


[77] Studies of oxygenate adsorption on Cu$_2$O(100) have shown similar reaction products as those observed from Cu(110) surfaces.


[91] Thermal desorption studies of CO₂ have shown that all CO₂ desorbs below 300 K on the Cu₂O(100).


[105] Unpublished results.


[108] Unpublished results. Thermal desorption experiments have shown that all CO$_2$ desorbs below 309 K after adsorption at 100 K on the Cu$_2$O(100) surface.


VITA

Kirk Herman Schulz, son of Carl A. and Judith J. Schulz, was born on May 11, 1963, in Portsmouth, Virginia. Upon graduation from Norfolk Christian High School in June of 1981, he enrolled as a chemistry major at Old Dominion University, in Norfolk, Virginia. In 1984, after three years of study at O.D.U., he transferred to Virginia Polytechnic Institute and State University to pursue a B.S. degree in Chemical Engineering. After graduation from Virginia Tech in 1986, he started work on his Ph.D. degree in Chemical Engineering. After completion of his doctoral studies, he joined the faculty of the University of North Dakota as an Assistant Professor of Chemical Engineering.