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S.S.-B. Fu
(Ph.D. Thesis)

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Surface Science Studies of Catalyzed Methanol Synthesis on Model Copper and Cu-Zn-O Surfaces

Sabrina Su-Bin Fu
Ph.D. Thesis

Department of Chemistry
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

June 1991

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Surface Science Studies of Catalyzed Methanol Synthesis on Model Copper and Cu-Zn-O Surfaces

by

Sabrina Su-Bin Fu

Abstract

Cu-Zn-O surfaces that are catalysts for methanol synthesis from CO, CO$_2$, and H$_2$ are modeled using zinc oxide overlayers on copper single crystals. These studies were performed in ultra-high vacuum (UHV) utilizing Temperature Programmed Desorption, Auger Electron Spectroscopy, and Low Energy Electron Diffraction techniques.

The chemisorption of O$_2$, CO, CO$_2$, and D$_2$ were compared on a stepped Cu(311), and a flat Cu(110). At low pressures (~10$^{-6}$ Torr), Cu(311) was found to be much more reactive than Cu(110) for the dissociative adsorption of CO$_2$ and D$_2$, and the formation of CO$_2$ from surface oxygen and CO. Since these reactions are important in methanol synthesis, these results suggest that methanol synthesis over copper may be a structure sensitive reaction.

The interaction of copper, zinc, and oxygen were examined by the deposition of submonolayers to multilayers of zinc and oxygen in UHV on Cu(110). Carbon monoxide adsorbs well on copper at 150 K and low pressures (<10$^{-6}$ Torr), but only poorly on the oxides of copper and zinc. Carbon dioxide adsorbs on ZnO at 150 K and low pressures (<10$^{-6}$ Torr), but not on copper or oxidized copper. We used a combination of CO and CO$_2$ adsorption to follow the initial growth of two-dimensional ZnO$_x$ islands and the effects of heat and oxygen treatments on these islands. Heating above 300 K leads irreversibly to three-dimensional island
formation. In addition, the behavior of ZnO$_x$ overlayers on Cu(311) and a high defect concentration Cu(111) were compared to ZnO$_x$ overlayers on Cu(110).

The interaction of methanol with these model Cu-Zn-O surfaces was also studied. Oxygen was adsorbed onto the exposed copper part of the surface to form ZnO$_x$/y ML O/Cu(110) surfaces. The roles of ZnO$_x$ islands and chemisorbed oxygen on copper were investigated by monitoring methanol decomposition, into surface formate and methoxy species, on these ZnO$_x$/y ML O/Cu(110) surfaces. The role of chemisorbed oxygen on Cu(110) in the ZnO$_x$/y ML O/Cu(110) system is to keep the zinc oxidized and to increase the amount of formate formed on the ZnO$_x$ component of the surface. The presence of ZnO$_x$ increases the surface formate to methoxy ratio from that of O/Cu(110).
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that this thesis is dedicated to.

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To Philip:
You have shown me love
Beyond all that I have imagined

and

To my parents:
When I behold the sacred liao wo* my thoughts return
To those who begot me, raised me, and now are tired.
I would repay the bounty they have given me,
But it is as the sky: it can never be approached.

From Huston Smith's *The Religions of Man*

* A species of grass symbolizing parenthood
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6.13 Amount of methanol desorbed for each 2.0 L dose of methanol for a $\text{ZnO}_x/0.5\text{ ML} \text{ O}/\text{Cu}(110)$ surface and a 0.5 ML $\text{O}/\text{Cu}(110)$ surface as a function of the number of methanol TPD experiments.
Chapter 1
Introduction

Catalyzed methanol synthesis is performed predominantly over Cu-Zn-O catalysts from CO, CO₂, and H₂. The production of methanol from CO, CO₂, and H₂ is defined by the following three reactions:

\[
CO + 2H₂ \leftrightarrow CH₃OH \quad \Delta G^{°}_{500K} = 19 \text{ kJ/mole} \quad (1.1)
\]

\[
CO₂ + 3H₂ \leftrightarrow CH₃OH + H₂O \quad \Delta G^{°}_{500K} = 40 \text{ kJ/mole} \quad (1.2)
\]

\[
CO + H₂O \leftrightarrow CO₂ + H₂ \quad \Delta G^{°}_{500K} = -20 \text{ kJ/mole} \quad (1.3)
\]

Only two of these pathways are independent. Methanol may be produced from both CO₂ and H₂ or from CO and H₂, with the water-gas shift reaction \((CO + H₂O \leftrightarrow CO₂ + H₂)\) controlling the availability of each route. Hence, it is important to understand the water-gas-shift reaction in studying methanol synthesis from CO, CO₂, and H₂. We will see in chapter 3 that the water-gas shift can be observed on Cu(311) surfaces in vacuum, but not on Cu(110) surfaces.

Of the three reactions written above, the water-gas shift reaction is the most thermodynamically favorable at 500 K. Because of thermodynamic constraints, high pressure is used for methanol synthesis in order to obtain reasonable amounts of product. Above 500 K, methanol synthesis is even less thermodynamically favorable due to a negative \(\Delta S\). Hence, it is desirable to perform methanol synthesis at
low temperatures. To date, Cu-Zn-O based catalysts have been found to be the lowest temperature methanol synthesis catalysts with high activity and selectivity. Typically, these catalysts work at temperatures of 500-570 K at a CO:CO$_2$:H$_2$ ratio of 1:1:8, adding to a total pressure of 40-100 atm.

In their simplest form, industrial Cu-Zn-O based catalysts are produced from a mixture of copper, zinc, and aluminium nitrates by coprecipitation with sodium carbonate followed by filtration, washing, drying, and calcination of the purified precipitate. This produces a catalyst containing many different surface species with a surface area of approximately 30 m$^2$/g.

Numerous attempts have been made to characterize these catalysts. Some of the major findings are:

1. Cu$^+$ species in ZnO interstitial sites are the active centers for methanol synthesis. Methanol is made from CO and H$_2$, with CO$_2$ needed to stabilize Cu$^+$ centers in the ZnO lattice [1,2].

2. The more active catalysts have 30-60% of their copper surface area covered with oxygen after methanol synthesis reaction [3,4].

3. There is a direct correlation between the $\frac{CO_2}{CO}$ feed ratio and the amount of chemisorbed oxygen on the copper component after reaction [5].

4. The specific activity of Cu/ZnO catalysts are at least $10^3$ times greater than unsupported copper [6].

5. There is no correlation between copper surface area and methanol synthesis activity among various copper/metal oxide catalysts, and Cu-Zn-O catalysts have higher activity per copper surface area than copper catalysts supported on other oxides [7,8]. This suggests that there is a synergistic behavior between the copper and the zinc oxide.

6. Chinchen and co-workers found comparable activity per unit copper surface area for unsupported copper and copper supported on various oxides [5,9].
Pan and co-workers found a direct correlation between copper surface area and methanol synthesis rate for Cu/ZnO catalysts [10].

7. Formate is the intermediate for methanol synthesis from CO₂ and H₂ [4].

8. Isotope labelling of the carbon in CO₂ shows CO₂ as the carbon source for methanol [11,12].

These conflicting results in the literature may be due to different catalyst preparations. All of the various catalyst preparations produce high surface area catalysts containing a wide variety of active sites. In order to reduce the number of surface species, several investigators have modeled Cu-Zn-O synthesis catalysts using single crystal materials. Work on ZnO single crystals has shown that methanol decomposition is a structure sensitive reaction on ZnO [13], and by the principle of micro-reversibility, methanol synthesis is therefore structure sensitive on ZnO. Relevant reactions over various copper single crystals have been examined, but of particular interest are studies demonstrating the effect of oxygen upon methanol decomposition over Cu(110). Wachs and Madix have found that, for a given methanol exposure, surface formate and methoxy production is maximized when 0.2-0.3 monolayers (ML) of oxygen is chemisorbed on Cu(110) [14]. We will see in chapter 5 how this effect changes upon adding ZnOₓ islands to Cu(110) and oxygen covered Cu(110) surfaces.

In addition, a few three-component systems have been examined. Campbell and co-workers [15] have characterized the growth of copper deposited on ZnO(0001) by X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), and low energy electron diffraction (LEED). By decomposing a droplet of ZnO-saturated water solution, these same researchers formed ZnOₓ on Cu(111) which they analyzed by XPS before performing catalytic studies. Chan and Griffin [16] examined the decomposition of methanol over copper deposited on oriented ZnO thin films, and found the properties of Cu/ZnO to be primarily a superposition of the separate copper and zinc oxide components. Didziulis and co-workers [17] performed a detailed surface science study of copper overlayers on ZnO(0001), (0001), and (1010).
Heating in UHV resulted in loss of copper XPS intensity which they interpreted as being due to three-dimensional clustering of the copper. They also found that copper deposited on Zn\textsuperscript{2+} terminated ZnO(0001) surfaces is most easily oxidized.

Although a number of studies have been done on modelling Cu-Zn-O catalysts, no one has examined the interaction of submonolayers to multilayers of zinc with oxygen on copper single crystals. In this thesis, I have used copper single crystals and ZnO\textsubscript{x} overlayers on copper single crystals to model Cu-Zn-O methanol synthesis catalysts.

We will see in chapter 3 that Cu(311) surfaces are much more reactive than Cu(110) surfaces to the dissociative adsorption of CO\textsubscript{2} and D\textsubscript{2}, to the formation of CO\textsubscript{2} from CO plus surface oxygen, and to the water-gas shift reaction. In chapter 4, we will see how zinc oxide overlayers on Cu(110) can be formed and characterized by a combination of CO and CO\textsubscript{2} temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED). In chapter 5, we will compare the formation and decomposition of ZnO\textsubscript{x} islands on Cu(311), Cu(110), and a high defect concentration Cu(111). And finally, in chapter 6, we will use the most well-characterized of these surfaces – ZnO\textsubscript{x} on Cu(110) – as a model catalyst to examine the rôles of zinc oxide and chemisorbed oxygen on copper for methanol synthesis.
References


Chapter 2

Experimental Techniques and Apparatus

2.1 Surface Analysis Techniques

Overview

Many surface analysis techniques have been developed over the past 25 years. A summary of these techniques, classified according to the nature of the probe and the mode of detection is shown in table 2.1. Many of these experimental methods, including the techniques used in this thesis (Auger Electron Spectroscopy and Low Energy Electron Diffraction), involve the detection of electrons in the energy range of 20-1000 eV. This range of energies is selected for surface studies because the mean-free path of the electron is then only a few interatomic spacings (see figure 2.1). Thus, surface sensitivity is maximized.

In order to perform well controlled studies of any surface phenomenon, one must begin with well characterized surfaces. Hence, the use of single crystal substrates for the work described in this thesis. In addition, the environment in which the surface is studied must not change the nature of the surface during the course of the experiment. At an ambient pressure of $10^{-6}$ Torr, each second, a monolayer of unwanted material can form on the surface by adsorption of background gases (assuming a sticking probability of unity). Hence, all the experiments described in this thesis where performed under ultra-high vacuum (UHV) conditions; an ambient pressure of less than $10^{-9}$ Torr. In this well controlled environment, a surface can
Figure 2.1: The mean free path of electrons as a function of their kinetic energy.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Probe Particle</th>
<th>Detected Particle</th>
<th>Information Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-Violet Photoemission Spectroscopy (UPS)</td>
<td>electrons</td>
<td>electrons</td>
<td>valence band structure of first few atomic layers</td>
</tr>
<tr>
<td>X-Ray Photoemission Spectroscopy (XPS)</td>
<td>photons</td>
<td>electrons</td>
<td>oxidation state of top $\approx 20,\text{Å}$</td>
</tr>
<tr>
<td>Photoemission of Adsorbed Xenon (PAX)</td>
<td>electrons or photons</td>
<td>electrons</td>
<td>local work function</td>
</tr>
<tr>
<td>Inverse Photoemission (IPES)</td>
<td>electrons</td>
<td>photons</td>
<td>unoccupied electronic states</td>
</tr>
<tr>
<td>Work Function</td>
<td>electrons</td>
<td>electrons</td>
<td>work function</td>
</tr>
<tr>
<td>Surface-Sensitive Extended X-Ray Adsorption Fine Structure (SEAXAFS)</td>
<td>photons</td>
<td>electrons</td>
<td>local geometry of adsorbates</td>
</tr>
<tr>
<td>Reflection High Energy Electron Diffraction (RHEED)</td>
<td>electrons</td>
<td>electrons</td>
<td>surface morphology</td>
</tr>
<tr>
<td>Medium Energy Electron Diffraction (MEED)</td>
<td>electrons</td>
<td>electrons</td>
<td>structure of top 10-20Å</td>
</tr>
<tr>
<td>Low Energy Electron Diffraction (LEED)</td>
<td>electrons</td>
<td>electrons</td>
<td>structure of top 5-10Å</td>
</tr>
<tr>
<td>High, Medium, and Low Energy Ion Scattering (HEIS), (MEIS), and (LEIS)</td>
<td>ions</td>
<td>ions</td>
<td>structure of top few layers</td>
</tr>
<tr>
<td>Ion Scattering Spectroscopy (ISS)</td>
<td>ions</td>
<td>ions</td>
<td>composition of top-most layer</td>
</tr>
<tr>
<td>Surface Penning Ionization (SPI)</td>
<td>metastable helium</td>
<td>electrons</td>
<td>electronic structure</td>
</tr>
<tr>
<td>High-Resolution Electron Energy Loss Spectroscopy (HREELS)</td>
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<td></td>
<td>vibrational modes</td>
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<td>electrons</td>
<td>structure of ultra-thin films</td>
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<td>Scanning Electron Microscopy (SEM)</td>
<td>electrons</td>
<td>electrons</td>
<td>surface topography</td>
</tr>
<tr>
<td>Scanning Tunneling Microscopy (STM)</td>
<td>electrons</td>
<td>electrons</td>
<td>local electronic structure &amp; morphology</td>
</tr>
<tr>
<td>Atomic Force Microscopy (AFM)</td>
<td></td>
<td></td>
<td>sensitive to forces in the 1nm range</td>
</tr>
<tr>
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<td>ions</td>
<td>surface structure of top-most layer</td>
</tr>
<tr>
<td>Auger Electron Spectroscopy (AES)</td>
<td>electrons, photons, or atoms</td>
<td>electrons</td>
<td>composition of top 5-20Å</td>
</tr>
<tr>
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<td>ions</td>
<td>clusters</td>
<td>chemical state &amp; composition of first few atomic layers</td>
</tr>
<tr>
<td>Temperature Programmed Desorption (TPD)</td>
<td>molecules or atoms</td>
<td>molecules or atoms</td>
<td>binding energy, composition, and reactivity of top-most layer</td>
</tr>
</tbody>
</table>
be characterized without appreciable changes in surface composition during the course of the experiment.

The following sections will summarize the three surface analysis techniques employed in the experiments described in this thesis. These techniques are: Auger Electron Spectroscopy (AES), Temperature Programmed Desorption (TPD), and Low Energy Electron Diffraction (LEED). For a more comprehensive description of each of these techniques, the reader is referred to [1] for AES, [2-5] for TPD, and [6,7] for LEED.

Auger Electron Spectroscopy (AES)

Fundamentals

Auger electron spectroscopy is one of the most widely used methods of surface analysis. In this technique, the surface is excited by impact with electrons, photons, or atoms which have sufficiently high energies to eject core level electrons from atoms within the surface. The Auger process begins when the core hole is filled by the de-excitation of a valence electron; the excess energy being transferred to a second electron which is emitted from the surface. It is this electron, the Auger electron, which is detected. The kinetic energy of the Auger electron is characteristic of the element from which it was ejected because the energy of the Auger electron is dependent only upon the relative energy levels of the hole and the two electrons. Hence, when an electron in energy level $E_{v1}$ is de-excited to fill the core-hole in energy level $E_c$, an electron from energy level $E_{v2}$ is ejected with kinetic energy $E_c - E_{v1} - E_{v2}$. The Auger process is shown schematically in figure 2.2A.

Auger electrons have kinetic energies in the range of 20-1000 eV. Due to the limited mean free path of electrons in this energy range within solids (see figure 2.1), only those Auger electrons ejected from the first 15 monolayers or less are detected.

In addition to providing the elemental composition of the near-surface region, AES can also be used to distinguish the local electronic states, if the resolution of
the analyzer is sufficient. In this thesis work, the simplest of Auger electronics was used in which the energy of the electrons is selected with a retarding field. However, the reader is referred to reference [1] for a discussion of more complete AES analyses which can be performed with more sophisticated energy analyzers.

**Technique**

To obtain the AES spectra shown in this thesis, the surface atoms were ionized using a 2.0 KeV electron beam incident at about $70^\circ$ from the surface normal. The energies of the emitted Auger electrons were determined using a four-grid LEED optics as a retarding field analyzer [8]. The AES spectra were recorded in the derivative mode by modulating the retarding field voltage on the $2^{nd}$ and $3^{rd}$ LEED grids at 10 eV and 5000 Hz. The second harmonic of the modulated signal was detected with an Ortec Brookdeal precision lock-in amplifier. A schematic illustration of the AES experimental set-up is shown in figure 2.2B.

AES spectra may be plotted simply as intensity of the detected Auger electrons versus energy. But often, AES spectra are plotted as the derivative of the intensity with respect to the energy ($dN/dE$) versus energy, especially when a retarding field energy analyzer is used. By differentiating the AES peaks, it is easier to distinguish between the small Auger peaks from the rising background of secondary electrons in the low energy region. This approach also increases the signal to noise ratio, especially needed in the high energy region. Therefore, all AES spectra shown in this thesis were obtained in the derivative mode. Needham, Driscoll, and Rao [9] have shown that if the Auger peaks in the intensity ($N$) vs. kinetic energy plot are Gaussian, then the peak-to-peak height in the $dN/dE$ vs. kinetic energy plot is proportional to coverage. Thus, AES peak ratios were used to determine $\text{ZnO}_x$ coverage, after having used CO$_2$ TPD to determine the monolayer point of $\text{ZnO}_x$.

A typical Auger spectrum for clean Cu(110) and 2.0 ML $\text{ZnO}_x$ on Cu(110) are shown in figure 2.3A and 2.3B. Copper and zinc both have Auger peaks at around 60 eV, 100 eV, and the 700-900 eV region. Because zinc and copper differ in atomic number only by one, they have many of their Auger peaks overlapping.
Figure 2.2: (A) The Auger process. A valence electron, from energy level $E_{v1}$, is de-excited to fill a core-hole in energy level $E_c$, with the energy from the de-excitation used to eject an electron from energy level $E_{v2}$. This ejected electron leaves the surface with kinetic energy $E_c - E_{v1} - E_{v2}$. (B) A schematic of the Auger experimental set-up using a retarding field analyzer.
Figure 2.3: (A) Auger spectrum of clean Cu(110) and (B) 2.0 ML ZnOx on Cu(110).
The only non-overlapping peaks have energies >900 eV, and those are the least surface sensitive of the possible AES peaks. Thus, in order to determine the surface composition of the Cu-Zn-O systems studied in this thesis, it was crucial to employ a more surface sensitive probe in tandem with AES. That probe was temperature programmed desorption (TPD), and will be discussed in the next section.

**Calibrations**

The AES spectra obtained during the course of the experiments described in this thesis were compared to the standard spectra of elements in reference [10] in order to determine the elements present in the near surface region. In the case of Auger emission from atomic overlayers, an estimate of the coverage can be obtained from the Auger peak heights once sensitivity factors and probabilities for transitions are taken into account. However, to obtain a quantitative measure of the coverage, calibrations need to be made. A LEED pattern corresponding to a well-ordered p(2x1) surface structure was used to define 0.5 ML coverage of oxygen on Cu(110), as this surface structure is associated with half monolayer of oxygen on Cu(110) [11]. The resulting $O/\text{Cu}$ AES ratio was then used to define 0.5 ML oxygen on Cu(111) and Cu(311).

To obtain quantitative coverages of ZnO$_x$, CO$_2$ titration was used to determine the monolayer point on Cu(110), and related to AES peak ratios. These calibrated AES peak ratios of zinc, oxygen, and copper for ZnO$_x$/Cu(110) were then used for ZnO$_x$ overlayers on Cu(311) and Cu(111).

**Temperature Programmed Desorption (TPD)**

**Fundamentals**

In a temperature programmed desorption (TPD) or thermal desorption spectroscopy (TDS) experiment, the surface is held at a well defined temperature and exposed to a controlled amount of gas. After adsorption and/or reaction of the gas with the surface, the temperature of the surface is increased, causing desorption of molecules from the surface. These molecules are detected with the mass
spectrometer, which is held in front of the sample monitoring a single or several \( m \) ratios.

As adsorption on clean metal surfaces is generally a non-activated process, the desorption activation energy is approximately equal to the differential heat of adsorption. Hence, TPD is one of the simplest experimental methods available for obtaining a measure of the bond energy in adsorption. The relation between bond energy and the temperature of desorption depends upon three factors; the heating rate, the pre-exponential factor, and the desorption order.

The rate of desorption from a unit surface area may be written as

\[
N(t) = -\frac{d\sigma}{dt} = \nu_n \sigma^n \exp\left(-\frac{E}{RT}\right)
\]

where

\( n \) is the order of the desorption reaction,

\( \sigma \) is the surface coverage in molecules/cm\(^2\),

\( \nu \)=the rate constant for the particular desorption process,

and \( E \) the activation energy of desorption.

If we assume \( E \) is independent of \( \sigma \) and use a linear change of sample temperature \((T=T_0+\beta t)\), where \( \beta \) is the heating rate, then we can solve equation (2.1) for various desorption orders:

\[
\ln\left(\frac{d\sigma}{dT_p}\right) = \ln\left(\frac{\nu \sigma_o}{\beta}\right) - \frac{E}{RT_p}
\]

\( \text{zero order desorption) (2.2) } \)

\[
\ln\left(-\frac{E}{RT_p}\right) = \ln\left(\frac{c\nu}{2\beta}\right)\sqrt{\sigma_o} + \ln\left(\frac{T_p}{\sqrt{\sigma_o}}\right) - \frac{E}{RT_p}
\]

\( \text{half order desorption) (2.3) } \)

\[
\frac{E}{RT_p^2} = \left(\frac{\nu}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right)
\]

\( \text{first order desorption) (2.4) } \)

\[
\frac{E}{RT_p^2} = \left(\frac{\sigma_o \nu}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right)
\]

\( \text{second order desorption) (2.5) } \)
where

\[ T_p = \text{the temperature at peak rate of desorption}, \]
\[ \sigma_p \] is the coverage at the temperature of peak desorption,
\[ \sigma_0 \] is the initial coverage,

and \( c \) is a constant.

The desorption order can be determined by fitting the observed desorption spectra to the equations for zero, half, first, and second order desorption. Once the order is known, the binding energy can be determined. For example, if we plot \( \frac{1}{T_p} \) vs \( \ln(\frac{d\sigma}{dT_p}) \) and obtain a straight line, the desorption is zero-order with the slope of the line equal to \( \frac{E}{RT} \). We will see an example of this in chapter 4.

In addition to determining coverage and bond energies, TPD can also be used to determine the reactivity of the surface. For example, by exposing oxygen-covered copper surfaces to a known amount of CO, we can determine if the reaction \( \text{CO} + \text{O}_{(\text{surface})} \rightarrow \text{CO}_2 \) can occur on copper surfaces under our experimental conditions by monitoring for \( \text{CO}_2 \) with the mass spectrometer. The reactivity of surface oxygen can be confirmed by AES (and for certain surfaces, by LEED) after TPD experiments. Hence, by a combination of TPD, LEED, and AES, we can determine the reactivity and changes which occur on the surface under various conditions, as we have a mass balance of what has left the surface and what remains behind.

This thesis uses TPD to determine the reactivity of the surface, the surface bond energies, and the coverage of the surface. More detailed information on the kinetics and interaction of surface species can be obtained from TPD, as described in references [2] through [5].

**Techniques**

In order to minimize the background contribution to the measured TPD spectra from molecules desorbed from the manipulator parts, the 0.8 cm\(^2\) sample was placed 2 mm in front of the 1 cm\(^2\) mass spectrometer orifice. The mass spectrometer had a
Figure 2.4: CO desorption from Cu(311) surfaces covered with various amounts of oxygen. Each surface was exposed to enough CO (20 L) to produce saturation coverages. As in all TPD spectra presented in this thesis, each TPD curve is offset for better viewing.
stainless steel shield surrounding this orifice, which shielded the spectrometer from molecules desorbed from the manipulator parts.

For the TPD experiments described in this thesis, all gases were dosed with the sample in front of the mass spectrometer, and the exposures reported were not corrected for ion gauge sensitivities. After the desired gas exposure, Cu(110) and Cu(111) crystals were heated at a linear rate of 30 K/s and Cu(311) was heated at 10 K/s. All of the TPD spectra shown in this thesis have been referenced to a common scale (in arbitrary units), with the multiplication factor given either on the graph or in the figure caption. When no multiplication factors are reported, the scale is that of the reference scale.

An illustration of some TPD spectra are shown in figure 2.4. From this plot of temperature versus CO desorption rate for various oxygen coverages on Cu(311), one can see that oxygen blocks the CO adsorption site whose desorption peak is centered at 203 K. In addition, information such as activation energy of desorption and surface coverage can be obtained from such plots, as was discussed above.

Calibrations

The mass spectrometer's sensitivity was monitored prior to each day of TPD experiments by measuring the intensity of the \( \frac{m}{e} = 28 \) peak when \( 1 \times 10^{-8} \) Torr of CO was admitted into the UHV chamber. This signal fluctuated as much as 50% over the two year period during which the experiments described in this thesis were performed. Quantitative comparisons of the amount of desorbed gases were made only after accounting for the changes for mass spectrometer sensitivity.

As was mentioned earlier, one advantage that TPD has over AES is its superior surface sensitivity. Since most molecules and atoms are adsorbed directly upon the surface and usually cannot penetrate the top-most atomic layer, TPD is inherently more surface sensitive than AES. Furthermore, it has been shown that if the pumping speed is fast enough (so that readsorption is negligible), the mass spectrometer signal is proportional to ambient pressure [2], and hence to the surface coverage prior to desorption. Thus, once a calibration is made to relate the number of molecules to
a particular area under TPD spectra (with known mass spectrometer conditions), the number of molecules desorbed can be determined. For the work described in this thesis, this calibration was done by determining the area under the CO desorption peak obtained from a CO overlayer on Cu(110), which, prior to desorption displayed a p(2×1) surface structure. Since this surface structure is associated with a 0.5ML coverage of CO on Cu(110) [12], the mass spectrometer could be calibrated by assuming that the area under the CO desorption peak corresponded to \(4.4 \times 10^{14}\) molecules of CO; half of the number of copper surface atoms on the 0.8 cm\(^2\) Cu(110) crystal. To obtain the number of CO\(_2\) molecules per unit area, the relative mass spectrometer sensitivity for CO and CO\(_2\) was determined using equal fluxes of both gases. The relative sensitivity of the mass spectrometer varied from 1.0 to 1.5 over the two year period of these experiments, and the variations have been accounted for in each set of experiments when the area under CO\(_2\) TPD spectra was converted to molecules of CO\(_2\).

**Low Energy Electron Diffraction (LEED)**

In low energy electron diffraction (LEED), electrons with kinetic energies between 20 to 300 eV are directed at a surface and the diffracted electrons observed with a fluorescent screen. A schematic diagram of a LEED experiment is shown in figure 2.5. Diffraction occurs because of the wave-like nature of electrons as postulated by deBroglie [13]. Electrons with kinetic energy \(E\) have a deBroglie wavelength: 

\[
\lambda(\text{Å}) = \frac{h}{p} = \frac{1594}{\sqrt{E(\text{eV})}}.
\]

Thus electrons with kinetic energies of 20 to 300 eV have wavelengths of 1-3 Å; a value which is comparable to interatomic distances within solids. Therefore electron diffraction is anticipated. If the atoms are in an ordered array, such as in a crystalline solid, then constructive interference implies that the electrons are reflected from the surface within discreet Bragg beams, which, when observed on a fluorescent screen, appear as diffraction spots. The diffraction patterns for Cu(110), Cu(311), and Cu(111) are shown in figure 2.6, along with their real space lattice. These diffraction patterns are reciprocal space mappings of the real space lattice parallel to the surface. Hence, LEED can be used
Figure 2.5: Schematic diagram of a low energy electron diffraction (LEED) experiment from an idealized two-dimensional crystal lattice.
Figure 2.6: LEED patterns of Cu(110) (at 151 eV), Cu(311) (at 100 eV), and Cu(111) (at 118 eV) used in this thesis, along with their idealized real space schematics.
to characterize the long range order of the surface. This is predominantly the mode in which LEED has been used in this work.

If an ordered overlayer is deposited onto the single crystal, the LEED diffraction pattern of the new unit cell, in reciprocal space, can be seen on the fluorescent screen. The 2D lattice formed by the overlayer atoms and molecules is superimposed on the substrate unit cell in reciprocal space. These patterns reveal the shape, and size of the overlayer unit cells with respect to the reference cell. However, the diffraction pattern cannot be used to determine the nature of the atoms/molecules within the surface unit cell; in particular, the adsorption site or number of molecules contained within the overlayer unit cell are usually inaccessible from the LEED pattern alone.

Much more complete structural information can be obtained from LEED by analysis of spot intensities as a function of energy; so called IV spectra. These IV spectra can be interpreted within the framework of multiple scattering theory to determine bond lengths and angles in the near-surface region, both parallel and perpendicular to the surface. For further details of the use of LEED as a complete structural tool, the reader is referred to [6,7]. Although no such analysis was performed in the work described in this thesis, we have compared IV spectra to determine if two different surfaces which produce the same diffraction pattern have the same surface structure. We employed LEED in this “fingerprint” mode to determine if the ordered (1x1) pattern is due to the ZnOx overlayer or the copper substrate.

2.2 Apparatus

The experiments described in this thesis were performed in a stainless-steel ultra-high vacuum (UHV) chamber operating at a base pressure less than $2 \times 10^{-10}$ Torr, pumped with a Varian ion pump at 500 liters/sec. The residual background gases consisted of water, carbon monoxide, methane, helium, hydrogen, and argon, (usually in that order of abundance) adding to a total pressure of $2 \times 10^{-10}$ Torr or less.
The chamber was equipped with the following:

An off-axis Varian manipulator
A retarding field analyzer (RFA) for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES)
A glancing incidence electron gun for AES mounted 70° from surface normal
A normal incidence electron gun for LEED
An ion gun for argon sputtering
A zinc source for zinc deposition
Leak valves
A UTI-100C quadrupole mass spectrometer for residual gas analysis and temperature programmed desorption (TPD)
A Pfeiffer TSU 170 turbomolecular pump (50 liters/sec) with roughening pump DUO 1.5A, used during argon sputtering
A pumping well consisting of a Varian ion pump and titanium sublimation pump

A schematic diagram of the chamber is shown in figure 2.7.

Everything mounted on the UHV chamber was obtained commercially except the zinc source which was designed specifically for the experiments described in this thesis. The zinc source consisted of 99.999% pure zinc wires (Aldrich) enclosed in a ceramic effusive source, built by Robert Wright of the LBL technical staff. This effusive source was mounted in a stainless steel casing equipped with bellows and a shutter. In addition, the zinc source was equipped with water cooling capabilities and chromel-alumel thermocouples to monitor the temperature of the zinc. A schematic diagram of the zinc source is shown in figure 2.8.

The zinc source requires three hours to equilibrate as indicated by a plateau in the temperature versus time and zinc signal (as measured by the mass spectrometer) versus time graphs. Typically, a current of 3.9 amps is used to heat the zinc. With this current, the thermocouples glued to the back of the inner ceramic indicate 110°C. This produces a monolayer of zinc oxide every 120 seconds when dosed in an ambient of \( \geq 1 \times 10^{-7} \) Torr \( O_2 \).
Figure 2.7: Schematic of the surface analysis chamber used for this thesis.
Figure 2.8: Diagram of the zinc source.
2.3 Experimental Procedure

Preparation of Single Crystals

The single crystals used for the experiments described in this thesis were obtained from three different sources:

1. One of the Cu(110) crystals was cut by Wini Heppler of the LBL technical staff.

2. Two of the Cu(110) crystals used were purchased from a commercial source (Monocrystals).

3. The Cu(311) and Cu(111) single crystals were obtained from the Université Libre de Bruxelles, Chimie Analytique, through Marie-Paule Delplancke.

All the crystals were 99.999% pure, and cut using standard metallurgical techniques. Four 21 mil (one thousandth of an inch) holes at the edge and one 10 mil hole on the bottom of the 0.8 cm² disks were spark-eroded (see sample mounting section). The single crystals were then polished, beginning with 20 micron Al₂O₃, and finishing mechanically with 0.3 micron α-alumina. The copper single crystals were then electropolished in a phosphoric acid bath by the application of a +1.8 eV potential between the crystal and the cathode. After electropolishing, the crystal was rinsed with 10% phosphoric acid in water solution, followed by high purity ethanol and acetone rinses, ending by drying with a heat gun. One must be careful to wash off all the phosphoric acid before placing the single crystal in vacuum. Sonicating the copper single crystal in ethanol destroys its surface order. Hence, careful washing in ethanol and acetone with a squirt bottle was used.

Once the copper single crystals were electropolished, they were mounted using 20 mil platinum wires, and 5 mil chromel-alumel thermocouples were attached to the 10 mil hole on the bottom of the crystal. This produced even heating in UHV as seen by a uniform glow across the crystal when it was heated to 790 K and above.

The copper single crystals were cleaned in UHV by argon bombardment in 5×10⁻⁵ Torr of argon with an ion gun voltage of 500 eV and emission current
of 20 mA. This produced a current of 10 μA between the crystal and the ground. The different single crystals contained various amounts of impurities, which segregated to the surface upon heating due to their endothermic heats of segregation. The main contaminants were carbon and sulfur, and the extent of sputtering needed to remove all bulk impurities from the crystal varied from 5 hours to 50 hours, depending on the source of the crystal. The temperature was cycled from 300 K to 910 K during sputtering. The crystals were then annealed in vacuum. The final annealing conditions for Cu(111) and Cu(110) crystals were 910 K for 15 minutes, and for the Cu(311) crystals, at 770 K for 60 minutes.

Sample Mounting and Manipulator

Each copper single crystal was mounted onto the manipulator by spark eroding four 21 mil holes at the edge of the crystal and one 10 mil hole on the bottom of the crystal before polishing. After mechanical and electropolishing the crystal, 20 mil platinum wires were physically attached to the copper through the holes as shown in figure 2.9. The 20 mil platinum supports are attached by screws onto copper blocks, which then are accessible to liquid nitrogen cooling and resistive heating through copper braids attached to the copper blocks of the cold fingers. The 10 mil hole on the bottom is used to attach the thermocouples to the copper crystal. The mounting of the crystal to the manipulator is also shown in figure 2.9. With this set-up, the temperature of the crystal could be brought down to 150 K routinely. For the experiments using a Cu(111) substrate, thicker copper braids were installed between the cold fingers and the copper blocks which enabled us to achieve a sample temperature of 130 K routinely.

Reagents

The reagents used in this thesis are given in table 2.2. All gases except the 18O enriched isotopes were obtained from metal gas cylinders. The 18O enriched gases were obtained in break-seal glass flasks which were fitted with o-ring-sealed, teflon stopcocks. Cajon ultra-torr fittings were used for glass to metal connection to the
Figure 2.9: Sample mounting and manipulator.
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<tr>
<td>CO</td>
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<td>O₂</td>
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<tr>
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<td>99% \textsuperscript{18}O enriched</td>
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<tr>
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<td>Aldrich</td>
<td>99.9%</td>
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</tr>
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stainless steel gas manifold.

All reagents were used as received except for methanol. The methanol was stored in a glass vial fitted with a teflon stopcock, and was taken through several freeze-pump-thaw cycles before use to remove gases trapped within the vial.

**Gas Dosing**

The manifold was pumped with sorption pumps to less than $10^{-3}$ Torr, and flushed several times with the gas to be used to avoid contaminants. Gases were admitted to the chamber through four variable leak valves, and gas purity was checked by mass spectroscopy before and after each set of experiments.

All gas exposures are reported in Langmuirs (L), 1.0 L being an exposure of $1 \times 10^{-6}$ Torr gas for one second. The reported exposures are not corrected for different ion gauge sensitivities of the gases. However, the ion gauge sensitivity was taken into account when the relative sensitivity of the mass spectrometer to CO and CO$_2$ was determined.

**General Experimental Procedure**

A typical experimental procedure was as follows: Once the copper crystal was cleaned and sample cleanness is checked by AES and its structure by LEED, various overlayers were deposited and characterized by AES and LEED. The sample was then cooled to 150 K (or 130 K for Cu(111)), positioned 2 mm in front of the mass spectrometer, dosed with a known amount of gas, and then the sample temperature was ramped linearly at 30 K/sec (or 10 K/sec for the Cu(311) crystals) with the mass spectrometer tuned to a particular mass. AES spectra were obtained between TPD experiments to correlate surface composition to the CO and CO$_2$ TPD spectra. For the methanol decomposition studies, methanol TPD experiments began after characterizing each surface by AES, LEED, CO and CO$_2$ TPD, with further characterization between methanol TPD experiments. After examining each Cu-Zn-O sample by various surface analysis techniques, the crystal temperature was
ramped to \( \sim 1100 \text{ K} \) while monitoring zinc, oxygen, copper, or carbon dioxide to further characterize these surfaces.

For TPD of CO, CO\(_2\), H\(_2\), D\(_2\), \(^{18}\)O\(_2\), H\(_2\)\(^{18}\)O, CH\(_2\)O, and H\(_2\)O, the respective parent \( \frac{m}{e} \) fragment was followed. For O\(_2\), the parent fragment of \( \frac{m}{e} = 32 \) was used except in the presence of zinc, as the signal from Zn\(^{2+}\) interferes with the O\(_2\) parent signal. Thus, when zinc was also present, \( \frac{m}{e} = 16 \) was used to monitor O\(_2\) signal. The \( \frac{m}{e} \) ratio of 63 (Cu\(^+\)) was used to follow copper, and the \( \frac{m}{e} \) ratio of 64 (Zn\(^+\)) was used to follow zinc. For CH\(_3\)OH, \( \frac{m}{e} = 31 \) (CH\(_3\)O\(^-\)) was followed as it is 50% greater in signal than \( \frac{m}{e} = 32 \).

Chemisorption studies on pure Zn were performed by depositing multilayers of the pure metal onto Cu(110). The term multilayers used throughout this thesis means that enough material was deposited so that the substrate AES peaks could not be detected. Chemisorption studies on submonolayers to multilayers of ZnO\(_y\) deposited on gold foils were performed to discern the relative rôle of copper compared to that of a more inert metal.

To determine the chemisorption properties of oxidized copper, a Cu\(_x\)O surface was prepared by oxidizing a copper foil in 190 mTorr of O\(_2\) at 470 K for 30 minutes. This Cu\(_x\)O surface appears to be mainly Cu\(_2\)O as shown by the lack of satellite peaks in the copper 2p XPS spectrum (analysis done by air transfer to a PHI 5300 system).

The contribution from background desorption (from the Pt supports, etc.) of CO, Zn, and CO\(_2\) was examined using a gold foil. For CO TPD using 2.0 L CO exposure, no contribution from background desorption was found. For Zn TPD, up to 2.0 ML zinc produced no contribution from the background. For CO\(_2\) TPD using 4.0 L CO\(_2\) exposure, the background contributed \( \sim 1\% \) of the CO\(_2\) TPD signal obtained from a freshly prepared 1.0 ML ZnO\(_x\) overlayer on Cu(110).
References


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Chapter 3

Interactions of O₂, CO, CO₂, and D₂ with the Stepped Cu(311) Crystal Face: Comparison to Cu(110)

3.1 Introduction

Cu-Zn-O catalysts are important methanol synthesis catalysts which produce over thirteen million tons of methanol each year from CO, CO₂, and H₂. Hence, it is not surprising that understanding the rôles the surface plays in catalyzing this reaction is of great interest [1,2]. In spite of the large number of works published on both the working Cu-Zn-O catalysts and model methanol synthesis catalysts, little work has been done on the structure sensitivity of methanol synthesis catalysts [3,4], or on the importance of copper surface structure in methanol synthesis.

A number of studies on Cu/metal oxide catalysts have suggested a direct correlation between methanol production and copper surface area [5-7]. However, other studies have shown that there is no correlation between activity and copper surface area [8,9]. This, along with the fact that Cu/metal oxides prepared differently do not give the same methanol activity per copper surface area (compare reference [7] to reference [9]), suggests methanol synthesis may be structure sensitive. In this chapter, we compare two copper surfaces – Cu(311) and Cu(110) – by examining their interaction with the reactant gases of methanol synthesis (CO, CO₂ and H₂.
(D₂)), and the effect pre-adsorbed oxygen has on their interactions. We concentrate on the pure copper component for we have seen that zinc oxide islands on Cu(110) and Cu(311) do not alter the binding of CO or CO₂ to the copper component [10,11]. We will show that Cu(311) is much more reactive to CO₂ and D₂ dissociative adsorption, and to the formation of CO₂ by the reaction

\[ \text{CO} + \text{O}_{\text{surface}} \leftrightarrow \text{CO}_2, \]

which is important under methanol synthesis reaction conditions. These chemisorption studies suggest that methanol synthesis over copper may be a structure sensitive reaction.

### 3.2 Results

**Interaction of Oxygen with Cu(311) and Cu(110)**

Oxygen dissociative chemisorption on Cu(311) produced streaks in the [233] direction from 0.1 ML to 0.2 ML oxygen. At 0.3 ML oxygen, half-order spots begin to appear in this direction for the LEED pattern, corresponding to a p(2×1) surface structure by 0.4-0.5 ML oxygen. This p(2×1) pattern is accompanied by a diffuse background at ≥0.4 ML oxygen. A coverage of >0.6 ML oxygen was achieved by dosing the Cu(311) surface with 6,000 L O₂. This high coverage produced no visible diffraction pattern.

Half-order spots also form on Cu(110) with oxygen chemisorption, but the diffraction pattern is much sharper than on Cu(311). Patches of a p(2×1) surface structure begin at 0.2 ML oxygen and becomes a well-ordered, sharp pattern by 0.5 ML oxygen. At oxygen coverages greater than 0.5 ML, extra spots in addition to the half order spots appear, forming a LEED pattern corresponding to a real-space p(2×1)+c(6X2) pattern [12].

Adsorption of oxygen onto Cu(311) appears to produce two types of oxygen, one which remains on the surface up to 1000 K, and one which desorbs as molecular oxygen in a broad peak, beginning at 180 K, as shown in figure 3.1A. We have used oxygen gas which is 50% enriched in \(^{18}\)O in order to obtain clear results on
Figure 3.1: (A) Oxygen on Cu(311). A small amount of oxygen initially desorbs from Cu(311) after exposure to 2.0 L or greater of $^{18}$O$_2$. The oxygen remaining on the surface after the initial desorption does not desorb as $^{18}$O$_2$ until $>1000$ K. Some of the surface oxygen reacts with background hydrogen to form $\text{H}_2^{18}$O ($^\circ_{\text{H}}=20$). The amounts of oxygen lost from the surface due to water formation in the time scale of TPD experiments is not detectable by AES. (B) Oxygen on Cu(110). Unlike oxygen on Cu(311), oxygen on Cu(110) is very unreactive. Oxygen does not desorb from Cu(110) until $>1000$ K. Scale for these spectra are 100× the sensitivity of the reference scale (CO TPD spectra).
the origin of the oxygen for several reactions. There is no additional desorption of molecular oxygen after the initial desorption. However, there is a slight loss of surface oxygen due to reaction with background H₂ as shown in figure 3.1A. The loss of atomic oxygen from the surface due to water formation is extremely small and a background check showed no change in the AES oxygen signal during the time span of each set of TPD experiments. Notice that the H₂¹⁸O desorption occurs at different temperatures depending on the type of oxygen on the surface.

Although the sticking coefficient of oxygen on Cu(311) and Cu(110) are roughly the same at 150 K, ¹⁸O₂ adsorption on Cu(110) does not produce any ¹⁸O₂ desorption until >1000 K. Additionally, no ¹⁸O is lost by water formation with background H₂ as shown in figure 3.1B. Thus, oxygen on Cu(110) is less reactive than oxygen on Cu(311). We will see further evidence of this in the following sections.

Interaction of CO with Clean and Oxygen Covered Cu(311) and Cu(110)

Carbon monoxide TPD near and at saturation coverage on Cu(311) is shown in figure 3.2A. The low temperature adsorption site has a T_p (temperature at peak desorption) of 203 K at saturation coverage. But in addition to the low temperature adsorption site, is a high temperature adsorption site at ~430 K. We will see that this high temperature adsorption site is responsible for the formation of CO₂ from surface CO and chemisorbed oxygen on Cu(311).

The change in CO adsorption with 0.5 ML O/Cu(311) is also shown in figure 3.2A. There are two adsorption sites in the low temperature region and oxygen blocks only one of these adsorption sites. The high temperature peak at ~430 K is not seen because at these saturation doses of 20 L CO, there is a high rising background due to desorption from the manipulator parts that hides the high temperature CO peak. At lower CO doses, we see that the high temperature CO peak at ~430 K remains unchanged with pre-adsorbed oxygen.

Saturation coverage of CO produces a similar CO TPD spectrum on Cu(110) as on Cu(311) (with T_p=218 K instead of T_p=203 K), but an order in magnitude
Figure 3.2: (A) The main CO peak from Cu(311) has $T_p=203$ K at saturation coverage. Adsorption at 303 K shows that the broad high temperature peak at $\sim 430$ K remains at this adsorption temperature. The monotonic rise in CO signal from TPD experiments at 150 K and 20 L CO is due to desorption from the manipulator parts which hides the small CO peak from Cu(311) centered at $\sim 430$ K. Saturation coverages of CO at 150 K on 0.5 ML O/Cu(311) shows that oxygen decreases the saturation coverage of CO by blocking one type of site. (B) CO TPD from Cu(110). Saturation dose (2.0 L) produces a desorption peak with $T_p=218$ K. Oxygen blocks CO adsorption more effectively on Cu(110) than on Cu(311).
less CO exposure is needed to reach saturation coverage on Cu(110) at 150 K. This is shown in figure 3.2B. Half monolayer of pre-adsorbed oxygen blocks more CO adsorption on Cu(110) than on Cu(311).

In addition to observing changes in CO adsorption as a function of temperature and oxygen coverage, we monitored for reaction products between CO and oxygen with the use of O₂ gas 50% enriched in ¹⁸O. Figure 3.3 shows the results of dosing 20 L CO onto Cu(311) pre-adsorbed with various amounts of 50% ¹⁸O and monitoring for CO¹⁸O. A few points are to be noted from this figure:

1. The same amount of CO¹⁸O (2×10¹² CO¹⁸O molecules/cm² of Cu(311), which means twice as much carbon dioxide was produced as only half of the oxygen are ¹⁸O) is produced with oxygen coverages ranging from 0.15 ML to 0.4 ML at 150 K.

2. No change for CO¹⁸O production is observed when the dosing temperature is changed from 150 K to 300 K.

3. CO dosed at 370 K produced less CO¹⁸O than at 300 K.

4. Cu(311) covered with 0.3 ML of 50% ¹⁸O in a background less than 2×10⁻¹⁰ Torr CO for 12 hours (less than 10 L CO) produced almost four times as much CO¹⁸O as a dose of 1×10⁻⁷ Torr CO for 200 seconds (20 L).

On the same figure, we show that ¹⁸O/Cu(110) does not react with CO to form CO¹⁸O. We checked background formation of CO¹⁸O by dosing a clean Cu(311) surface with 20 L CO, and found no CO¹⁸O formation.

The overnight dose of background CO was done with all filaments in the vacuum chamber off. The reason for this is the observation that CO¹⁸O formation can be accelerated by an electron beam. The electron beam used for LEED has no detectable effect on the time scale of <5 minutes exposure, but the 2.0 KeV electron beam used for AES does produce CO¹⁸O from background CO plus surface ¹⁸O. Hence, the crystal was flashed to 700 K after each exposure to the Auger electron beam. This brings us to the possibility that the whole CO¹⁸O formation is stimulated by
Figure 3.3: Reaction of CO with surface $^{18}$O to form CO$^{18}$O. CO was dosed at $1 \times 10^{-7}$ Torr for 200 seconds for the 20 L dose. The same amount of CO$^{18}$O was produced between oxygen coverages of 0.15 ML and 0.4 ML with a 20 L dose of CO. Adsorption of CO at 300 K instead of 150 K did not change the amount of CO$^{18}$O produced, but changing the CO adsorption temperature to 370 K did decrease the amount of CO$^{18}$O produced. Exposing a 0.3 ML $O/Cu(311)$ surface with background CO for 12 hours (<10 L CO), with all filaments off, produced almost four times the quantity of CO$^{18}$O than with a 20 L dose of CO given over 200 seconds. In comparison, Cu(110) does not form carbon dioxide from CO and surface oxygen under these low pressures and temperatures. Y-axis scale is $10^x$ the reference scale.
the one filament it is necessary to turn on – the mass spectrometer filament. Two checks were make concerning this possibility: 1) The O/Cu(311) sample was held at a -90 eV bias during the TPD experiment and this was shown to have no effect on the amount of CO$^{18}$O produced. 2) A Cu(311) covered with 0.3 ML 50% $^{18}$O was left in the chamber with about 2x$10^{-10}$ Torr CO and all filaments turned off in the chamber for 28 hours (20 L). This process produced greater than an order in magnitude amount of CO$^{18}$O (4x$10^{13}$ molecules/cm$^2$ of Cu(311)) as dosing a 0.3 ML 50% $^{18}$O on Cu(311) with 20 L of CO in a 200-second period. These experiments show that although the formation of carbon dioxide can be accelerated by an electron beam, the process does occur in the absence of an electron beam.

The fact that dosing 20 L of CO in a 200-second period produces an order in magnitude less CO$_2$ from the same surface than dosing the 20 L over a 28 hour time period, suggests that the reaction of CO plus surface oxygen is activated. The fact that less CO$_2$ is produced when Cu(311) is exposed to CO at 370 K instead of 300 K suggests a surface reaction rather than an Eley-Rideal reaction.

The consumption of surface oxygen can be observed by AES and LEED. Continually dosing the surface with 20 L of CO followed by desorption of CO$^{18}$O shows a slow decline in the oxygen AES signal and loss of the half-order spots in the LEED pattern. But the most dramatic change is seen when the sample is left overnight: a diffuse p(2×1) pattern is observed from O/Cu(311) the night before with a specific oxygen AES signal, and the next morning, the AES spectrum looks the same but the half-order spots in the LEED pattern are gone. Desorption indicates CO$^{18}$O formation, and AES after desorption shows a large loss in oxygen signal.

If a 0.3 ML O/Cu(311) surface is left in the UHV chamber with the ion guage filament on for 20 hours, the sample produces both H$_2$O and CO$_2$, leaving the Cu(311) surface oxygen free after desorption of these molecules. We have a calibration for CO$_2$, but not for H$_2$O. Assuming H$_2$O has about the same mass spectrometer sensitivity as CO$_2$, we determined that 1.0x$10^{14}$ molecules of CO$_2$ and 1.0x$10^{14}$ molecules H$_2$O desorbed from the surface. As we assume that the CO$_2$ we detect is from background CO plus surface oxygen and the H$_2$O is from background hy-
drogen plus surface oxygen, we conclude that $2.0 \times 10^{14}$ atoms of oxygen existed on the surface prior to reaction. We had started out with 0.3 ML oxygen (AES calibration) on a 0.8 cm$^2$ Cu(311) - $2.2 \times 10^{14}$ oxygen atoms. Hence, the calibrations for quantitative analysis by Auger and mass spectrometry appear to be consistent.

**Interaction of CO$_2$ with Clean and Oxygen Covered Cu(311) and Cu(110)**

Carbon dioxide TPD spectra from clean Cu(311) and Cu(110) are shown in figure 3.4. Cu(110) surfaces do not adsorb CO$_2$, while Cu(311) surfaces do adsorb CO$_2$ at 150 K and $<10^{-7}$ Torr pressure. The CO$_2$ desorption from Cu(311) consists of a low temperature peak, and a very broad high temperature peak. The low temperature peak, centered at $\sim$200 K, appears first at low coverages of CO$_2$, followed by the broad high temperature peak. The low temperature state appears to be a precursor for the high temperature states as no CO$_2$ adsorption could be detected at an adsorption temperature of 300 K.

In addition to CO$_2$ adsorption on Cu(311) and Cu(110), we investigated CO$_2$ adsorption on oxygen covered Cu(311) and Cu(110). This is shown in figure 3.5. Pre-adsorbed oxygen does not change CO$_2$ interaction with Cu(110); there is no CO$_2$ desorption with oxygen modified Cu(110). Pre-adsorbed oxygen on Cu(311) increases the CO$_2$ population on the higher energy adsorption sites.

We had seen, in the previous section, that CO reacts with surface oxygen to produce CO$_2$. We investigated the reverse reaction of CO$_2$ dissociation by use of C$^{18}$O$_2$ and found that a small amount (approximately $6 \times 10^{12}$ molecules/cm$^2$) of carbon dioxide does dissociate to form carbon monoxide for a 4.0 L dose of C$^{18}$O$_2$. (We stayed at low C$^{18}$O$_2$ exposures to avoid ion pump dissociation of C$^{18}$O$_2$.) This is shown in figure 3.6. The amount of oxygen from this dissociation process cannot be detected by AES until $>3 \times 10^{13}$ molecules CO$_2$/cm$^2$ has dissociated on clean Cu(311). No $^{18}$O$_2$ was detected, but approximately $\leq 1 \times 10^{11}$ H$^2$O molecules/cm$^2$ could be detected during each TPD experiment. This is due to the reaction C$^{18}$O$_2$+H$_2$(background) $\rightarrow$C$^{18}$O+H$_2$O, the water-gas shift reaction. In con-
Figure 3.4: CO$_2$ desorption from Cu(311) and Cu(110). Cu(110) does not adsorb CO$_2$ at these low temperatures and pressures. On the other hand, Cu(311) does adsorb CO$_2$. The low energy CO$_2$ site fills first, and then the high energy sites. The low energy state appears to be a precursor for the high energy states as no CO$_2$ adsorption was detected at an adsorption temperature of 300 K. Notice that the peak due to CO$^{18}$O formation from CO and $^{18}$O$_{\text{surface}}$ lies within the broad high temperature CO$_2$ peak. Y-axis scale is 10× the reference scale.
Figure 3.5: Effect of oxygen on $^{18}$O$_2$ desorption from Cu(311) and Cu(110). Pre-adsorbed oxygen does not change CO$_2$ interaction with Cu(110). Pre-adsorbed oxygen on Cu(311) increases the CO$_2$ population of the higher energy binding states. Y-axis scale is $10 \times$ the reference scale.
Figure 3.6: Decomposition of $^{18}$O$_2$ on Cu(311) and Cu(110). On Cu(311), $^{18}$O$_2$ decomposes to form $^{18}$O and surface oxygen. The oxygen produced from this reaction is not detectable by AES until >20 L $^{18}$O$_2$ exposure. Up to 0.4 ML oxygen does not alter the dissociative probability of $^{18}$O$_2$ on Cu(311). The ability to dissociate carbon dioxide at these low pressures and temperatures have not been seen on Cu(110) or oxygen modified Cu(110). Y-axis scale is $10\times$ the reference scale.
trast to Cu(311), on Cu(110) and oxygen modified Cu(110), carbon dioxide does not dissociate to carbon monoxide and oxygen.

One may argue that the $^{18}\text{O}$ detected is due to impurities in the $^{18}\text{O}_2$ gas. This was checked as follows: $1\times10^{-8}$ Torr $^{18}\text{O}_2$ and a 2.0 KeV electron beam were simultaneously exposed to $^{16}\text{O}$ covered Cu(311) surfaces for 10 minutes. Then the crystal was ramped and $^{16}\text{O}^{18}\text{O}$ ($m=46$) monitored. No signal was detected. If there was $\geq1\%$ $^{18}\text{O}$ impurities in the $^{18}\text{O}_2$, we would have detected a signal for $^{16}\text{O}^{18}\text{O}$ formation under those conditions. Hence, we are confident that the decomposition of carbon dioxide occurs as well as the formation of carbon dioxide on oxygen covered Cu(311) surfaces.

**Interaction of D$_2$ with Clean and Oxygen Covered Cu(311) and Cu(110)**

Figure 3.7 shows that D$_2$ does adsorb on Cu(311) at low pressures and 150 K. Pre-adsorbed oxygen enhances the ability of Cu(311) to adsorb D$_2$. In contrast, we see that D$_2$ does not interact with Cu(110) or oxygen modified Cu(110) at $<10^{-7}$ Torr and 150 K. This is in agreement with studies which have shown that H$_2$ dissociation on low Miller index copper surfaces and O/Cu(110) is an activated process [13-15], while H$_2$ dissociation on Cu(311) is spontaneous [16].

**Some Co-Adsorption Studies**

Some co-adsorption studies of CO and D$_2$, and CO$_2$ and D$_2$ were performed on Cu(311). All co-adsorption studies were performed at a total pressure of $1\times10^{-7}$ Torr, with 50% of each gas, uncorrected for different ion guage sensitivities. On clean Cu(311), CO blocks D$_2$ adsorption almost to 100%, and to a lesser extent on 0.4 ML O/Cu(311).

The co-adsorption of $^{18}\text{O}_2$ and D$_2$ on Cu(311) produced adsorption similar to the absence of each other. Hence, the adsorption sites for $^{18}\text{O}_2$ and D$_2$ on Cu(311) appear to be independent of each other.
D$_2$ desorption rate (arb. units)

Figure 3.7: D$_2$ does adsorb on Cu(311), and the amount of adsorption increases with 0.4 ML O/Cu(311). In contrast, D$_2$ does not adsorb on either Cu(110) or oxygen modified Cu(110). Y-axis scale is 10x the reference scale.
3.3 Discussion

We have shown that Cu(311) is much more reactive toward CO-CO$_2$ exchange than Cu(110), and Cu(311) faces adsorb CO$_2$ and D$_2$ at low pressures (<10$^{-6}$ Torr) while Cu(110) does not interact with either CO$_2$ or D$_2$ under low pressures and temperatures of <10$^{-6}$ Torr and 150 K. We choose Cu(311) because our earlier work on copper foil [17] led us to believe that atomic steps may play an important rôle by interacting with CO$_2$, and Cu(311) has one of the highest step densities available, and is an open surface.

The greater reactivity of O/Cu(311), compared to oxygen chemisorbed on low Miller index copper faces, to H$_2$ and CO have been shown by Arlow and Woodruff [18] at higher pressures. They examined a cylindrical single crystal which contained the three low Miller index faces, the (311) face, and vicinal faces, all pre-adsorbed with 0.5 ML oxygen. This O/Cu cylindrical single crystal was then rotated in 10$^{-6}$-10$^{-4}$ Torr of CO or H$_2$. The rate of oxygen consumption was monitored by AES. They showed that oxygen disappeared two to five times faster from the (311) and (311)/(100) (orientation between (311) and (100)) and (311)/(111) faces than from the low Miller index faces. Hence, this structure sensitivity for CO-CO$_2$ exchange at higher pressures of 10$^{-6}$-10$^{-4}$ Torr is consistent with our UHV studies.

In addition to showing that CO$_2$ forms from CO and surface oxygen on Cu(311) at low pressures and temperatures, we showed that the reverse reaction of CO$_2$ dissociation also occurs on Cu(311). This is important because CO-CO$_2$ exchange is believed to be part of the mechanism for methanol synthesis over Cu-Zn-O catalysts [19,20] and the ability for this exchange may be important in determining the activity and selectivity of methanol synthesis.

The importance of copper structure in methanol synthesis under industrial conditions could explain the discrepancy in the catalytic literature between various copper/metal oxide catalysts, as has been suggested by Burch and Chappell [9]. It would be interesting to determine the effect of stepped copper sites on the activity of methanol synthesis by comparing the methanol synthesis activity of Cu(110) crystals to those of Cu(311) crystals.
Dissociation of \( \text{CO}_2 \) and \( \text{H}_2 \) are important steps in methanol synthesis. The ability for \( \text{CO}-\text{CO}_2 \) exchange can also be a significant step as the competing reaction of the water-gas shift reaction \( (\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2) \) occurs under industrial conditions. As we have shown that \( \text{Cu}(311) \) is much more reactive for these processes than \( \text{Cu}(110) \), methanol synthesis from \( \text{CO}, \text{CO}_2, \text{and} \text{H}_2 \) is likely a structure sensitive reaction.

3.4 Conclusion

We have compared the reactivity of \( \text{Cu}(110) \) and \( \text{Cu}(311) \) to the reactant gases of methanol synthesis (\( \text{CO}, \text{CO}_2, \text{and} \text{D}_2 (\text{H}_2) \)) in UHV. It is shown that important differences exist between the two surfaces: (1) \( \text{CO}_2 \) and \( \text{D}_2 \) chemisorb on \( \text{Cu}(311) \) and oxygen modified \( \text{Cu}(311) \), but not on \( \text{Cu}(110) \) or \( \text{O/Cu}(110) \). (2) The forward and reverse reaction of \( \text{CO} + \text{O}_{(\text{surface})} \leftrightarrow \text{CO}_2 \) can be seen on \( \text{Cu}(311) \), but not on \( \text{Cu}(110) \).
References


11. S.S. Fu and G.A. Somorjai, to be published.


17. S.S. Fu and G.A. Somorjai, unpublished work.


Chapter 4

Surface Studies of Zinc Oxide Growth on Cu(110)

4.1 Introduction

In the previous chapter, we examined, in vacuum, the different reactivities of Cu(311) and Cu(110) to the reactant gases of methanol synthesis – CO, CO₂, and H₂ (D₂). We now examine Cu-Zn-O interaction on the Cu(110) face.

Since Cu-Zn-O species are important as methanol synthesis catalysts, it is not surprising that several studies on the interaction of copper, zinc, and oxygen have been published [1-6], although none on the growth and characterization of submonolayers to multilayers of zinc and oxygen on copper single crystals. Campbell and co-workers [3] deposited copper on ZnO(0001) and characterized its growth by XPS, ISS, and LEED. These same researchers formed ZnOₓ on Cu(111) by depositing in air, a droplet of ZnO-saturated water solution and then analyzed the resulting surface by XPS before catalytic studies. Chan and Griffin [5] examined the decomposition of methanol over copper deposited on oriented ZnO thin films, and found the properties of Cu/ZnO to be primarily a superposition of the separate copper and zinc oxide components. Didziulis and co-workers [6] performed a detailed surface science study of copper overlayers on ZnO(0001), (0001), and (1010). Heating in UHV resulted in loss of copper XPS intensity which they interpreted as being due to three-dimensional clustering of the copper. They also found that copper deposited on Zn²⁺ terminated ZnO(0001) surfaces are most easily oxidized.
In this chapter we present the results of our studies on the growth and chemical properties of the system formed when zinc vapor and oxygen are deposited onto copper single crystal surfaces of (110) orientation. The probes we used are AES, LEED, chemisorption of CO and CO₂, and Zn TPD. Carbon monoxide has been known to adsorb mainly on the copper part of reduced Cu-Zn-O catalysts [7], and this was confirmed by our studies of CO adsorption on Cu(110), half a monolayer of oxygen on Cu(110) (henceforth denoted 0.5 ML O/Cu(110)), Zn, and ZnOₓ. Carbon dioxide, on the other hand, adsorbs only on ZnO [8] and not on clean Cu(110) [9], or O/Cu(110), or Zn at 150 K. By using selective CO and CO₂ adsorption to determine surface composition in Cu-Zn-O systems, we found rapid clustering of the initial two-dimensional ZnOₓ islands above 300 K.

4.2 Experimental

In addition to the experimental chapter, a few experimental notes for this particular chapter are given below.

A typical experimental procedure is as follows: The copper single crystal is cleaned by cycles of sputtering with 5×10⁻⁵ Torr argon at 300 K and 910 K, and then annealed at 950 K for fifteen minutes. Sample cleanness is then checked by AES and its structure by LEED. Once the sample is cleaned, the desired amount of zinc and oxygen are deposited. Unless otherwise noted, all zinc depositions reported in this chapter are done in an ambient of 1×10⁻⁷ Torr O₂. Only zinc, oxygen, and copper could be detected by AES after zinc and oxygen depositions onto the copper. After producing the desired amount of ZnOₓ, TPD experiments begin. The sample is cooled to 150 K, an AES spectrum is taken, the sample is positioned 2 mm in front of the mass spectrometer, dosed with a known amount of gas, and then the sample temperature is ramped linearly at 30 K/s with the mass spectrometer tuned to a particular mass. AES spectra were obtained after each TPD experiment to correlate composition to CO and CO₂ TPD spectra. After characterizing each surface by AES, LEED, CO and CO₂ TPD, the sample temperature was ramped to ~1100 K while monitoring zinc, oxygen, or copper to further characterize these
surfaces.

All CO and CO₂ TPD data presented in this chapter were obtained from saturation coverages after dosing 2.0 L of CO and 3.0 L of CO₂ (without correction for ion gauge sensitivity). All TPD data in this chapter were collected using a 30 K/s linear ramp, and by monitoring \( m_e = 44 \) for CO₂ and \( m_e = 28 \) for CO.

For zinc TPD, \( m_e = 64 \), corresponding to the most abundant zinc isotope, was used. Mass 63 was monitored to determine copper desorption. There is no natural isotope of zinc at this mass. For oxygen desorption, \( m_e = 16 \) was used since there is contribution from zinc to \( m_e = 32 \) signal but not to \( m_e = 16 \) signal as determined by TPD of pure zinc from Cu(110).

4.3 Results

There are several difficulties in forming and studying zinc oxide overlayers on copper. We can see some of these difficulties when we examine and compare the interactions of the various two-component systems. For example, oxygen is readily dissociated onto Cu(110) at room temperature [10] and can dissolve into the bulk of copper [11]. In our laboratory, we have observed both the dissolution and segregation of oxygen on Cu(110). Not only does oxygen readily dissolve into copper, but so does zinc. Hence, we have the possibility of both zinc and oxygen dissolved in copper. Zinc can be oxidized in the presence of O₂, but the dissociation of oxygen on zinc is a slow process relative to the dissociation of oxygen on Cu(110). In addition, the oxidation of zinc occurs via three-dimensional zinc oxide island formation surrounded by elemental zinc [12,13]. Figure 4.1 shows schematically the different possibilities for zinc oxide growth on Cu(110).

Although figure 4.1 creates a very complicated picture of the Cu-Zn-O system, we will see that by combining several surface sensitive probes, we can understand what occurs upon deposition of zinc and oxygen onto Cu(110) and the effects that heat and further oxygen treatment has on these surfaces. In order to comprehend the three-component system of copper, zinc, and oxygen, an understanding of simpler one and two-component systems must be known. The first two subsections are
Figure 4.1: Schematic drawing of some of the species possible in Cu-Zn-O interaction on Cu(110).
Table 4.1
CO and CO$_2$ Desorption from Various Surfaces
(Adsorption at 150K)

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>CO $T_p$</th>
<th>CO $\theta_{sat.}$</th>
<th>CO$_2$ $T_p$</th>
<th>CO$<em>2$ $\theta</em>{sat.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(110)</td>
<td>218K</td>
<td>0.5ML</td>
<td>no ads.</td>
<td>—</td>
</tr>
<tr>
<td>0.5ML O/Cu(110)</td>
<td>222K &amp; 180K</td>
<td>&lt;0.05ML</td>
<td>no ads.</td>
<td>—</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>222K &amp; 180K</td>
<td>&lt;0.03ML</td>
<td>no ads.</td>
<td>—</td>
</tr>
<tr>
<td>Zn</td>
<td>no ads.</td>
<td>—</td>
<td>no ads.</td>
<td>—</td>
</tr>
<tr>
<td>ZnO$_y$</td>
<td>203K</td>
<td>&lt;0.05ML</td>
<td>340K &amp; 175K</td>
<td>0.2ML</td>
</tr>
</tbody>
</table>

a. Each surface prepared as described in the experimental section.
b. $T_p$=temperature at peak desorption and $\theta_{sat.}$=saturation coverage where $\theta=1$ is defined as $1.1 \times 10^{15}$ molecules/cm$^2$ corresponding to the number of copper atoms on the Cu(110) surface.
devoted to present the results of several one and two component systems.

**CO and CO₂ Chemisorption Properties on Cu, O/Cu, CuₓO, Zn, and ZnO**

Table 4.1 summarizes the chemisorption properties of CO and CO₂ on Cu(110), 0.5 ML O/Cu(110) (0.5 ML O/Cu is defined by a sharp LEED pattern corresponding to a well-ordered p(2×1) surface structure [10]), oxidized copper, zinc, and zinc oxide. On Cu(110), CO adsorbs readily at 150 K giving a narrow desorption peak at Tₚ=218 K, with a saturation coverage of 0.5 ML CO. Carbon dioxide, on the other hand, does not adsorb on Cu(110) at 150 K [9]. Exposing Cu(110) to oxygen decreases its CO adsorption capacity [14]. Molecular oxygen does not desorb below 1000 K. With 0.5 ML O/Cu(110), the saturated CO adsorption has decreased to <10% of that on clean Cu(110). Carbon dioxide does not adsorb onto the oxygen covered Cu(110) surface.

In addition to O/Cu(110), we examined CO and CO₂ chemisorption on a CuₓO surface, prepared by bulk oxidation of a copper foil. This surface behaves similarly to that of 0.5 ML O/Cu(110); it adsorbs <0.05 ML CO and does not adsorb detectable amounts of CO₂ at 150 K.

We examined CO and CO₂ adsorption on multilayers of zinc deposited onto both gold foil and Cu(110). In both cases, we observed no detectable adsorption of CO or CO₂ on zinc.

Finally, we examined the CO and CO₂ TPD spectra of ZnO₇ on gold substrates. Saturated CO adsorption by multilayers of ZnO₇ is less than 0.05 ML with a desorption peak centered at ~200 K. In contrast, CO₂ adsorption is readily observed and reaches saturation at about 2.5×10¹⁴ molecules/cm² (see experimental section for determination). This corresponds to a CO₂ coverage of θ≈0.23 (θ=1 is defined as 1.1×10¹⁵ molecules/cm²). The CO₂ desorption peak from submonolayers to multilayers of ZnO₇ on gold is always centered at 340 K and 175 K, even after annealing to 1170 K. This indicates that ZnO₇ overlayers on gold substrates are stable even
after exposure to such elevated temperatures.

**LEED patterns**

Oxygen on Cu(110) forms a sharp LEED pattern corresponding to a well-ordered p(2×1) surface structure at 0.5 ML oxygen [10]. But various domains of a p(2×1) pattern can be seen above a coverage of 0.2 ML oxygen. No new LEED pattern could be seen upon the deposition of ZnOₓ onto Cu(110). By comparing I-V curves of (1×1) and p(2×1) surface structures, with and without ZnOₓ on the surface, we can show that all LEED patterns are due to long range order of either Cu(110) or O/Cu(110), and are not due to the ZnOₓ overlayer.

**Preparation and Thermal Stability of Oxidized Zinc Layers on Cu(110)**

The oxidation state of zinc layers on copper depends upon the oxygen content of the surface. AES shows a peak at 988 eV (Zn LVV) for all surfaces independent of the oxygen treatment condition (temperature and exposure) except for zinc on clean copper, in which case the LVV transition occurs at 992 eV. (note: Although we cannot resolve the 988 eV and 992 eV peaks, we can detect the 4 eV shift.) The shift in the LVV zinc transition is indicative of the oxidation of zinc, but is not a good indicator of the stoichiometry of the oxide. From the oxygen AES peak alone, we cannot distinguish between the oxygen associated with copper and that associated with zinc.

The stability of the zinc layers as a function of oxidation extent was studied by TPD and the results are shown in figure 4.2. Zinc was adsorbed at 300 K under four different conditions; 1) on clean Cu(110), 2) on 0.5 ML oxygen preadsorbed on Cu(110), 3) in an ambient of 1×10⁻⁷ Torr O₂, and 4) same as (3) with additional oxidation in 5×10⁻⁷ Torr O₂ for 20 minutes at 300 K. Zinc desorbs from the surface in the range of 700-1100 K, depending on oxidation treatments. It is interesting to note that the two highest zinc desorption peaks from ZnOₓ/Cu(110) occur at about the same temperature as two of the zinc desorption peaks from ZnO(0001)
Figure 4.2: Desorption of 0.1 ML zinc adsorbed on Cu(110) under various oxidation conditions. All zinc and oxygen depositions were done at 300 K. Similar results are obtained for zinc and oxygen depositions at 150 K. AES shows a peak at 988 eV for all these surfaces except for zinc on clean copper (i), which has its LVV transition at 992 eV. No zinc could be detected by AES after each TPD ending at 1100 K. As reference, zinc desorption from multilayers of pure zinc and zinc desorption from ZnO(0001) [15] are shown. The zinc desorption from ZnO(0001) [15] is not on the same scale as the rest of the data. TPD spectra are 100× the reference scale.
surfaces [15]. No zinc could be detected by AES after each of our zinc TPD experiment. Only oxygen was left on the copper surface as detected by AES, except where pure zinc was deposited on clean Cu(110) (figure 4.2(i)).

Although the vast majority of zinc has desorbed by 1000 K, oxygen and copper desorption from these Cu-Zn-O surfaces are not detected below 1000 K. Both the copper and oxygen signal continues to rise from 1000 K to 1100 K, where the TPD experiments end. Only when the temperature of the crystal approaches the melting point of copper does oxygen desorb. This indicates that the species on these Cu-Zn-O surfaces decompose by desorption of Zn(g) atoms, leaving oxygen adsorbed on the copper surface and also absorbed into the bulk of copper. The absorption of oxygen into copper is clearly observed when >2 ML ZnOx is heated to 1000 K. No O2 desorption is detected by the mass spectrometer (and virtually no H2O) and yet the AES oxygen signal decreases considerably (always down to ~0.6 ML oxygen) after heating the surface to 1000 K.

In addition to examining the thermal stability of ZnOx overlayers on Cu(110), we calculated the desorption energy for ZnOx, as represented by peak d of figure 4.2. The Tp of peak d of figure 4.2 increases with increasing ZnOx surface coverage. This is indicative of zero and half order desorption processes. Hence, zinc desorption from ZnOx, as represented by peak d of figure 4.2, was analyzed using a zero order and half order analysis, as described in chapter 2. From that discussion, the equations for zero and half order desorptions are:

\[
\ln\left(\frac{\text{d}n}{\text{d}p}\right) = \ln\left(\frac{\text{d}n}{\text{d}A}\right) - \frac{E}{RT_p}\ 
\text{(zero order)}
\]

and

\[
\ln\left(\frac{E}{RT_p}\right) = \ln\left(\frac{\text{d}n}{\text{d}A}\right)\sigma_p^{1/2} + \ln\left(\frac{T_p}{\sigma_p}\right) - \frac{E}{RT_p}
\text{(half order)}.
\]

where

- \(T_p\) the temperature at peak rate of desorption,
- \(\sigma_p\) is the coverage at the temperature of peak desorption,
- \(\sigma_0\) is the initial coverage,
\( \nu = \text{the rate constant for the particular desorption process,} \)

\( c \) is a constant,

and \( E \) is the desorption energy.

A plot of \( \ln \left( \frac{dP}{dT_p} \right) \) vs \( \frac{1}{T_p} \) and \( \ln \left( \frac{\sigma_P}{o_p} \right) \) vs. \( \frac{1}{T_p} \) shows that the desorption of zinc from ZnO\(_x\) overlayers on Cu(110) is best described as a half order process. This is shown in figure 4.3. The slope of the plot of \( \ln \left( \frac{\sigma_P}{o_p} \right) \) vs. \( \frac{1}{T_p} \) is equal to \( \frac{E}{RT} \), giving a value of 150 kJ/mole for the desorption energy of zinc from ZnO\(_x\) on Cu(110).

**Initial two-dimensional growth of ZnO\(_x\) and the effect of heat**

Oxygen produces a sharp p(2\( \times \)1) structure on Cu(110) after an exposure of \( \geq 10 \) L O\(_2\) corresponding to a coverage of half monolayer. For exposures between 10 L and \( > 300 \) L O\(_2\) at 150-300 K, the AES spectrum and LEED pattern do not change. In contrast, even a 3000 L O\(_2\) exposure at 300 K is not sufficient to form a uniform ZnO surface from Zn(0001) surfaces [12]. Since oxygen is much more readily dissociated on Cu(110) than on zinc, we began all our preparations of ZnO\(_x\) overlayers with 0.5 ML O/Cu(110).

In figure 4.4(i), we plot AES signal intensities of copper, zinc, and oxygen versus zinc deposition time. Zinc was dosed in an ambient of \( 1 \times 10^{-7} \) Torr O\(_2\) onto a 0.5 ML O/Cu(110) (p(2\( \times \)1)) surface at 150 K (the need for low temperatures will become clear later). The p(2\( \times \)1) surface structure disappears after 10 minutes deposition time. From the plot of AES intensities versus deposition time, it is hard to determine the monolayer completion point. A better determination is by CO\(_2\) adsorption on each freshly prepared ZnO\(_x\) surface. This is shown in figure 4.4(ii). A plot of the amount of CO\(_2\) at saturation adsorption versus deposition time indicates the ZnO\(_x\) monolayer is completed after 20 minutes deposition time. The attenuation of the copper signal from its clean value is 25%, which is approximately the expected reduction for 918 eV electrons going through one monolayer.
Figure 4.3: Zero and half order desorption analyses of zinc desorption, as represented by peak d of figure 4.2, from ZnOx on Cu(110). Half order analysis shows the best fit. The slope of the plot of ln(T_p/T_d) versus 1/T is equal to E/RT, giving a value of E=150 kJ/mole for the desorption energy of zinc from ZnOx overlayers on Cu(110).
Figure 4.4: (i) AES intensities of Cu, Zn, and O peaks vs. zinc deposition time. Zinc was dosed in $1 \times 10^{-7}$ Torr O$_2$ at 150 K. Arrow points to copper AES intensity from clean Cu(110). By depositing 0.5 ML oxygen onto Cu(110), the copper 918 eV AES signal attenuates by 10%. (ii) Accompanying saturation CO$_2$ adsorption for each coverage in (i). From the CO$_2$ adsorption versus zinc and oxygen deposition time, monolayer completion occurs after 20 minutes deposition time. Each surface is prepared fresh from 0.5 ML O/Cu(110).
Carbon monoxide and carbon dioxide TPD spectra from freshly prepared 1.0 ML ZnO_x surfaces are shown in figure 4.5(i). These surfaces adsorb less than 10% of the amount of CO that can adsorb on clean Cu(110) surfaces (and has CO desorption peak at T_p=190 K rather than T_p=218 K), and adsorbs $6.3 \times 10^{13}$ CO_2 molecules/cm^2. This indicates that at saturation $\theta \sim 0.06$ for CO_2 adsorption. A value of $\theta \sim 0.1$ was found for the saturation coverage of CO_2 adsorption on ZnO(0001) surfaces [16]. The most strongly bound CO_2 molecules on these two-dimensional ZnO_x islands desorb at T_p=510 K, 170 K higher than CO_2 from ZnO_y overlayers on gold.

This initial ZnO_x overlayer on Cu(110) undergoes very drastic changes after heating to 700 K. The new surface obtained after cooling to 150 K does not adsorb CO_2, and CO adsorption is restored to 100% of clean Cu(110) capacity with the same temperature at peak desorption (T_p=218 K) as CO from Cu(110). This is shown in figure 4.5(ii). At this point, LEED shows a diffuse (1×1) pattern. AES shows only a 20% loss in zinc and oxygen intensities after the heat treatment.

The effect of heat upon 1.0 ML ZnO_x overlayers can be seen by performing the following experiment; dose 2.0 L CO onto a freshly prepared 1.0 ML ZnO_x/Cu(110) surface, observe the CO desorption from the surface to >250 K, cool the surface back down, and titrate with CO all over again, each time increasing the temperature at which the TPD experiment ends. This is shown in figure 4.6. The ability of the surface to adsorb CO increases as the surface is exposed to higher temperatures.

For a more detailed study of the effect of temperature upon the two-dimensional ZnO_x overlayers on Cu(110), the following experiments were performed: We deposited zinc and oxygen at 150 K, and increased the temperature of the crystal to a particular value. We then examined first the CO and CO_2 adsorption capacity of the surface, and finally, we examined the zinc desorption spectrum. Each experiment required the preparation of a fresh surface, since above 300 K, the initial ZnO_x overlayer changes. A plot of the area of CO and CO_2 desorption peaks versus the annealing temperature is shown in figure 4.7. The ability of ZnO_x overlayers to adsorb CO_2 decreases by 350 K, and the ability to adsorb CO begins to increase,
Figure 4.5: (i) CO and CO₂ TPD from a freshly prepared surface of 1.0 ML ZnOₓ on Cu(110). (ii) After the first TPD; saturation CO adsorption is now 100% of that from clean Cu(110), and the surface no longer adsorbs CO₂. The third, the fourth, the fifth, etc. TPD spectrum are all exactly like (ii). The CO₂ spectra are offset from the CO spectra for clearer viewing. There is no visible order by LEED for the freshly prepared surfaces. After the first TPD, LEED shows a diffuse (1×1) pattern.
Figure 4.6: The effect of heat on the amount of CO adsorbed on 1.0 ML ZnO$_x$/Cu(110). The sample was prepared at 150 K. Each TPD experiment consisted of a 2.0 L dose of CO at 150 K, with each consecutive CO TPD experiment ending at a higher temperature.
Figure 4.7: CO and CO₂ adsorption capacity vs. annealing temperature of the ZnOₓ overlayer on Cu(110). Each experiment requires the preparation of a fresh surface, since above 300 K, the ZnOₓ/Cu(110) surface changes.
slowly first at 350 K, and then rapidly above 500 K. Both these changes, along with no detectable desorption of zinc from the surface for temperatures \( \leq 700 \) K point to either clustering of the ZnO\(_x\) overlayer into three-dimensional islands or diffusion of ZnO\(_x\) into the copper single crystal.

If ZnO\(_x\) dissolved into the subsurface region of copper, further annealing at 670 K would dissolve more of the ZnO\(_x\) into the bulk of copper, and hence, less zinc would be detected during zinc TPD. Figure 4.8 shows the resulting zinc TPD from a) 0.8 ML ZnO\(_x\), and b)-c) same as (a) but with the addition of annealing at 670 K for 5 minutes (b) and 10 minutes (c). In all three cases, the amount of zinc desorbed remains the same within a 10\% experimental error. This could only be true if the ZnO\(_x\) overlayer formed three-dimensional islands since increased ZnO\(_x\) dissolution into copper would result in smaller amounts of zinc desorption after annealing treatments. AES indicates that there may be further clustering of the ZnO\(_x\) islands as there is a 30-40\% loss in zinc AES intensity after 5 minutes of annealing at 670 K. There is no difference by AES between the 5 minutes and 10 minutes annealing treatments.

We have seen from zinc TPD and CO chemisorption that upon heating to 700 K, the initial two-dimensional ZnO\(_x\) overlayer clusters to form three-dimensional ZnO\(_x\) islands. We believe that these ZnO\(_x\) islands are oxygen deficient due to the inability of these islands to adsorb CO\(_2\). The detection limit of CO\(_2\) by our mass spectrometer is about \( 2 \times 10^{11} \) molecules which is about \( \left( \frac{1}{300} \right)^{th} \) of the CO\(_2\) adsorption capacity on the initial two-dimensional ZnO\(_x\) overlayer. Within this detection limit, we do not observe any CO\(_2\) adsorption after annealing the initial surface (prepared at 150 K) to \( \geq 600 \) K for a fraction of a second. This inability of ZnO\(_x\) islands to adsorb CO\(_2\) may be due to a slight loss of oxygen during the clustering process. Cheng and Kung [17] have noted that reduced ZnO single crystals of (10\( \overline{1} \)0) orientation do not adsorb CO\(_2\). If it is true that these ZnO\(_x\) islands are unable to adsorb CO\(_2\) because they are oxygen deficient, then adding oxygen should restore their CO\(_2\) adsorption capability. We will see in the next section that this is indeed so.
Figure 4.8: Effect of annealing on Zn TPD: a) 0.8 ML ZnO\textsubscript{x}, b) same as (a) but annealed at 670 K for 5 minutes before Zn TPD, and c) same as (b) but annealed for 10 minutes at 670 K. TPD spectra are 100\times the reference scale.
Effect of further oxygen and heat treatments on three-dimensional ZnOx islands on Cu(110)

We show in figure 4.9(i) the effect of treating oxygen deficient three-dimensional ZnOx islands on Cu(110) with more oxygen. We took the surface described in figure 4.5(ii) (a surface seen by AES to contain zinc, oxygen, and copper, but shown by CO and CO2 TPD to be predominantly Cu(110)) and exposed it to $5 \times 10^{-7}$ Torr O2 for 10 minutes at 300 K followed by annealing at 700 K for 2 seconds. This treatment restores the ability of the ZnOx islands to adsorb CO2 (note that the highest Tp is now at 550 K) and decrease the CO adsorption capacity by $\sim 40\%$. This may be interpreted as the spreading of ZnOx islands onto Cu(110) or oxygen incorporation into deficient ZnOx islands and adsorption of some oxygen on Cu(110). We believe the latter case to be true as patches of diffuse p(2 x 1) domains appear on the surface after the oxygen and annealing treatments described above, indicating oxygen adsorption on Cu(110).

Another indication that the oxygen and annealing treatments restore oxygen to deficient ZnOx islands is that of CO and CO2 adsorption capacity with the annealing treatment as compared to no annealing treatment. If CO is dosed onto the surface after O2 treatment, the CO adsorption capacity decreases by 95%. But with each TPD experiment, CO adsorption capacity increases (up to that shown in figure 4.9(ia)) as each TPD experiment effectively anneals the surface for a fraction of a second at 700 K. In addition, these non-annealed oxygen treated surfaces exhibit increasing CO2 adsorption capacity with each TPD (up to that shown in figure 4.9(ib)). All this indicates diffusion of oxygen from Cu(110) to the oxygen-deficient ZnOx islands when the surface is heated to 700 K, hence increasing both the CO and CO2 adsorption capacity of the surface.

We can continue oxygen treatment by an additional $5 \times 10^{-7}$ Torr O2 exposure for 10 minutes at 300 K. Carbon dioxide TPD indicates that the ZnOx islands have remained unchanged, while the CO TPD indicates further oxygen adsorption on Cu(110). This is shown in figure 4.9(ii). Annealing this surface at 700 K for a few seconds does not change the CO and CO2 chemisorption properties. It is because
Figure 4.9: (i) Chemisorption of surface produced after surface represented in figure 4.5(ii) was exposed to $5 \times 10^{-7}$ Torr O$_2$ for 10 minutes at 300 K and annealed at 700 K for 2 seconds. (ii) CO and CO$_2$ desorption spectra after an additional exposure of $5 \times 10^{-7}$ Torr O$_2$ for 10 minutes at 300 K. All TPD data were obtained from saturation coverages of CO or CO$_2$. Surfaces which give CO$_2$ desorption spectra similar to figure 4.9 contain the highest zinc desorption peak (peak d of figure 4.2) in their zinc TPD spectra. LEED shows diffuse p(2x1) patterns throughout these oxygen treatments.
Table 4.2
Effect of Co-Adsorption on CO & CO₂ Adsorption Capacity

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Amount of CO desorbed molecules/cm²</th>
<th>Amount of CO₂ desorbed molecules/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>3L CO₂ then 2L CO</td>
<td>4.1\times 10^{14}</td>
<td>9.0\times 10^{13}</td>
</tr>
<tr>
<td>2L CO alone</td>
<td>4.0\pm0.1\times 10^{14}</td>
<td>---------</td>
</tr>
<tr>
<td>2L CO then 3L CO₂</td>
<td>3.9\times 10^{14}</td>
<td>8.8\times 10^{13}</td>
</tr>
<tr>
<td>3L CO₂ alone</td>
<td>---------</td>
<td>8.7\pm0.3\times 10^{13}</td>
</tr>
</tbody>
</table>
the ZnO$_x$ islands no longer need oxygen that annealing at 700 K for 2 seconds does not result in loss of oxygen from the copper to the ZnO$_x$ islands.

Zinc TPD from these stable three-dimensional ZnO$_x$ islands always contain the highest zinc desorption peak at $T_p \sim 1000$ K (the desorption is half order so it is hard to define one $T_p$). This is the main difference between the zinc TPD spectra from the oxygen deficient ZnO$_x$ islands and these “stoichiometric” ZnO$_x$ islands.

The hypothesis that the CO and CO$_2$ TPD spectra shown in figure 4.9(i) are due to ZnO$_x$ islands on Cu(110) may be further tested by co-adsorption of CO and CO$_2$. If there are ZnO$_x$ clusters on Cu(110), co-adsorption of saturation coverages of CO and CO$_2$ should have little or no effect on CO and CO$_2$ adsorption capacities. Table 4.2 shows the amount of CO and CO$_2$ adsorbed on a “3.0 ML ZnO$_x$” overlayer on Cu(110). From CO titrations, this surface has $\sim 70\%$ of the copper surface area of clean Cu(110). No change in either CO$_2$ or CO adsorption capacity could be detected by co-adsorption of the two molecules, further indicating the model of three-dimensional ZnO$_x$ islands on bare Cu(110).

We can obtain reproducible CO$_2$ and CO TPD spectra ending at 700 K from these three-dimensional ZnO$_x$ islands on Cu(110). But as TPD experiments are performed with a heating rate of 30 K/s, each TPD only anneals the surface for a fraction of a second at 700 K. If we anneal these Cu-Zn-O surfaces for longer periods of time, we see changes by AES, LEED, and CO and CO$_2$ TPD. The changes in CO$_2$ TPD spectra for a 3.0 ML ZnO$_x$/Cu(110) surface are shown in figure 4.10 and all the changes observed are summarized in table 4.3. Carbon dioxide TPD spectra show changes in the ZnO$_x$ overlayer from the heat treatments at 700 K. A new peak at 340 K appears and increases with annealing treatment. This indicates new adsorption sites for CO$_2$. But the total CO$_2$ adsorption capacity does not increase; on the contrary, it decreases slightly due to a decrease in the other types of adsorption sites. Auger indicates a loss in both zinc and oxygen intensity after annealing at 700 K for 2.0 minutes. This is most likely due to additional clumping of ZnO$_x$ islands. There are no changes in either CO adsorption or in the LEED
Figure 4.10: Effect of annealing at 700 K on CO₂ chemisorption properties: a) 3.0 ML ZnO₂/Cu(110), b) after annealing (a) to 700 K for 2.0 minutes, and c) after an additional 10 minutes anneal at 700 K. TPD spectra are 10× the reference scale.
Table 4.3
Summary of AES, LEED, and CO & CO₂ TPD data for 3.0ML ZnOₓ/Cu(110) annealed at 700K

<table>
<thead>
<tr>
<th>Surface</th>
<th>AES Intensities (Arb. Units)</th>
<th>LEED Pattern</th>
<th>CO Adsorption Capacity (molecules/cm²)</th>
<th>CO₂ Adsorption Capacity from Tₚ=340K (molecules/cm²)</th>
<th>Amount of CO₂ from all other desorption peaks (molecules/cm²)</th>
<th>Total CO₂ Adsorption Capacity (molecules/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) &quot;3.0ML ZnOₓ&quot;**</td>
<td>39 10 40</td>
<td>(1×1)</td>
<td>4.0×10¹⁴</td>
<td>&lt;3×10¹¹</td>
<td>9.0×10¹³</td>
<td>9.0×10¹³</td>
</tr>
<tr>
<td>(b) After 700K/2.0 min.</td>
<td>39 6.7 32</td>
<td>(1×1)</td>
<td>4.1×10¹⁴</td>
<td>6.1×10¹³</td>
<td>7.5×10¹³</td>
<td></td>
</tr>
<tr>
<td>(c) After an additional 700K/10.0 min.</td>
<td>39 6.0 32</td>
<td>diffuse p(2×1)</td>
<td>1.2×10¹⁴</td>
<td>2.9×10¹³</td>
<td>4.4×10¹³</td>
<td>7.3×10¹³</td>
</tr>
</tbody>
</table>

*Coverage determined by AES
pattern after the 2.0 minutes annealing treatment. However, after an additional 10.0 minutes of annealing at 700 K, CO adsorption capacity does decrease by 70%. This decrease in CO adsorption capacity is accompanied by a diffuse LEED pattern corresponding to a poorly ordered p(2×1) surface structure, indicating that the decrease in CO adsorption capacity is due to oxygen adsorption on Cu(110). The oxygen is believed to surface from the bulk of copper as the annealing is done in vacuum. Similar results were obtained for a wide range of ZnO<sub>x</sub> coverages from 0.5 ML to 3.0 ML ZnO<sub>x</sub>.

The heat treatments were performed in an attempt to spread the three-dimensional ZnO<sub>x</sub> islands onto Cu(110). Since heating in vacuum failed to spread these islands, heating in oxygen was attempted; up to 5×10<sup>-8</sup> Torr O<sub>2</sub> was used. There was no additional effect of the oxygen ambient other than to create an oxygen covered Cu(110) surface more rapidly.

We can continue to deposit zinc and oxygen and obtain approximately the same CO<sub>2</sub> and CO adsorption capacity (9×10<sup>13</sup> molecules/cm<sup>2</sup> and 4×10<sup>14</sup> molecules/cm<sup>2</sup> respectively) from about 3.0 ML to 7 ML ZnO<sub>x</sub> (coverage determined by AES). A diffuse (1×1) LEED pattern due to the copper substrate can still be observed at ~7 ML ZnO<sub>x</sub>. At coverages above 7 ML, the ZnO<sub>x</sub> islands begin to collapse as evidenced by an increase in CO<sub>2</sub> adsorption capacity. The diffuse (1×1) LEED pattern does not completely disappear until >8 ML ZnO<sub>x</sub>, and evidence of bare Cu(110) as detected by CO adsorption remains until >15 ML ZnO<sub>x</sub>.

### 4.4 Discussion

We have seen evidence of some of the complexities anticipated in attempting to grow ZnO<sub>x</sub> overlayers on copper single crystals; oxygen adsorption onto copper as well as zinc oxide formation, diffusion of oxygen into and out of bulk copper, and so on. We have also seen an additional complication of rapid clustering of ZnO<sub>x</sub> into three-dimensional islands at temperatures above 300 K. Hence, to avoid three-dimensional islands, we evaporated zinc in an oxygen ambient at 150 K.
Ideally, we would like an ordered ZnO overlayer on copper. Examining the unit cells of various zinc oxide and copper single crystals, the best fit is between ZnO(10\bar{1}0) and Cu(110): For Cu(110), a=3.61 Å, b=2.55 Å, and for ZnO(10\bar{1}0), a=3.2495 Å, b=5.2069 Å. There is a 10% mismatch between the Cu(110) and ZnO(10\bar{1}0) faces for one side of their unit cell, and taking twice the distance of b=2.55 Å for Cu(110) (so the overlayer is a p(2×1)), there is a 2% mismatch between the other side of the two faces. Hence, by requirement of similar unit cell dimensions, ordered ZnO layers on Cu(110) seemed plausible. However, we have seen that even with an ordered Cu(110) p(2×1)O surface prior to zinc deposition, the resulting ZnO\textsubscript{x} overlayer displayed no long range order.

We have seen that by depositing zinc vapor and oxygen onto Cu(110), a surface species forms which adsorbs CO\textsubscript{2}. This indicates the formation of zinc oxide. The temperature at maximum rate of desorption of CO\textsubscript{2} from this ZnO\textsubscript{x} surface is 510 K, 170 K higher than from submonolayers to multilayers of ZnO\textsubscript{y} on gold foils. This shift in binding energy may be due to interactions between copper and zinc oxide or it may be due to the structure of the ZnO\textsubscript{x} overlayer on Cu(110). Reports in the literature have shown CO\textsubscript{2} desorption to occur between T\textsubscript{p}=350 K and 400 K for ZnO single crystal orientation of (10\bar{1}0), (4041), and (5051) [8,17]. In contrast, the polar ZnO single crystal of (0001) orientation interacts with CO\textsubscript{2} more strongly, as indicated by the maximum rate of desorption of 670 K [17]. Hence, the difference in binding energy of CO\textsubscript{2} on the three-dimensional ZnO\textsubscript{x} islands/Cu(110) and on ZnO\textsubscript{y}/Au may be due to differences in the overlayer structure (i.e. dipole moment and defect density).

We have noted that the temperature of peak desorption changes for CO\textsubscript{2} from the two-dimensional ZnO\textsubscript{x} islands to the three-dimensional islands. For example, the highest T\textsubscript{p} for the two-dimensional ZnO\textsubscript{x} overlayer is at 510 K, while for the three-dimensional ZnO\textsubscript{x} islands, the highest T\textsubscript{p} is at 550 K. This is most likely due to different faces of ZnO exposed in the two different cases. With additional annealing, we obtained more and more CO\textsubscript{2} adsorption indicative of non-polar faces of ZnO (T\textsubscript{p}=340 K).
While we have observed various CO$_2$ desorption peaks depending on preparation of the surface, CO desorption is always a narrow peak centered at $T_p=218$ K except when the copper is covered with $\geq 0.4$ ML oxygen. It may be surprising that ZnO$_x$ islands have no influence on the binding energy of CO to Cu(110), but this insensitivity of CO adsorption on copper has been previously seen for CO adsorption on cobalt modified Cu(100) [18].

It would be interesting to observe the interaction of copper, zinc, and oxygen by scanning tunneling microscopy (STM) in the barrier height mode; the initial two-dimensional structures, the three-dimensional island formation upon heating above 300 K, and changes in structure and composition upon further oxygen and heat treatments.

4.5 Conclusion

It is possible to grow two-dimensional ZnO$_x$ islands on Cu(110), but these islands cluster into three-dimensional islands above 300 K. These three-dimensional ZnO$_x$ islands do not adsorb detectable amounts of CO$_2$ because of oxygen deficiency. Once these oxygen deficient ZnO$_x$ islands are oxidized, CO$_2$ adsorption capacity increases to detectable levels. Carbon dioxide chemisorption properties on three-dimensional islands vary depending upon heat treatments. At first, strong adsorption associated with polar faces and/or defect sites are observed. With increasing heat treatments at 700 K, adsorption indicative of non-polar faces of ZnO increases.

Carbon monoxide adsorption on Cu(110) is unaffected by the presence of ZnO$_x$. Hence, CO titration can be used to determine the amount of exposed Cu(110). From a combination of CO and CO$_2$ titrations, it appears that zinc oxide prefers to grow as three-dimensional islands on Cu(110). These ZnO$_x$ islands do not collapse until AES indicates $>7$ ML ZnO$_x$. Heating in vacuum and in oxygen failed to spread these islands onto the copper substrate.
References


Chapter 5

A Comparative Study of $\text{ZnO}_x$ Overlayers on Cu(311), Cu(110), and high defect concentration Cu(111)

5.1 Introduction

We began our work on $\text{ZnO}_x$ overlayers on copper with Cu(110) as the substrate (chapter 4 and reference [1]). The (110) face of copper was used as it has a small mismatch to a ZnO face; a 2% mismatch on one side of the unit cell and a 10% mismatch on the other side to a ZnO(10I0) face. Unfortunately, we found no ordered $\text{ZnO}_x$ overlayer on Cu(110). Instead, we found $\text{ZnO}_x$ to be most stable as three-dimensional islands at temperatures greater than 300 K in vacuum. As Cu(110) is an open, flat surface, we decided to investigate $\text{ZnO}_x$ formation on two surfaces which represent two other distinct types of surfaces; a close-packed surface, Cu(111), and a stepped surface, Cu(311), and compare them to $\text{ZnO}_x$ formation on Cu(110).

In this chapter, we show that upon heating above 300 K, $\text{ZnO}_x$ clusters on all three surfaces. The clustering appears to be most extensive on the (110) and (111) faces of copper. Our use of a high defect density Cu(111) shows $\text{ZnO}_x$ prefers to cluster to the defect sites. In addition, we show that the temperature of $\text{ZnO}_x$ decomposition is dependent on the structure of the copper substrate.
5.2 Results

CO and CO$_2$ Desorption from copper (311), (110), and (111), and oxygen covered copper (311), (110), and (111)

Figure 5.1 shows CO desorption after saturation exposures on Cu(110), a high defect concentration Cu(111), and Cu(311), along with CO desorption from their 0.5 ML oxygen covered counterparts. CO desorption from Cu(110) occurs with $T_p=218$ K. This is in agreement with previous work which shows CO desorption with $T_p=223$ K [2]. CO desorption from Cu(111) produces two peaks – one centered at 165 K and the other one centered at 225 K. The peak centered at 165 K is in agreement with previous work which shows CO desorption at 168 K [3]. We believe that the peak centered at 225 K is due to defects on the Cu(111) surface. We shall see later that this defect site appears to be favored by ZnO$_x$ islands. No previous work other than ours has been reported on CO TPD from Cu(311) (chapter 3 and reference [4]).

The common feature observed from CO TPD is that when oxygen is pre-adsorbed on the three copper surfaces, it blocks CO adsorption. From figure 5.1, we see that of the three surfaces, oxygen blocks CO adsorption most effectively on the Cu(110) surface.

Though CO desorption from the three different copper surfaces is very similar, CO$_2$ desorption is not. In chapter 3, we found CO$_2$ to adsorb on Cu(311), whilst no adsorption is observed on Cu(110) [4]. Although it has been reported that CO$_2$ does not interact with Cu(111) [5], we have observed some CO$_2$ adsorption on our Cu(111), as shown in figure 5.2. We believe this is due to adsorption by the defects on our Cu(111). Note that for the high defect density Cu(111), pre-adsorbed oxygen decreases subsequent CO$_2$ adsorption and blocks the defect site represented by CO desorption at $T_p=225$ K.

CO and CO$_2$ Titration of 1.0 ML ZnO$_x$/Cu before and after heating to 700 K

We have shown in chapter 4 (and reference [1]) that CO and CO$_2$ are good
Figure 5.1: CO desorption from Cu(110), a defective Cu(111), and Cu(311), and the effect of pre-adsorbed oxygen upon CO adsorption. Enough CO was exposed to each surface to produce saturation coverages – 2.0 L CO for Cu(110), 10 L CO for Cu(111), and 20 L CO for Cu(311).
Figure 5.2: CO$_2$ desorption from Cu(110), a defective Cu(111), and Cu(311), and the effect of pre-adsorbed oxygen upon CO$_2$ adsorption. TPD spectra are 10× the reference scale of CO TPD spectra.
titration probes for Cu(110) and zinc oxide surfaces, respectively. We will use similar techniques to probe changes of the ZnO\textsubscript{x} overlayers on the Cu(111) and Cu(311) surfaces.

Figure 5.3 shows CO and CO\textsubscript{2} desorption from a freshly prepared 1.0 ML ZnO\textsubscript{x}/Cu(110) surface, and the effect heating to 700 K has on that surface. The freshly prepared ZnO\textsubscript{x} overlayer adsorbs CO\textsubscript{2}, but very little CO, and shows no visible LEED pattern. This surface changes dramatically after heating to 700 K. The surface then adsorbs as much CO as clean Cu(110) and with the same temperature at peak desorption. There is only a 20-30% decrease in zinc and oxygen AES signal upon heating to 700 K.

Similar changes in CO adsorption capacity occur after heating 1.0 ML ZnO\textsubscript{x}/Cu(311) and 1.0 ML ZnO\textsubscript{x}/Cu(111) to 700 K, as shown in figures 5.4 and 5.5. Additionally, upon heating to 700 K, we found that the amount of CO\textsubscript{2} desorbed between 400-500 K decreases on all three surfaces. Remember that, in the absence of ZnO\textsubscript{x}, CO\textsubscript{2} adsorbs on both the Cu(311) and defective Cu(111). Hence, the interpretation of CO\textsubscript{2} TPD spectra for the ZnO\textsubscript{x} overlayers on Cu(311) and Cu(111) surfaces is not as clear-cut as it was for the Cu(110) substrate. However, it is apparent that the copper surface area increases upon heating the ZnO\textsubscript{x} overlayer on all three copper surfaces. As with 1.0 ML ZnO\textsubscript{x}/Cu(110), no visible LEED pattern could be seen on a freshly prepared 1.0 ML ZnO\textsubscript{x}/Cu(311) and 1.0 ML ZnO\textsubscript{x}/Cu(111). After annealing to 700 K, all three surfaces displayed a poorly ordered (1\times1) surface structure together with a reduction of the zinc and oxygen Auger signal by approximately 30%.

The change in the CO TPD spectrum of 1.0 ML ZnO\textsubscript{x}/Cu(111) upon heating is of particular interest. Comparing figure 5.5B to figure 5.1, one can see that CO desorption from a 1.0 ML ZnO\textsubscript{x}/Cu(111) surface heated to 700 K is very similar to that of CO desorption from Cu(111) except for the peak centered at 225 K. This high temperature peak is not visible on the ZnO\textsubscript{x}/Cu(111) surface, indicating that ZnO\textsubscript{x} has clustered onto the defect sites of Cu(111).

We have seen that drastic changes in chemisorption properties of 1.0 ML ZnO\textsubscript{x}
Figure 5.3: (A) CO and CO$_2$ TPD from freshly prepared 1.0 ML ZnO$_x$/Cu(110) surfaces. (B) The effect of annealing a 1.0 ML ZnO$_x$/Cu(110) surface to 700 K as seen by CO and CO$_2$ titration. AES zinc and oxygen signals decrease by 20-30% and a visible (1×1) LEED pattern appears after annealing to 700 K.
Figure 5.4: (A) CO and CO$_2$ TPD from freshly prepared 1.0 ML ZnO$_x$/Cu(311) surfaces. (B) The effect of annealing a 1.0 ML ZnO$_x$/Cu(311) surface to 700 K as seen by CO and CO$_2$ titration. AES zinc and oxygen signals decrease by $\sim$30\% and a visible (1$x$1) LEED pattern appears after annealing to 700 K.
Figure 5.5: (A) CO and CO₂ TPD from freshly prepared 1.0 ML ZnOₓ/Cu(111) surfaces. (B) The effect of annealing a 1.0 ML ZnOₓ/Cu(111) surface to 700 K as seen by CO and CO₂ titration. AES zinc and oxygen signals decrease by ~30% and a visible (1×1) LEED pattern appears after annealing to 700 K.
overlayers on three different copper surfaces occur upon heating to 700 K. Next, we examined the effect of heat upon CO and CO₂ adsorption capacities of 1.0 ML ZnOₓ overlayer on Cu(110), Cu(311), and Cu(111) substrates. This is shown in figure 5.6. Each sample was heated to the annealing temperature indicated for a fraction of a second, cooled back down to 150 K (or 130 K for Cu(111)), and then CO or CO₂ TPD experiments performed. Each sample had to be freshly prepared as the surface changes after heating above 300 K. For 1.0 ML ZnOₓ/Cu(110), CO adsorption capacity increases and CO₂ adsorption capacity decreases with increasing annealing temperature. For 1.0 ML ZnOₓ/Cu(311) and 1.0 ML ZnOₓ/Cu(111), the CO adsorption capacity also increases as the annealing temperature is raised.

We have shown that for 1.0 ML ZnOₓ on Cu(110), this change in adsorption capacity is due to clustering of ZnOₓ (chapter 4 and reference [1]). The extent of ZnOₓ clustering is large enough for 1.0 ML ZnOₓ/Cu(110) to obtain 90-100% of the CO adsorption capacity of clean Cu(110) after annealing to >650 K. For 1.0 ML ZnOₓ/Cu(111), the extent of clustering is again large enough to obtain 90-100% of the CO adsorption capacity of clean Cu(111). These two cases contrast with that of 1.0 ML ZnOₓ/Cu(311) annealed to 700 K, which achieves only 60-70% of the adsorption capacity of clean Cu(311). This may be due to a larger ZnOₓ island perimeter in the case of 1.0 ML ZnOₓ/Cu(311), but it is difficult to conclude anything without knowledge of CO and ZnOₓ adsorption sites on Cu(311).

One may argue that it is excess oxygen on the Cu(311), and not ZnOₓ islands, which is blocking CO adsorption. Excess oxygen may also be responsible for the blocking of the CO adsorption site with Tₚ=225 K on the Cu(111). To investigate this, we performed the following experiment: half a monolayer of oxygen was deposited on each copper surface, and then, in an ambient pressure of 10⁻¹⁰ Torr, zinc was evaporated onto each copper single crystal, annealed at 700 K for a second, and the resulting surface titrated with CO. By evaporating zinc onto the oxygen covered copper surface, and annealing to 700 K, the zinc combines with oxygen adsorbed on the copper surfaces to form ZnOₓ islands. Thus, the resulting surface has more free copper surface area than the 0.5 ML O/Cu we began the experiments with.
Figure 5.6: (A) CO and CO\textsubscript{2} adsorption capacities as a function of annealing temperature for 1.0 ML ZnO\textsubscript{x}/Cu(110). Each surface was prepared at 150 K, and heated to the indicated annealing temperature for a fraction of a second, and then the CO or CO\textsubscript{2} adsorption capacity measured. (B) CO adsorption capacity as a function of annealing temperature for 1.0 ML ZnO\textsubscript{x} overlayers on Cu(311) and Cu(111). The ZnO\textsubscript{x}/Cu(111) surfaces were prepared at 130 K and the ZnO\textsubscript{x}/Cu(311) surfaces were prepared at 150 K. Each experiment requires the preparation of a fresh surface since above 300 K, the ZnO\textsubscript{x}/Cu surfaces change.
change in copper surface area is monitored by CO titration. For all three copper substrates, a plateau in the CO adsorption capacity was reached after 0.4-0.5 ML zinc had been deposited onto 0.5 ML O/Cu and annealed to 700 K. The maximum CO adsorption capacity on ZnO\textsubscript{x}/Cu(111) and ZnO\textsubscript{x}/Cu(110) is, again, 90-100% of the adsorption capacity of the corresponding clean surface, as shown in figure 5.7. The CO adsorption from a 0.5 ML O/Cu(111) that has reacted with 0.5-0.7 ML zinc is just like figure 5.5B – the CO peak with \(T_p=225\) K is missing. For 0.5 ML O/Cu(311) reacted with 0.5-0.7 ML zinc, the CO adsorption capacity reached upon annealing to 700 K is only 60-70% of the CO adsorption capacity of clean Cu(311). This is also shown in figure 5.7. These studies suggest that it is ZnO\textsubscript{x} islands, and not surface oxygen chemisorbed on copper, that is blocking the CO adsorption sites.

**Zn Desorption from ZnO\textsubscript{x}/Cu(311), ZnO\textsubscript{x}/Cu(110), and ZnO\textsubscript{x}/Cu(111)**

Zinc desorption from Cu(110), Cu(311), and Cu(111) under various oxidation conditions is shown in figure 5.8. The temperature at peak desorption of zinc from the various surfaces is dependent on:

1) The crystal face of the substrate.

2) The extent of oxidation, which is dependent on crystal face as well as oxidation conditions.

Oxygen dissociation is a prerequisite for ZnO\textsubscript{x} formation from zinc and O\textsubscript{2}. Molecular oxygen can be dissociated on zinc or on the copper substrate. We have found that the formation of a 0.5 ML coverage of oxygen requires an order of magnitude greater O\textsubscript{2} exposure for Cu(111) than for either Cu(110) or Cu(311) between 150-300 K. This indicates that dissociation of molecular oxygen occurs at a rate which is an order of magnitude slower on Cu(111) than on Cu(311) and Cu(110). Similar results have been found for oxygen interaction with Cu(111) and Cu(110) by other investigators [7,8]. In addition, we have observed that zinc is at
Figure 5.7: Removal of oxygen on copper single crystals with elemental zinc. Zinc takes away the chemisorbed oxygen on copper to form ZnO islands. The extent of the clustering is titrated by saturation coverages of CO.
Figure 5.8: The desorption of zinc after various oxidation treatments for three different copper substrates. (A) 0.3 ML of zinc from Cu(111). (B) 0.3 ML of zinc from Cu(311). (C) 0.1 ML of zinc from Cu(110). AES shows that no zinc is left on any of these Cu-Zn-O surfaces after heating to 1100 K. As reference, zinc from multilayers of zinc on Cu(110) and zinc from a ZnO(0001) single crystal are shown. The desorption of zinc from ZnO(0001) is reproduced with permission from the authors of reference [6] and is not on the same scale as the rest of the TPD curves. All Zn TPD spectra are 100x the reference scale.
least an order in magnitude slower at dissociation of molecular oxygen than Cu(110).
Hence, it is not surprising that highly oxidized zinc (represented by zinc desorption at $T_p \sim 1000$ K) requires more severe oxidation conditions to form on Cu(111) than on Cu(311) or Cu(110). This is shown in figure 5.8.

We believe that the temperature of peak desorption of zinc is dependent on crystal face as well as oxidation conditions. This can be seen by comparing zinc desorption from Cu(110) and Cu(311). The difference between the $T_p$ for zinc desorption from Cu(110) and for zinc desorption from 0.5 ML O/Cu(110) is 70 K, whilst the difference is 175 K for the case of Cu(311). This difference in temperature is much greater than our ±5 K error bar. AES shows that no zinc is left on any of these Cu-Zn-O surfaces after heating to 1100 K.

We did not find simultaneous copper and oxygen desorption with the zinc from any of the model Cu-Zn-O surfaces. Oxygen from ZnO\textsubscript{x} decomposed to form surface oxygen on the copper substrate, and does not begin to desorb until greater than 1000 K, along with the copper.

5.3 Discussion

We have compared the formation of ZnO\textsubscript{x} overlayers on three different copper surfaces. By CO titration, AES, and LEED, we see that zinc oxide clusters above 300 K on all three surfaces, and appears to cluster more extensively on the Cu(111) and Cu(110) surfaces than on the Cu(311) surface. We cannot be certain that the differences seen by CO titration are due to differences in ZnO\textsubscript{x} cluster size on each substrate since we do not know the binding sites of CO nor of ZnO\textsubscript{x} islands on Cu(311). It would be interesting to see the difference in ZnO\textsubscript{x} island perimeter size on Cu(311) and Cu(110) substrates by scanning tunneling microscopy (STM). Even more interesting would be to observe the image, on an atomic scale, of CO interaction to these Cu-Zn-O surfaces; the adsorption sites of CO on Cu(311) and the changes in CO adsorption on Cu(311) in the presence of ZnO\textsubscript{x} islands.

Zinc desorption resulting from the decomposition of ZnO\textsubscript{x} on the three different copper surfaces appears to depend on the structure of the copper substrate as well.
as the extent of oxidation. Although $\text{ZnO}_x$ decomposes at different temperatures on the three substrates studied, in all cases, $\text{ZnO}_x$ decomposition produces surface oxygen and zinc vapor. It would be interesting to observe, by a combination of STM and TPD, the adsorption sites corresponding to the various binding energies observed by TPD. In addition, the decomposition process of

$$\text{ZnO}_x \rightarrow O_{(\text{surface})} + \text{Zn}_g$$

should be investigated on the atomic scale in order to understand the reaction pathway.

### 5.4 Conclusions

We have seen that $\text{ZnO}_x$ clusters above 300 K on all three copper substrates, and that the $\text{ZnO}_x$ clusters on Cu(311) block more CO adsorption sites on Cu(311) than on the Cu(110) and Cu(111) substrates. By comparing the CO TPD of a high defect density Cu(111) and the CO TPD of 1.0 ML $\text{ZnO}_x$/Cu(111) that has been annealed to 700 K, we see that $\text{ZnO}_x$ clusters at the defect sites. The decomposition of submonolayers of $\text{ZnO}_x$ on copper substrates produces zinc vapor and surface oxygen. The temperature at which $\text{ZnO}_x$ decomposes on copper is dependent on the structure of the copper substrate.
References


Chapter 6

The Rôles of Chemisorbed Oxygen and Zinc Oxide Islands on Cu(110) surfaces for Methanol Decomposition

6.1 Introduction

We have seen, in chapters 4 and 5, that ZnOₓ clusters to three-dimensional islands upon heating above 300 K on Cu(110), Cu(311), and Cu(111). In this chapter, we use the most well-characterized of these surfaces – ZnOₓ on Cu(110) – and add chemisorbed oxygen onto the copper part of the surface. We then examine methanol interaction with these model Cu-Zn-O surfaces.

Several investigators [1,2] have found that after reaction in CO/CO₂/H₂ gases, the more active Cu-Zn-O catalysts have 30-60% of their copper surface area covered with oxygen. Ren and co-workers [3] have shown that CO₂ has an inhibiting effect on methanol synthesis catalysts that do not contain copper but has a promotional effect on catalysts containing copper. This, along with studies which have shown that CO₂ produces chemisorbed oxygen on the copper component of the catalysts [4], suggests that chemisorbed oxygen on the copper component has a promotional effect on methanol synthesis over Cu-Zn-O surfaces. It has been proposed by Chinchen, Spencer, Waugh, and Whan [4] that the rôle of chemisorbed oxygen on supported copper catalysts is to promote CO₂ adsorption on the copper component of the
catalysts. In this chapter, we will show that chemisorbed oxygen on the copper component also plays a rôle in promoting the total amount of formate formation.

In addition to studies of Cu-Zn-O catalysts, various investigations concerning methanol interaction with zinc oxide and oxygen modified Cu(110) have been reported. Wachs and Madix [5] monitored methoxy and formate formation upon chemisorption of methanol on oxygen modified Cu(110) (henceforth denoted O/Cu(110)) surfaces by observing their decomposition into CH$_3$O and CO$_2$, respectively. They found that both the amount of [CH$_2$O]$_{methoxy}$/CH$_3$OH (to emphasize the relationship between the various species, we have used the notation [X]$_Y$/Z, where X is the decomposed product from intermediate Y, produced by adsorption of Z) and [CO$_2$]$_{formate}$/CH$_3$OH production increased, and then decreased with increasing oxygen coverage, forming a characteristic volcano plot. Investigations of the interaction of methanol with ZnO powders, oriented thin films, and single crystals [6-12] have shown that methanol decomposes sequentially into methoxy and formate species. Chan and Griffin [11] have observed methanol decomposition over copper overlayers on zinc oxide oriented thin films. They observed a new CO$_2$ desorption peak (from methanol decomposition) which they interpreted as evidence for dispersed copper cation sites.

In this chapter, we take a new approach to the modelling of Cu-Zn-O catalysts: We use ZnO$_x$ islands on Cu(110) that is covered with various amounts of oxygen as a model for studying the interaction of methanol with Cu-Zn-O surfaces.

Electron microscopy studies of Cu-Zn-O methanol synthesis catalysts [13] have shown copper and zinc oxide components in separate phases; hence, the appropriateness of using ZnO$_x$ islands on copper as our model. Our previous studies have shown that ZnO$_x$ overlayers on Cu(110) can be characterized by a combination of CO$_2$ and CO TPD (along with AES and LEED), since CO preferentially chemisorbs on copper while CO$_2$ chemisorbs on ZnO$_x$ [14, chapter 4]. We use the same characterization techniques to follow changes in our model Cu-Zn-O surfaces after methanol decomposition. We show that the rôle of chemisorbed oxygen on Cu(110) is two-fold. There is transfer of oxygen from the copper to the zinc oxide
which keeps the zinc oxidized under the reducing conditions of formate production from methanol. Furthermore, oxygen on copper promotes the total amount of surface formate produced by methanol decomposition. The role of ZnO₇ islands is to increase the surface formate:methoxy ratio, from 1:9 in the absence of ZnO₇, to 1:3 in the presence of ZnO₇.

6.2 Experimental

General experimental comments are the same as chapter 2. In addition to chapter 2, there are some additional experimental notes needed to understand this chapter. They are discussed below.

All of the ZnO₇ overlayers described in this chapter were prepared in the same manner so as to obtain approximately “2.0 ML” (AES calibration) of ZnO₇. The procedure used was as follows: Zinc vapor was deposited onto Cu(110) which had been pre-dosed with 0.5 ML oxygen (henceforth denoted 0.5 ML O/Cu(110)) at 150 K in an oxygen ambient of \(1 \times 10^{-7}\) Torr O₂. After zinc deposition, the surface was further oxidized with 300 L O₂ at 250 K. This last step determines the difference between oxygen deficient zinc oxide, which cannot adsorb CO₂ under our conditions, and zinc oxide, which can adsorb CO₂. Finally, the surface was annealed at 710 K for 2 seconds to produce three-dimensional ZnO₇ islands on essentially oxygen-free Cu(110). (The presence of oxygen adsorbed on Cu(110) can be detected by CO₂ production from CH₃OH decomposition.)

A typical experimental procedure is as follows: The copper single crystal is cleaned by cycles of sputtering with \(5 \times 10^{-5}\) Torr argon at 300 K and 910 K, and then annealed at 910 K for fifteen minutes. Sample cleanliness is then checked by AES and surface order by LEED. Once the sample is cleaned, ZnO₇ and/or oxygen overlayers are produced and characterized as described above, and then TPD experiments begin. The sample is cooled to 150 K, positioned 2 mm in front of the mass spectrometer, dosed with a known amount of gas, and then the sample temperature is ramped linearly at 30 K/sec with the mass spectrometer tuned to a particular mass. After characterizing each surface by AES, LEED, CO and CO₂.
TPD [14], the interaction of methanol with the model Cu-Zn-O surface was determined. Each methanol TPD experiment ended at 710 K because that is the temperature where oxidized zinc begin to desorb. AES spectra and LEED patterns were obtained after TPD experiments, to correlate composition and structure of the surface to methanol decomposition. By the end of each day of methanol TPD studies, the surface had accumulated ~5% of a monolayer of carbon. This does not alter the data as shown by performing the same set of experiments over again on this 5% carbon contaminated surface.

As methanol reduces zinc oxide and takes away oxygen from Cu(110) (see results), each ZnO$_x$/O/Cu(110) (or O/Cu(110)) surface changes after each methanol TPD. The same procedure was used for each methanol TPD reported in this chapter: We dose the surface with 1×10^{-8} Torr methanol at 150 K for 200 seconds (2.0 L CH$_3$OH), wait 200 seconds to pump out the methanol, and then ramp the temperature of the crystal at 30 K/second while monitoring a particular mass. It takes 300-400 seconds (variation in cooling rates from day to day) to cool back down to 150 K after each TPD ending at 710 K.

During TPD experiments, only one $m/e$ unit at a time was followed in order to obtain the best signal to noise ratio possible. Hence, many surfaces had to be prepared to check reproducibility. As an extra check on reproducibility, in some of the experiments, two masses which produced signals in different temperature ranges were followed. For example, after methanol adsorption, $m/e=31$ (methanol) would be followed up to 450K, after which the $m/e$ center was switched to $m/e=44$ (CO$_2$) in order to obtain the products from 450 K to 710 K. All these experiments indicated that these model Cu-Zn-O surfaces are very reproducible.

The products observed were identified by comparing their observed cracking pattern in the mass spectrometer with those in the literature. Once the products were identified, the parent $m/e$ fragment was followed except for CH$_3$OH, in which case $m/e=31$ methoxy signal was followed as it is 50% greater in signal than $m/e=32$. 

99
Table 6.1a: Products from methanol adsorption on 0.5 ML O/Cu(110)

<table>
<thead>
<tr>
<th>CH$_3$OH</th>
<th>CH$_2$O</th>
<th>H$_2$</th>
<th>CO</th>
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<th>H$_2$O</th>
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<td>183 K</td>
<td></td>
<td>410 K</td>
<td>200 K</td>
<td>490 K</td>
<td>230 K</td>
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<td>220 K</td>
<td></td>
<td></td>
<td>410 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>275 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>420 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1b: Products from methanol adsorption on ZnO$_x$/0.5 ML O/Cu(110)

<table>
<thead>
<tr>
<th>CH$_3$OH</th>
<th>CH$_2$O</th>
<th>H$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>183 K</td>
<td>410 K</td>
<td>260 K</td>
<td>660 K</td>
<td>490 K</td>
<td>220 K</td>
<td>starts</td>
</tr>
<tr>
<td>220 K</td>
<td>(490 K)</td>
<td>410 K</td>
<td>660 K</td>
<td></td>
<td>300 K</td>
<td>desorbing</td>
</tr>
<tr>
<td>270 K</td>
<td>560 K</td>
<td>560 K</td>
<td>660 K</td>
<td>490 K</td>
<td>490 K</td>
<td>at 600 K</td>
</tr>
<tr>
<td>310 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>660 K</td>
<td></td>
</tr>
<tr>
<td>440 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3 Results

Methanol Decomposition on Cu(110)

The products from methanol TPD on Cu(110) are shown in figure 6.1. On clean Cu(110), the decomposition of methanol produces simultaneous formaldehyde and hydrogen desorption at $T_p=370$ K. Wachs and Madix also obtained simultaneous desorption of formaldehyde and hydrogen at $T_p=365$ K and have assigned this result to the decomposition of methoxy surface species [5]. Our results agree well with those of Wachs and Madix except for the desorption of undissociated methanol. This discrepancy is due to a difference in adsorption temperature between our studies and theirs: our adsorption temperature is 150 K while their adsorption temperature is 180 K.

Methanol Decomposition from O/Cu(110)

In addition to methanol decomposition on clean Cu(110), we investigated how oxygen on Cu(110) influences methanol decomposition. The products from methanol TPD from 0.5 ML oxygen on Cu(110) surfaces are shown in figure 6.2. This was the highest coverage of oxygen investigated. Several differences can be seen between this spectra and that obtained for methanol decomposition over clean Cu(110) (figure 6.1):

1) CO$_2$ and H$_2$O are now products of methanol decomposition, with both CO$_2$ and H$_2$O desorbing at $T_p=490$ K. This indicates the presence of chemisorbed formate parent species [5].

2) CH$_3$OH desorption peaks change, with the appearance of a peak at $T_p=420$ K, disappearance of the peak at $T_p=380$ K, and a decrease in the amount of undissociated methanol.
Figure 6.1: Products from 2.0 L methanol adsorption on Cu(110) at 150 K. Methanol decomposes to methoxy which then decomposes to formaldehyde and hydrogen at 370 K. All the products which could be detected from methanol decomposition are shown above.
Figure 6.2: Products from 2.0 L methanol adsorption on 0.5 ML oxygen covered Cu(110) (0.5 ML O/Cu(110)) at 150 K. Methanol decomposes to formate and methoxy intermediates. Formate decomposes to CO$_2$ and H$_2$O at 490 K and methoxy decomposes to formaldehyde and hydrogen at 410 K.
3) There is a decrease in the amount of \([\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}\) production indicating that there are less methoxy parent species chemisorbed than on clean Cu(110).

4) The \([\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}\) and \([\text{H}_2]_{\text{methoxy}}/\text{CH}_3\text{OH}\) peak decomposition temperature increases from 370 K on clean Cu(110) to 410 K in the presence of 0.5 ML chemisorbed oxygen on Cu(110).

Similar results were obtained by Wachs and Madix [5] who observed simultaneous CO\(_2\), H\(_2\)O, and H\(_2\) desorption at \(T_p=470\) K and a shift in the simultaneous CH\(_2\)O and H\(_2\) desorption peaks to \(T_p=390\) K for 0.4 ML O/Cu(110). We do not detect H\(_2\) desorption with CO\(_2\) and H\(_2\)O desorption at \(T_p=490\) K. We believe this is due to the high H\(_2\) background in our chamber. All the products and their temperatures at peak desorption from methanol adsorption on 0.5 ML O/Cu(110) are summarized in table 6.1a.

The effect of oxygen coverage on Cu(110) for \([\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}\), \([\text{CO}_2]_{\text{formate}}/\text{CH}_3\text{OH}\), and CH\(_3\)OH/CH\(_3\)OH production is shown in figure 6.3. Both the \([\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}\) and \([\text{CO}_2]_{\text{formate}}/\text{CH}_3\text{OH}\) production exhibit a maximum at 0.2-0.3 ML O/Cu(110), in agreement with work by Wachs and Madix [5]. We find that the amount of CH\(_3\)OH/CH\(_3\)OH production decreases at >0.3 ML oxygen, but Wachs and Madix [5] found a maximum in methanol desorption at 0.2-0.3 ML oxygen. This discrepancy is due to our use of 150 K as the adsorption temperature for methanol rather than 180 K, as used by Wachs and Madix.

We will note that the ratio of the maximum in \([\text{CO}_2]_{\text{formate}}/\text{CH}_3\text{OH}\) to \([\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}\) production is 1:9 (uncorrected for mass spectrometer sensitivities) in the absence of ZnO\(_x\), and we will see in the next section how this ratio changes in the presence of ZnO\(_x\).

**Methanol Decomposition from ZnO\(_x\)/O/Cu(110)**

Products from methanol adsorption on ZnO\(_x\)/0.5 ML O/Cu(110) are shown in figure 6.4. All the desorption temperatures of products from methanol interaction
Figure 6.3: The effect of $O_{\text{Oxygen}}$ on Cu(110) upon the production of CH$_3$OH, CH$_2$O, and CO$_2$, following 2.0 L CH$_3$OH exposure at 150 K. To emphasize the relationship between the various species, we have used the notation [X]$Y/Z$, where X is the decomposed product from intermediate Y, produced by adsorption of Z.
Figure 6.4: Products from 2.0 L methanol adsorption on ZnOx/0.5ML O/Cu(110) at 150 K. Methanol decomposition on ZnOx/0.5 ML O/Cu(110) is qualitatively like the addition of methanol decomposition on 0.5 ML O/Cu(110) and ZnOx. Note that ZnOx is being reduced as indicated by the detection of Zn(g) beginning at ~600 K.
Table 6.2:
Temperature at peak desorption of species from CH₃OH decomposition on ZnO

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorbed Species</th>
<th>Decomposition Products</th>
<th>Tₚ</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;2ML&quot; ZnOₓ/Cu(110)</td>
<td>Formate, Methoxy</td>
<td>CO₂+CO+H₂O, CH₂O+H₂</td>
<td>660 K</td>
<td>this work</td>
</tr>
<tr>
<td>Polycrystalline</td>
<td>Formate, Methoxy</td>
<td>CO₂+H₂</td>
<td>580 K</td>
<td>6</td>
</tr>
<tr>
<td>ZnO with large fraction of polar faces</td>
<td>Formate, Methoxy</td>
<td>CO₂+H₂O, CH₂O</td>
<td>540 K</td>
<td>6</td>
</tr>
<tr>
<td>Thin Films</td>
<td>Formate</td>
<td>CO₂+CO+H₂</td>
<td>580 K</td>
<td>7</td>
</tr>
<tr>
<td>ZnO(0001)</td>
<td>Formate, Methoxy</td>
<td>CO₂+CO+H₂O, CH₂O+H₂</td>
<td>575 K</td>
<td>8</td>
</tr>
<tr>
<td>ZnO(1010) and (5051)</td>
<td>Formate</td>
<td>CO₂+CO+H₂</td>
<td>650 K</td>
<td>9,10</td>
</tr>
<tr>
<td>ZnO(0001)</td>
<td>Formate, Methoxy</td>
<td>CO₂+CO+H₂O, CH₂O+H₂</td>
<td>750 K</td>
<td>9,10</td>
</tr>
<tr>
<td>C-axis oriented ZnO thin films</td>
<td>Formate, Methoxy</td>
<td>CO₂+CO+H₂</td>
<td>635 K</td>
<td>11</td>
</tr>
<tr>
<td>ZnO(0001)</td>
<td>Formate</td>
<td>CO₂+CO+H₂</td>
<td>470 K</td>
<td>12</td>
</tr>
<tr>
<td>&gt;15ML ZnOₓ/Cu(110)</td>
<td>Formate, Methoxy</td>
<td>CO₂+CO+H₂O, CH₂O</td>
<td>650 K</td>
<td>this work</td>
</tr>
<tr>
<td>ZnOₓ/Au foil</td>
<td>Formate, Methoxy</td>
<td>CO₂+CO+H₂O+CH₄, CH₂O+H₂</td>
<td>570 K</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂+H₂O+CH₄, CH₂O+H₂</td>
<td>670 K</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂O+H₂</td>
<td>620 K</td>
<td>this work</td>
</tr>
</tbody>
</table>
with 0.5 ML O/Cu(110) are essentially unchanged. The desorption products from 
ZnO$_x$/0.5 ML O/Cu(110) surfaces are summarized in table 6.1b.

We attribute the simultaneous desorption of formaldehyde and hydrogen at
560 K to methoxy decomposition on ZnO$_x$ islands. The simultaneous desorption
of CO, CO$_2$, and H$_2$O at 660 K is attributed to formate decomposition from ZnO$_x$
islands. Table 6.2 summarizes the decomposition temperatures of formate and
methoxy species from various zinc oxide surfaces. The peak temperatures for for-
mate and methoxy decomposition vary over a wide range, depending on the surface
structure of ZnO. It is difficult to compare our zinc oxide overlayer with any par-
ticular surface. The products from formate and methoxy decomposition on our
zinc oxide overlayer is most like that from ZnO(0001) as reported in [8], but our
peak temperatures of decomposition are between those reported in [8] ($T_p=575$ K
for formate decomposition and $T_p=520$ K for methoxy decomposition) and [9,10]
($T_p=750$ K for formate decomposition and $T_p=670$ K for methoxy decomposition).

We have seen in the previous section that changing the chemisorbed oxygen cov-
erage on Cu(110) changes the amount of [CO$_2$]$_{formate}$/CH$_3$OH, [CH$_2$O]$_{methoxy}$/CH$_3$OH,
and CH$_3$OH/CH$_3$OH production from O/Cu(110). What is surprising is the dra-
matic difference in the amount of [CO$_2$]$_{formate}$/CH$_3$OH and [CO]$_{formate}$/CH$_3$OH
produced from the ZnO$_x$ component of the surface by changing oxygen coverage
on Cu(110). This is illustrated in figure 6.5, which shows the amount of zinc,
CH$_2$O, CO, and CO$_2$ desorbed from a ZnO$_x$/0.5 ML O/Cu(110) and a ZnO$_x$/0.2
ML O/Cu(110) surface. Four points should be noted in comparing the ZnO$_x$/0.2
ML O/Cu(110) surface to the ZnO$_x$/0.5 ML O/Cu(110) surface:

1) The amount of zinc desorbed from a ZnO$_x$/0.2 ML O/Cu(110) surface is
about fives times greater than the amount of zinc desorbed from a ZnO$_x$/0.5
ML O/Cu(110) surface.

2) The amount of formate from the ZnO$_x$ component increases while the amount
of methoxy from ZnO$_x$ remain the same.
Figure 6.5: The amount of zinc, CH$_2$O, CO, and CO$_2$ desorbed from a ZnO$_x$/0.5 ML O/Cu(110) surface and a ZnO$_x$/0.2 ML O/Cu(110) surface after 2.0 L exposures of methanol at 150 K.
3) The amount of formate and methoxy from the O/Cu(110) component both increases when changing the oxygen coverage from 0.5 ML to 0.2 ML (similar to O/Cu(110) behavior toward methanol in the absence of ZnOx).

4) The total [CO$_2$+CO]$_{formate}$ : [CH$_2$O]$_{methoxy}$ ratio increases, suggesting greater formate formation in the case of ZnOx/0.2 ML O/Cu(110) surfaces.

The following sections will further develop these points.

We noted in the previous section that at 0.2-0.3 ML O/Cu(110), the ratio of [CO$_2$+CO]$_{formate}$ : [CH$_2$O]$_{methoxy}$ was 1:9. We see from figure 6.5 that for ZnOx/0.2 ML O/Cu(110) surfaces, the [CO$_2$+CO]$_{formate}$ : [CH$_2$O]$_{methoxy}$ ratio has increased to 1:3, indicating an increase in the relative surface formate concentration.

No other thermal decomposition products apart from those shown in figures 6.1, 6.2, and 6.4 were observed; in particular, we searched for, but did not see, methane, methyl formate, methylal, and dimethyl ether. Oxygen does not desorb from the Cu(110) surface until >1000 K. The oxygen from ZnOx decomposition between 710 K and 1100 K is adsorbed (and absorbed) by the Cu(110) [14].

**Effect of O/Cu(110) on ZnOx Reduction**

Figure 6.6A shows the amount of zinc desorbed by 710 K versus the number of methanol TPD experiments for two different ZnOx/0.5 ML O/Cu(110) surfaces. These surfaces produce a p(2×1) surface structure which slowly diminishes with each methanol TPD experiment, since formate formation and decomposition takes away oxygen from the surface. The initial rise in the amount of zinc reduced for each 2.0 L dose of methanol is due to the depletion of oxygen from the copper component, chemisorbed oxygen on Cu(110) being used to re-oxidize the reduced zinc. After the initial rapid rise in the amount of zinc reduced with each 2.0 L dose of methanol, there is a slow decline in the amount of zinc reduced. This is most likely due to the decrease in ZnOx left to reduce. (The first ten methanol TPD experiments reduces the original AES zinc signal by 30%.) By AES, the oxygen signal decreased by 35% after the first four methanol TPD experiments, while the zinc signal decreased by only 15%. The oxygen loss is mainly from the copper, as
Figure 6.6: (A) Amount of zinc desorbed by 710 K (for each 2.0 L dose of methanol) versus the number of methanol TPD experiments from two separate ZnO/0.5 ML O/Cu(110) surfaces. With increasing reduction of the Cu-Zn-O surface (each methanol TPD reduces the surface), the amount of zinc reduced first increases and then slowly decreases. The first ten methanol TPD experiments reduces the original AES zinc signal by 30%. (B) The influence of $\theta_{\text{oxygen}}$/Cu(110) on the amount of reduced zinc following 2.0 L CH$_3$OH exposure at 150 K for ZnO/0/Cu(110) surfaces. Oxygen on the Cu(110) part helps keep the ZnO$_x$ islands oxidized.
can be seen by an order in magnitude increase in CO adsorption capacity (due to bare copper), and the transformation of a \( p(2\times1) \) surface structure, at the beginning of the first methanol TPD, to a \( (1\times1) \) surface structure, after the fourth methanol TPD.

The effect of \( O/Cu(110) \) on the \( \text{ZnO}_x \) component can be seen in another set of experiments where the amount of zinc reduced is monitored from surfaces with different oxygen coverage on Cu(110) but the same amount of \( \text{ZnO}_x \). This is shown in figure 6.6B: Less zinc desorbs because less \( \text{ZnO}_x \) is reduced with greater \( \theta_{\text{oxygen}} \) on the Cu(110) component. This suggests oxygen spillover from the Cu(110) component to the \( \text{ZnO}_x \) to keep zinc oxidized. Hence, we see that one of the rôles of chemisorbed oxygen on the copper component is to help keep the zinc oxidized.

**Effect of \( O/Cu(110) \) on [CO\(_2\)+CO]\(_{\text{formate/CH}_3\text{OH}}\) Production from the \( \text{ZnO}_x \) Component**

A more surprising finding is shown in figure 6.7, in which the amount of chemisorbed oxygen on the copper component influences the production of CO\(_2\)+CO from CH\(_3\)OH decomposition (henceforth denoted [CO\(_2\)+CO]\(_{\text{formate/CH}_3\text{OH}}\)) on the zinc oxide component. Remember that the amount of CO\(_2\)+CO desorbed with \( T_p=660 \) K is the amount of surface formate species decomposed from the \( \text{ZnO}_x \) component of the surface. To determine that this volcano plot is indeed due to the chemisorbed oxygen on the copper component, we performed two sets of experiments, summarized in figures 6.8 and 6.9. With figure 6.8, we show the results of the amount of [CO\(_2\)+CO]\(_{\text{formate/CH}_3\text{OH}}\) produced as a function of the number of methanol TPD experiments for three different surfaces – \( \text{ZnO}_x/Cu(110) \), \( \text{ZnO}_x/0.2 \) ML \( O/Cu(110) \), and \( \text{ZnO}_x/0.5 \) ML \( O/Cu(110) \). Two points should be noted from this figure:

1) the maximum for [CO\(_2\)+CO]\(_{\text{formate/CH}_3\text{OH}}\) production from the \( \text{ZnO}_x \) component of the \( \text{ZnO}_x/0.2 \) ML \( O/Cu(110) \) is four times greater than that produced from the \( \text{ZnO}_x/Cu(110) \) surface, and

2) the maximum in [CO\(_2\)+CO]\(_{\text{formate/CH}_3\text{OH}}\) formation from the \( \text{ZnO}_x \) component of the Cu-Zn-O surface is reached at about 0.2-0.3 ML oxygen on
Figure 6.7: Production of CO$_2$ and CO from the ZnO$_x$ component of a ZnO$_x$/0.5 ML O/Cu(110) surface for 2.0 L exposures of CH$_3$OH as a function of the number of methanol TPD experiments.
Figure 6.8: The effect of reduction on $[CO_2+CO]_{\text{formate}}/CH_3OH$ production for three different surfaces. It does not seem to matter whether we start with 0.2-0.3 ML oxygen on the Cu(110) component of the surface or reach those oxygen coverages by reduction with methanol; in both cases, the maximum amount of $[CO_2+CO]_{\text{formate}}/CH_3OH$ production from the ZnO$_x$ component is obtained when there is 0.2-0.3 ML oxygen on the Cu(110) component, producing about $2 \times 10^{13}$ molecules of $[CO_2+CO]_{\text{formate}}/CH_3OH$ from the ZnO$_x$ component. Each CH$_3$OH exposure was 2.0 L.
the Cu(110) component, regardless of whether one starts with a ZnOx/0.2 ML O/Cu(110) surface or a ZnOx/0.5 ML O/Cu(110) surface reduced by methanol to an oxygen coverage of 0.2-0.3 ML.

Multilayers of ZnOx/Au reproducibly give the same amount of [CO₂+CO]formate/CH₃OH with each methanol TPD. Hence, the amount of chemisorbed oxygen on Cu(110) does indeed influence the amount of [CO₂+CO]formate/CH₃OH production, or formate formation, on the ZnOx component of our model Cu-Zn-O surface.

In figure 6.9, we show the effect of exposing a ZnOx/0.2 ML O/Cu(110) surface, that has been reduced by methanol, to oxygen. We begin with ZnOx/0.2 ML O/Cu(110) surface. The ZnOx component of this surface produces \( \approx 2 \times 10^{13} \) molecules CO₂+CO for a 2.0 L dose of methanol. By the seventh methanol TPD, the ZnOx component produces only \( \approx 3 \times 10^{12} \) molecules [CO₂+CO]formate/CH₃OH, and the original zinc AES signal has been reduced by \( \approx 20\% \). At this point, enough oxygen (30 L O₂) to form a 0.5 ML oxygen coverage on the bare Cu(110) part of the surface was introduced into the UHV chamber. After the introduction of oxygen, methanol TPD experiments showed the formation of a volcano plot with regards to the amount of [CO₂+CO]formate/CH₃OH from the ZnOx component of the surface as a function of the number of methanol TPD experiments. The maximum in this volcano plot occurs, again, when there is 0.2-0.3 ML oxygen on the Cu(110) part of the surface. But this time, the maximum amount of [CO₂+CO]formate/CH₃OH production from the ZnOx component is \( 1 \times 10^{13} \) molecules, half of what was obtained at the beginning of these experiments with the ZnOx/0.2 ML O/Cu(110) surface. This is most likely due to the smaller amount of ZnOx left on the surface by the twelfth methanol TPD as compared to the first methanol TPD. (Remember that methanol reduces zinc oxide.) As reference, the amount of [CO₂+CO]formate/CH₃OH from the ZnOx component of a ZnOx/0.2 ML O/Cu(110) surface with increasing reduction is shown to continually decline (due to decreasing amounts of ZnOx).

The effect of oxygen exposure on the various surface areas was determined by CO and CO₂ TPD. Saturation doses of CO₂ before and after the oxygen exposure
Figure 6.9: Effect of oxygen on formate production from the ZnO$_x$ component of our model Cu-Zn-O surface. Dark square boxes indicate a ZnO$_x$/0.2 ML O/Cu(110) surface continually reduced with methanol. The x marks indicate a ZnO$_x$/0.2ML O/Cu(110) surface that was exposed to 30 L O$_2$ at 150 K after the 7$^{th}$ methanol TPD experiment. CO$_2$ TPD before and after the introduction of O$_2$ showed that the ZnO$_x$ component remain unchanged. CO TPD after the introduction of O$_2$ show that there is a great decrease in exposed Cu(110) area; this along with the formation of a p(2×1) surface structure indicates oxygen adsorption on the Cu(110) component of the surface. Hence, the volcano plot formed after the introduction of O$_2$ is due to chemisorbed oxygen on the Cu(110) part of the surface.
showed no changes in either the size of the desorption peaks or the desorption temperatures. This suggests that ZnO$_x$ islands remain unaltered. On the other hand, saturation doses of CO after oxygen exposure showed a dramatic decrease in CO adsorption capacity; this along with the formation of a p(2×1) surface structure points to oxygen adsorption on the Cu(110) component. Thus, we conclude that oxygen adsorbed on the Cu(110) component of the Cu-Zn-O surface does affect the amount of [CO$_2$+CO]$_{formate}$/CH$_3$OH from the ZnO$_x$ component of the ZnO$_x$/O/Cu(110) surfaces.

**Effect of ZnO$_x$ Islands on [CO$_2$]$_{formate}$/CH$_3$OH Production from the O/Cu(110) Component**

Figure 6.10 shows the amount of CO$_2$ produced from a 2.0 L dose of methanol at 150 K from the O/Cu(110) component in the absence and presence of ZnO$_x$ islands. We see that:

1) The O/Cu(110) component is more quickly reduced in the presence of ZnO$_x$ islands, and

2) The maximum in [CO$_2$]$_{formate}$/CH$_3$OH production is three times greater in the absence of ZnO$_x$ than in its presence.

These observations suggest that oxygen is being taken away from the copper. As there is no oxygen desorption except in the form of formate decomposition, the oxygen is most likely migrating to the ZnO$_x$ islands to re-oxidize the ZnO$_x$ reduced by methanol. Earlier, we had obtained this same conclusion from the change in the amount of reduced zinc as a function of the number of methanol TPD experiments for ZnO$_x$/0.5 ML O/Cu(110) surfaces. Although the presence of ZnO$_x$ decreases the amount of formate decomposed on the O/Cu(110) component, the amount of formate from the ZnO$_x$ islands is increased by a greater amount in the presence of 0.2-0.3 ML O/Cu(110). We will examine this promotional effect on total formate production in the next section.
Figure 6.10: Amount of $[\text{CO}_2]_{\text{formate}}/\text{CH}_3\text{OH}$ from the O/Cu(110) component in the presence and absence of ZnO$_2$. The O/Cu(110) component is more quickly reduced in the presence of ZnO$_2$ islands and the maximum in $[\text{CO}_2]_{\text{formate}}/\text{CH}_3\text{OH}$ production from the O/Cu(110) component is about three times greater in the absence of ZnO$_2$ islands than in its presence. This figure, along with figure 6.6, show that oxygen is transferred from the copper to the ZnO$_2$ component to help keep the ZnO$_2$ oxidized. Note that although the presence of ZnO$_2$ decreases the amount of formate decomposed on the O/Cu(110) component, the amount of formate from the ZnO$_2$ is increased by a greater amount in the presence of 0.2-0.3 ML O/Cu(110).
[CO₂+CO]enate/CH₃OH Production on the Three Component System versus the Addition of the Two Separate Components

We have seen that oxygen on Cu(110) can promote both the amount of [CO₂+CO]enate/CH₃OH produced from the ZnOₓ component and the O/Cu(110) component of our model Cu-Zn-O surface. But as the oxygen is taken away from the copper to the ZnOₓ component of the ZnOₓ/O/Cu(110) surface, less [CO₂+CO]enate/CH₃OH is produced on the O/Cu(110) component in the presence of ZnOₓ islands. To determine the overall effect on total [CO₂+CO]enate/CH₃OH production on the O/Cu(110) and ZnOₓ components in the presence and absence of each other, experiments were performed on three types of surfaces: O/Cu(110) surfaces in which the oxygen coverage was varied, ZnOₓ/Cu(110) surface, and ZnOₓ/O/Cu(110) surfaces in which the oxygen coverage was again varied. We show the amount of [CO₂+CO]enate/CH₃OH produced from the components of ZnOₓ and O/Cu(110) of the three-component system – ZnOₓ/O/Cu(110) – and compare that to the addition of the separate components – ZnOₓ/Cu(110) + O/Cu(110) – as a function of the oxygen coverage on the copper component of the surface (as seen by CO titration). The results are plotted in figure 6.11 and show that:

1. The oxygen/Cu(110) effect [CO₂+CO]enate/CH₃OH production from both the ZnOₓ and O/Cu(110) components of ZnOₓ/O/Cu(110) surfaces, and

2. The maximum for [CO₂+CO]enate/CH₃OH production from the ZnOₓ and O/Cu(110) components of ZnOₓ/O/Cu(110) surfaces is twice that of the addition of the separate surfaces of ZnOₓ/Cu(110) plus O/Cu(110). (The plot in figure 6.11 did not correct for surface area so that the promotional effect seen is a minimum.)
Figure 6.11: The amount of $[\text{CO}_2 + \text{CO}]_{\text{formate/CH}_3\text{OH}}$ from the ZnO$_x$ and O/Cu(110) components in the three-component system, and the addition of the separate components as a function of $\theta_{\text{oxygen}}$/Cu(110). Experiments were done on three different types of surfaces and the amount of $[\text{CO}_2 + \text{CO}]_{\text{formate/CH}_3\text{OH}}$ from the two separate surfaces of O/Cu(110) and ZnO$_x$/Cu(110) were added up and compared to the amount of formate from the separate components of the three-component surface. As oxygen-free copper does not produce any $[\text{CO}_2]_{\text{formate/CH}_3\text{OH}}$, the ZnO$_x$/Cu(110) plus O/Cu(110) has only 20-30% more surface area than the ZnO$_x$/O/Cu(110) surface. Area was not corrected for in order to obtain the most conservative view of any promotional effect.
[CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH Production from the Three Component System versus the Addition of the Two Separate Components

In order to assess the effect of O/Cu(110) and ZnO\textsubscript{x} on each other in [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH production, similar experiments were performed to those for the observation of [CO\textsubscript{2}+CO]_{formate}/CH\textsubscript{3}OH production. We find that for ZnO\textsubscript{x}/O/Cu(110) surfaces, the amount of [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH from Cu(110) changes with \( \theta \text{ oxygen} \), but methoxy decomposition from ZnO\textsubscript{x} remain unchanged in the presence of O/Cu(110). Comparing the amount of [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH from the ZnO\textsubscript{x} and the O/Cu(110) components of ZnO\textsubscript{x}/O/Cu(110) surfaces to the addition of the two separate surfaces of ZnO\textsubscript{x}/Cu(110) and O/Cu(110), we see that there is no effect of O/Cu(110) and ZnO\textsubscript{x} on each other in terms of [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH production. This is best summarized in figure 6.12, which plots [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH production from the ZnO\textsubscript{x} and O/Cu(110) components of the three-component system, and the addition of the separate components. In order to make this the same type of comparison as figure 6.11, the amount of [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH from the copper component of the ZnO\textsubscript{x}/Cu(110) surface was discarded as [CO\textsubscript{2}+CO] is not produced from methanol decomposition on the bare Cu(110) component, while CH\textsubscript{2}O is produced; hence, the ZnO\textsubscript{x}/Cu(110) + O/Cu(110) data has 20-30\% greater surface area than the ZnO\textsubscript{x}/O/Cu(110) surface, as in the comparison of figure 6.11. But, unlike figure 6.11, where we saw a promotional effect of a factor of two in [CO\textsubscript{2}+CO]_{formate}/CH\textsubscript{3}OH production from the three-component system, indicating the promotion of formate formation, we see no promotional effect for [CH\textsubscript{2}O\textsubscript{methoxy}/CH\textsubscript{3}OH production, and hence, no promotional effect for methoxy formation on the three-component system.

Total Methanol Desorption

Comparing figure 6.2 and 6.4, one can see that methanol desorption from ZnO\textsubscript{x}/0.5 ML O/Cu(110) is dominated by methanol desorption from oxygen covered Cu(110). (The only difference is an additional desorption peak at \( T_p = 310 \) K for the ZnO\textsubscript{x}/0.5
Figure 6.12: The amount of $[\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}$ from the ZnO$_x$ and O/Cu(110) components of the three-component system, and the addition of the separate components as a function of the oxygen coverage on the copper component. To make this graph the same type of comparison as figure 6.11, the amount of $[\text{CH}_2\text{O}]_{\text{methoxy}}/\text{CH}_3\text{OH}$ from the copper component of the ZnO$_x$/Cu(110) surface was discarded as [CO$_2$]$_{\text{formate}}$/CH$_3$OH is not produced from the copper component of ZnO$_x$/Cu(110) surfaces while [CH$_2$O]$_{\text{methoxy}}$/CH$_3$OH is produced.
ML O/Cu(110) surface.) This is consistent with previous studies which have shown methanol to be a minor product in methanol TPD from ZnO(0001) surfaces [9] while methanol has been shown to be a major product from methanol interaction with oxygen modified Cu(110) [5].

Figure 6.13 shows that the amount of methanol desorbed as a function of the number of methanol TPD experiments for both a ZnOx/0.5 ML O/Cu(110) and a 0.5 ML O/Cu(110) surface is the same, and increases with decreasing amounts of \( \theta_{\text{oxygen}}/\text{Cu(110)} \). It is surprising, at first, that the amount of desorbed methanol is the same for the two surfaces. If the amount of desorbed methanol was a function only of the oxygen coverage on Cu(110), then we would expect to see one curve offset from the other on the y-axis, with the ZnOx/O/Cu(110) surface obtaining the maximum more rapidly due to a faster loss of chemisorbed oxygen on Cu(110). Instead, we have overlapping curves for the two surfaces. The offset is within our 20% error bar for methanol desorption area. Hence, it is difficult to say whether the total amount of methanol desorption changes in the presence of ZnOx islands.

**Source for Surface Oxygen**

We used O\(_2\) in our studies to produce surface oxygen. Under industrial conditions, surface oxygen is produced from CO\(_2\), either by

\[
\text{CO}_2 \rightarrow \text{O}_{(\text{surface})} + \text{CO}
\]

or

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO} \rightarrow \text{O}_{(\text{surface})} + \text{CO} + 2\text{H}_{(\text{surface})}.
\]

Hence, we attempted to oxidize the Cu-Zn-O surfaces with CO\(_2\) and H\(_2\)O after reduction of the surface with methanol TPD experiments. ZnO\(_x\)/Cu(110) surfaces were annealed at 560 K in \(1 \times 10^{-4}\) Torr CO\(_2\) for 10 minutes. There was an increase in the AES spectrum for both the oxygen and carbon peaks due to carbonate formation. After the surface carbonates had been decomposed by heating in vacuum, methanol TPD indicates that the surface has not been oxidized by CO\(_2\). Heating
Figure 6.13: Amount of methanol desorbed for each 2.0 L dose of methanol for a ZnOx/0.5 ML O/Cu(110) surface and a 0.5 ML O/Cu(110) surface as a function of the number of methanol TPD experiments.
the reduced ZnOx/Cu(110) surface in $1 \times 10^{-8}$ Torr H$_2$O at 560 K for 10 minutes produced no change as detected by AES, LEED, and methanol TPD.

We were unable to produce surface oxygen from either CO$_2$ or H$_2$O due to our limits to low pressures. It has been shown that under the high pressures used in industry (>20 atm), there is a direct correlation between CO$_2$/CO feed ratio and the amount of chemisorbed oxygen on the copper surface [4]. Hence, although the source of surface oxygen under industrial conditions is CO$_2$, we have used O$_2$ due to the inability of CO$_2$ to dissociate on ZnOx/Cu(110) surfaces at low pressures.

6.4 Discussion

Wachs and Madix [5] have shown that [CO$_2$]$_{formate}$, [CH$_2$O]$_{methoxy}$, and CH$_3$OH production from CH$_3$OH exposure are all affected by pre-adsorbed oxygen on Cu(110). We show in this chapter that for the three-component system of ZnOx/O/Cu(110), O/Cu(110) affect [CO$_2$+CO]$_{formate}$/CH$_3$OH production on the ZnOx component as well. In addition to promoting [CO$_2$+CO]$_{formate}$/CH$_3$OH production on the ZnOx component, the oxygen on the copper component helps to keep zinc oxidized.

By following the decomposition products of CO$_2$, CO, and CH$_2$O, we have shown that the three-component system of ZnOx/O/Cu(110) has a promotional effect on the production of formate species, but not on the production of methoxy species. In addition, the relative ratio of [CO$_2$]$_{formate}$/CH$_3$OH to [CH$_2$O]$_{methoxy}$/CH$_3$OH changes from 1:9 on 0.2-0.3 ML O/Cu(110) to 1:3 on ZnOx/0.2-0.3 ML O/Cu(110) surfaces, indicating that the three component system has a higher concentration of surface formate. Detailed studies by various investigators [2,15] have shown formate species to be the common and most long-lived intermediate on Cu/ZnO/Al$_2$O$_3$ catalysts, ZnO catalysts, and polycrystalline copper. They argue that methanol is produced from carbon dioxide and hydrogen reacting to form formate species. These investigators [2], along with others [1], have also found that the more active Cu-Zn-O methanol synthesis catalysts have 30-60% of their copper surface area covered with oxygen after reaction in CO$_2$, CO, and H$_2$. Assuming each oxygen atom blocks two copper sites (this is a good approximation in the O/Cu(110) case), these methanol
synthesis catalysts are covered with 0.15-0.30 ML of oxygen. We have shown above that the maximum in total formate production ([CO₂+CO]formate/CH₃OH production) on the three-component system occurs when the Cu(110) component contains 0.2-0.3 ML oxygen. Though the maximum in formate production from the addition of the separate components is also 0.2-0.3 ML oxygen on Cu(110), its maximum is only half of the maximum produced in the three-component system. We propose that one of the roles of oxygen on the copper component is to increase the amount of formate formation. This suggestion is consistent with recent findings that Cu/ZnAl₂O₄ catalysts produce 20 times the amount of formate than ZnAl₂O₄ catalysts from CO₂+H₂ feed [16]. These Cu/ZnAl₂O₄ catalysts were shown to contain chemisorbed oxygen on the copper component. Hence, both the model ZnOₓ/O/Cu(110) surfaces and the working Cu/ZnAl₂O₄ catalysts show a promotional effect for formate formation with chemisorbed oxygen on the copper component.

We have seen that the other effect of O/Cu(110) is to help keep the ZnOₓ component oxidized. This role is most likely not a prominent one in the working catalyst as there is bulk ZnOₓ to draw surface oxygen from in the industrial catalyst, but this role of O/Cu(110) may be important in avoiding Cu-Zn alloy formation which could reduce the active surface area.

6.5 Conclusion

We have shown that the amount of surface oxygen on the Cu(110) part of the catalyst determines the amount of formate produced on the ZnOₓ component of the surface as well as the O/Cu(110) component of the surface. The three component system of ZnOₓ islands on Cu(110) with 0.2-0.3 ML oxygen on the Cu(110) part produced twice the amount of formate than the maximum reached with the addition of the separate components. In contrast, we saw no promotional effect of the three-component system on methoxy formation. The relative ratio of surface formate to methoxy species increases from 1:9 in the case of 0.2-0.3 ML O/Cu(110) to 1:3 in the case of ZnOₓ/0.2-0.3 ML O/Cu(110). In addition to promoting total formate
production, the O/Cu(110) helps keep the ZnO\textsubscript{x} islands oxidized.
References

Appendix A

High Pressure Studies

Throughout this thesis, a number of suggestions have been made concerning the rôle of different copper faces and the rôle of chemisorbed oxygen on the copper component of Cu-Zn-O methanol synthesis catalysts. These suggestions need to be tested under methanol synthesis conditions; high pressure (>20 atm) and 500-570 K.

In order to do this, we attempted high pressure studies in a combined ultra-high vacuum/high pressure (UHV/HP) chamber. The model catalysts were characterized in UHV, and then enclosed in a high pressure cell and heated resistively to reaction temperatures. This approach proved unsuccessful because of the limitations of the existing high pressure apparatus to be tailored to the Cu-Zn-O system. I do believe that it is possible to perform high pressure studies on model copper and Cu-Zn-O catalysts, but not without major changes from the experimental approach I had started with. Below, I discuss the major problems I have encountered while working with this particular catalytic system and some of the possible solutions:

1. In order to resistively heat the sample to 500 K, extremely large currents (100 amps) were required. When such large currents are passed through the sample, then manipulator parts and the high pressure reaction cell and loop are heated, and produce reaction products. Large amounts of current were needed to heat the copper samples due to the low electrical resistivity of copper (1.678 microhm-cm for copper at 293 K) and the high pressures of hydrogen which removed the heat from the copper by thermal conduction. Using resistive heating with 1.0 inch long 20 mil gold support wires, and
10 mil copper foil as the model catalyst, a current of 100 amps was needed in order to reach a sample temperature of 500 K, the point at which methanol production can be detected by gas chromatography. The current required to reach a sample temperature of 500 K could be reduced to 50 amps by using 20 mil gold wires, 0.5 inch long, and copper foil 1.0 mil thick. Clearly, one needs as thick and as short a supporting wire as is experimentally feasible in order to reduce the current needed to heat the sample. However, it became difficult to spot-weld copper to gold once the copper foil was thinner than 1.0 mil and the gold support wires were thicker than 20 mil. Copper support wires at 0.5 inch was as short as experimentally feasible to mount a sample 0.4 inch long. In spite of the reduction in current to 50 amps, manipulator parts and the high pressure loop and cell still produced reaction products on the order of those produced by the model copper catalyst; a clearly undesirable situation.

2. The second problem is that of low surface area and reactivity of the copper surface compared to the high surface area and reactivity of the reaction cell. The stainless steel cell and loop has a total surface area of 250 cm$^2$. The model catalysts have a surface area $\sim$1 cm$^2$ and consist of one of the least reactive of metals – copper. In order to minimize the background activity, water cooling lines around the high pressure cell were installed. Cooling the high pressure cell with ice water reduced its activity, but it was not possible to reduce the background activity to an order in magnitude less than that of the sample.

It is evident that resistive heating of copper under high pressures is inappropriate. A more suitable method of heating under these circumstances would be using microwaves. The microwaves would heat up the reactant gases of CO, CO$_2$, and H$_2$, which in turn would heat up the copper sample. This method of heating the 1 cm$^2$ model catalyst should reduce the temperature of the manipulator during reaction. To further reduce reaction on the manipulator parts, the manipulator should be coated with approximately 1 mil gold film.
In addition to reducing the temperature of the manipulator parts during reaction, microwave heating will also enable the use of copper samples thicker than 1.0 mil. This is an essential prerequisite to working with copper single crystals, as it is difficult to polish single crystals thinner than ~10 mil.

Although the use of microwaves should reduce the heating up of manipulator parts, the high partial pressures of hydrogen under reaction conditions will most likely carry significant amounts of heat to the manipulator, and the high pressure cell and loop. In order to reduce the activity of the reaction cell and loop, it is best to use an inert substrate such as glass. I believe that with a glass reactor and the sample heated with microwaves, the formation of methanol under high pressures from small area copper samples can be examined. This will enable the elucidation of the effect of copper structure and ZnO₂ overlays on methanol production under industrial conditions.
Appendix B

Cu-Zn-O Phase Diagram

In this thesis, we examined Cu-Zn-O interaction on the surface of copper single crystals. For comparison to bulk studies, I have reproduced a copy of a Cu-Zn-O phase diagram below. This phase diagram was obtained from Dr. Church at the International Copper Association.

1.20 Solubility limits, Cu-Zn-O.