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The Surface Chemistry of Vanadium Oxide Catalysts

K.B. Lewis, Jr.
(Ph.D. Thesis)

September 1988

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THE SURFACE CHEMISTRY OF VANADIUM OXIDE CATALYSTS

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Ph.D. Thesis

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September, 1988

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
The Surface Chemistry of Vanadium Oxide Catalysts

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Ph.D. Thesis

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Abstract

The surface chemistry of vanadium oxide catalysts was studied using UHV surface techniques and catalytic experiments at atmospheric pressure. In UHV, vanadium oxide films were grown on single crystal vanadium, Au(111), and Au foil substrates. Silica supported $V_2O_5$ was used in the catalytic experiments.

Auger electron spectroscopy and low energy electron spectroscopy revealed temperature dependent surface segregation of contaminants on the V(110) surface. Several cleaning procedures were used to remove persistent sulfur contamination. High temperature hydrogen treatment and argon ion sputtering at several temperatures were effective. Temperature programmed desorption revealed both a surface and a bulk desorption state for hydrogen, and two desorption states for potassium on V(110). Recrystallized foils containing large grains with a V(100) orientation were also examined.

Vanadium oxide films grown on a Au(111) substrate were ordered and exhibited a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. The growth mode and preparation of these films is discussed. The structure and Auger spectrum of the films were consistent with a $V_2O_3$ surface. The TPD of hydrogen, ethanol, and ethylene were examined on this surface. The peak temperatures for the desorption of $H_2O$, CO, and $CO_2$ were sensitive to the surface oxidation state.

Polycrystalline $V_2O_5$ supported on Au foil was also studied. An oxidized surface was maintained through the facile surface segregation of lattice oxygen above 750 K. Two water desorption peaks were observed after the adsorption of pre dissociated hydrogen. CO, $CO_2$, and $C_2H_4$ were the principle desorption products after
ethanol adsorption in UHV and at atmospheric pressure.

The partial oxidation of methane and ethanol over V$_2$O$_5$-SiO$_2$ was investigated. Methane oxidation with N$_2$O proceeded very slowly, however activation energies and rate laws were determined.. Ethanol oxidation with O$_2$ was more rapid. Catalyst dispersions were measured using irreversible oxygen uptake following reduction at 641 K. Ethanol partial oxidation was structure insensitive. The catalytic results were consistent with the the UHV results from gold-supported samples.
## Contents

Dedication \( \text{v} \)

Acknowledgements \( \text{vi} \)

List of Figures \( \text{viii} \)

List of Tables \( \text{xi} \)

1 Introduction \( \text{1} \)
   1.1 Vanadium Oxide Surfaces \( \text{2} \)
   1.2 Solid State Chemistry of Vanadium Oxide \( \text{5} \)
   1.3 Catalytic Properties of Vanadium Oxide \( \text{9} \)
   1.4 Summary and Questions to be Addressed \( \text{11} \)

2 Experimental \( \text{13} \)
   2.1 Introduction \( \text{13} \)
   2.2 General \( \text{16} \)
      2.2.1 Materials Preparation \( \text{16} \)
      2.2.2 Sample Mounting \( \text{18} \)
      2.2.3 Electron, Ion and X-Ray Formation \( \text{20} \)
      2.2.4 Energy and Mass Selection \( \text{26} \)
      2.2.5 Electron and Ion Detection \( \text{30} \)
   2.3 Utilization of Specific UHV Techniques \( \text{32} \)
      2.3.1 LEED \( \text{32} \)
# CONTENTS

2.3.2 Auger Electron Spectroscopy ........................................... 33  
2.3.3 XPS ................................................................. 36  
2.3.4 Ion Scattering Spectroscopy ........................................... 39  
2.3.5 Temperature Programmed Desorption .................................. 39  
2.4 Preparation and Characterization of Gold-Supported $V_2O_5$ .......... 41  
2.4.1 Epitaxial $V_2O_3$ on Au(111) ..................................... 41  
2.4.2 $V_2O_5$ on Au Foil .................................................. 42  
2.5 Preparation and Characterization of High Surface Area Catalysts .... 46  
2.5.1 Catalyst Preparation .................................................. 46  
2.5.2 Apparatus and Methods ................................................ 47  
2.5.3 Raman Spectroscopy ................................................... 51  

3 The Surface Chemistry of Vanadium Metal .................................. 53  
3.1 Introduction ........................................................................ 53  
3.2 Results ............................................................................. 55  
3.2.1 Sample Cleaning: Hydrogen Treatment and Contaminant Segregation .......................................................... 55  
3.2.2 LEED ................................................................. 59  
3.2.3 Reactivity, TPD and Oxidation Experiments ....................... 62  
3.3 Discussion ....................................................................... 66  
3.4 Conclusions and Recommendations ....................................... 70  

4 Vanadium Oxide on Au(111) ..................................................... 72  
4.1 Introduction ...................................................................... 72  
4.2 Methodology .................................................................... 73  
4.3 Results ........................................................................... 75  
4.3.1 Vanadium Deposition and Oxidation ................................ 75  
4.3.2 Film Growth Mechanism and Coverage Determination .......... 76  
4.3.3 Composition of Vanadium Oxide on Au(111) ....................... 78  
4.3.4 Structure of Vanadium Oxide on Au(111) ......................... 78  
4.3.5 Chemisorption of Hydrogen, Ethanol, and Ethylene ............... 80
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4.2 Film Growth Mechanism and Coverage Determination</td>
<td>84</td>
</tr>
<tr>
<td>4.4.3 Composition of Vanadium Oxide on Au(111)</td>
<td>85</td>
</tr>
<tr>
<td>4.4.4 Structure of Vanadium Oxide on Au(111)</td>
<td>85</td>
</tr>
<tr>
<td>4.4.5 Chemisorption of Hydrogen, Ethanol, and Ethylene</td>
<td>86</td>
</tr>
<tr>
<td>4.5 Summary</td>
<td>87</td>
</tr>
<tr>
<td>5 V$_2$O$_5$ on Gold Foil</td>
<td>89</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>89</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>90</td>
</tr>
<tr>
<td>5.3 Results</td>
<td>91</td>
</tr>
<tr>
<td>5.3.1 Temperature Programmed Decomposition</td>
<td>91</td>
</tr>
<tr>
<td>5.3.2 Temperature Programmed Reduction</td>
<td>93</td>
</tr>
<tr>
<td>5.3.3 Adsorption of Ethanol and Related Molecules</td>
<td>96</td>
</tr>
<tr>
<td>5.4 Discussion</td>
<td>98</td>
</tr>
<tr>
<td>5.5 Conclusions</td>
<td>102</td>
</tr>
<tr>
<td>6 Catalysis over V$_2$O$_5$-SiO$_2$</td>
<td>105</td>
</tr>
<tr>
<td>6.1 Introduction</td>
<td>105</td>
</tr>
<tr>
<td>6.1.1 CH$_4$ Partial Oxidation with N$_2$O</td>
<td>108</td>
</tr>
<tr>
<td>6.1.2 Oxygen Chemisorption</td>
<td>112</td>
</tr>
<tr>
<td>6.1.3 Dispersion of V$_2$O$_5$-SiO$_2$ Catalysts</td>
<td>114</td>
</tr>
<tr>
<td>6.1.4 Ethanol Partial Oxidation with O$_2$</td>
<td>114</td>
</tr>
<tr>
<td>6.1.5 Raman Spectroscopy of V$_2$O$_5$-SiO$_2$</td>
<td>121</td>
</tr>
<tr>
<td>6.2 Discussion</td>
<td>121</td>
</tr>
<tr>
<td>6.3 Conclusions</td>
<td>126</td>
</tr>
<tr>
<td>7 Conclusions</td>
<td>127</td>
</tr>
<tr>
<td>A Chamber Design</td>
<td>134</td>
</tr>
<tr>
<td>A.1 Pumping and Bell Jar</td>
<td>134</td>
</tr>
<tr>
<td>A.2 Analytical Instrumentation</td>
<td>138</td>
</tr>
</tbody>
</table>
CONTENTS

A.1 Pumping and Bell Jar ............................................. 134
A.2 Analytical Instrumentation ....................................... 138
A.3 Sample Manipulation .............................................. 141
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## List of Figures

1.1 Reactions on oxide surfaces ........................................ 3  
1.2 V-O phase diagram ................................................... 5  
1.3 Structure of $V_2O_5$ ................................................ 7  
1.4 Pressure-temperature phase diagram for Vanadium-Oxygen .... 8  

2.1 Universal curve for the escape depth of electrons ............. 15  
2.2 Methods of mounting samples. ...................................... 19  
2.3 Components of an electron gun ................................... 20  
2.4 Secondary electron emission ....................................... 23  
2.5 Relative geometry and potentials of a gas ionizer. .......... 24  
2.6 Ion gun modification ............................................... 25  
2.7 Retarding field analyzer showing potentials for LEED and AES. 27  
2.8 Double pass cylindrical mirror analyzer ........................ 29  
2.9 Channeltron ........................................................... 31  
2.10 Effect of operating parameters on Auger peak heights ....... 34  
2.11 Effects of scan rate on relative Auger peak heights .......... 35  
2.12 Changes in Auger electron spectra accompanying vanadium oxidation 37  
2.13 Plot of Auger electron spectra changes as a function of oxidation state. ......................................................... 38  
2.14 Aperature and shield surrounding quadrupole mass spectrometer. . 40  
2.15 SEM of $V_2O_5$/Au foil ............................................ 43  
2.16 XPS spectra of $V_2O_5$/Au foil ................................... 44  
2.17 Raman spectra of $V_2O_5$/Au foil ................................. 45  

viii
LIST OF FIGURES

2.18 Flow adsorption measurement technique ........................................ 48
2.19 Packed-bed catalytic reactor ......................................................... 50

3.1 V(110) and V(100) surfaces ............................................................ 55
3.2 V-H phase diagram ........................................................................... 57
3.3 Surface segregation of contaminants .................................................... 58
3.4 LEED: V(110)-O c(6×2) .................................................................. 60
3.5 Recrystallized vanadium foil ............................................................. 61
3.6 TPD spectra after D₂ adsorption on V(110) .......................................... 63
3.7 TPD spectra after potassium adsorption on V(110) ............................... 64
3.8 Oxidation of V(110) ........................................................................... 65
3.9 Oxide precipitates on V(110) .............................................................. 67

4.1 Growth of vanadium oxide films on Au(111) ....................................... 74
4.2 Dissolution of metallic vanadium in Au(111) ....................................... 75
4.3 Uptake of vanadium oxide on Au(111) ................................................ 77
4.4 LEED: vanadium oxide on Au(111) .................................................... 79
4.5 TPD spectra of H₂O desorption from vanadium oxide on Au(111) ......... 81
4.6 TPD spectra after ethanol adsorption on vanadium oxide on Au(111) .... 82
4.7 TPD spectra after ethylene adsorption on vanadium oxide on Au(111) 83

5.1 O₂ desorption from V₂O₅/Au foil ....................................................... 92
5.2 H₂O desorption from V₂O₅/Au foil + hydrogen ................................... 94
5.3 AES spectra of V₂O₅/Au foil + hydrogen ........................................... 95
5.4 TPD spectra after D₆-ethanol adsorption on V₂O₅/Au foil ................. 97
5.5 TPD spectra after C₂H₄ adsorption on V₂O₅/Au foil ............................ 98
5.6 TPD of V₂O₅/Au foil + 10 Torr ethanol .............................................. 99

6.1 Energetics of methane oxidation ....................................................... 106
6.2 Activation energies for methane partial oxidation ............................... 110
6.3 Dependence of reaction rates on steam concentration ........................ 111
6.4 TPR spectrum of V₂O₅ ................................................................. 112
LIST OF FIGURES

6.5 Oxygen uptake on V₂O₅ ............................................. 113
6.6 Oxygen uptake as a function of reduction temperature .......... 115
6.7 XRD spectra of reduced V₂O₅ ....................................... 116
6.8 O₂ uptake on V₂O₅-SiO₂ Catalysts ................................. 117
6.9 Dispersion curve for V₂O₅-SiO₂ catalysts .......................... 118
6.10 Conversion and selectivity for ethanol oxidation .................. 119
6.11 Activation energies for ethanol oxidation ........................... 120
6.12 Raman spectra of V₂O₅-SiO₂ catalysts .............................. 122
6.13 Raman spectra of 1.4% V₂O₅-SiO₂ + ethanol ..................... 123

A.1 Schematic diagram of the pumping and gas manifold for the UHV
    chamber. ................................................................. 135
A.2 Photograph and schematic diagram of UHV chamber ............... 139
## List of Tables

1.1 Vanadium oxide-catalyzed reactions ............................. 9

2.1 Molar sensitivity factors for mass spectrometer signal .......... 40

6.1 Reaction rates for methane partial oxidation .................. 109
Chapter 1

Introduction

Vanadium (IV and V) oxides exhibit catalytic activity for a wide variety of partial oxidation reactions. Common to all these reactions are high selectivity for partial oxidation products and a multistep oxidation-reduction mechanism. The high selectivity arises from the participation of lattice oxygen rather than chemisorbed oxygen in the oxidation reaction. During catalytic reactions over vanadium oxide, the surface is continuously reduced and reoxidized as lattice oxygen is removed and replaced. An understanding of the changes in the vanadium oxide surface accompanying each step in a catalytic reaction is necessary to understand the high selectivity of these catalysts. In the following chapters I will discuss the preparation of several vanadium oxide samples in high and Ultra-High Vacuum (UHV) environments. These samples were used to study the changes in vanadium oxide surfaces which accompany the adsorption and desorption of molecules relating to catalytic oxidation. Catalytic studies on model vanadium oxide catalysts will also be discussed.

Much of the published literature on vanadium oxide relates to either the physics of clean, low surface area vanadium oxide samples or the catalytic properties of poorly characterized, high surface area catalysts. This work combines these two types of studies by examining specific reaction steps from the catalytic oxidation of methane and ethanol on low surface area samples in UHV and comparing the energetics of these reactions with kinetic data from parallel studies on vanadium oxide catalysts. Figure 1.1 illustrates some of the processes occurring on a vanadium
oxide surface during a catalytic reaction:

1. The adsorption reactant molecules
2. The abstraction of surface oxygen and desorption of oxidized products
3. The replacement of surface oxygen via adsorption from the gas phase or diffusion of bulk oxygen to the surface

The adsorption of molecules as a function of the oxidation state and the structure of the surface can be studied in UHV. Desorption processes can also be observed using mass spectrometry. Whether in UHV or in an atmospheric pressure reaction mixture, the reoxidation reaction is generally rate limiting. However, in both UHV and catalytic studies, limited oxidation will occur even in the absence of gas phase oxidant through diffusion of bulk oxygen to the surface. The temperature at which this occurs can be determined from UHV studies and provides an estimate of the degree of interaction between bulk and surface at various temperatures.

1.1 Vanadium Oxide Surfaces

Previous research on vanadium oxide and other oxide surfaces illustrates some common problems encountered in UHV studies of oxides. All oxide surfaces undergo reduction in the presence of electron beams and ion beams. Electron beams stimulate oxygen desorption and ion beams reduce the surface through selective sputtering of oxygen. The rate of damage appears to be inversely related to the electrical conductivity of the sample, with insulating samples being damaged the most. Vanadium pentoxide, $V_2O_5$ is an insulator. However, slightly non-stoichiometric $V_2O_5$ and the lower oxide derived through its reduction, $V_6O_{13}$, are conductive. $V_6O_{13}$ grown on $V_2O_5$ is stable even when exposed to an electron beam[1]. The presence of hydrogen or carbon impurities, which are always present under catalytic conditions, increases reduction rates through $H_2O$, CO and $CO_2$ desorption.
Figure 1.1: Processes occurring on a vanadium oxide surface during a reaction. The surface is reduced when the oxidized products desorb and is later reoxidized from the gas phase or bulk oxygen diffusion.
The temperature dependent reduction in an electron beam can be used to determine at what temperature facile diffusion of oxygen from the bulk to the surface occurs. This is necessary to understand whether gas-surface-bulk or gas-surface reactions are occurring in a particular temperature range. At temperatures slightly below that for vacuum decomposition of vanadium oxide (800 K), diffusion of oxygen from the bulk of the sample rapidly reoxidizes the surface. This effect can be observed by following the temperature dependence of the LEED pattern for V_2O_5 (010) and topotactic V_6O_{13}. At room temperature the electron beam reduces the V_2O_5 surface to V_6O_{13} while at 750 K the surface remains oxidized to V_2O_5. At 750 K the surface oxygen desorbed by the electron beam is immediately replaced by oxygen from the bulk[2]. Even though vanadium is difficult to oxidize to the +5 oxidation state at low pressures of O_2, the surface segregation of bulk oxygen can be used to maintain highly oxidized surfaces on bulk oxide samples[3].

Similar behavior has been seen with MoO_3 and WO_3 surfaces. Facile diffusion of oxygen occurs in the same temperature range as for V_2O_5[4]. In several of these studies Ultra-Violet Photoelectron Spectroscopy (UHV) was used to monitor the occupation of the metal valence bands. Any exposure of the sample to an electron beam reduced the surface. The reduction observed in UPS spectra was reversible. Annealing at approximately 750 K restored the oxidized surface. Auger Electron Spectroscopy (AES), my principle spectroscopic technique, will not detect such changes. I use surface structure and adsorption behavior as more sensitive probes of the oxidation state of the surface.

The reactivity of the vanadium oxide will be determined by the oxidation state and structure of the surface. At low temperatures, reduction and reaction is limited to the surface of vanadium oxide. At higher temperatures (750 K) diffusion of oxygen couples reactions at the surface with reactions in the bulk. This is not the case for metal surfaces, where surface and solid state reactions are independent or occur on very different time scales.
1.2 Solid State Chemistry of Vanadium Oxide

Working vanadium oxide catalysts have a formal stoichiometry between $V_2O_4$ and $V_2O_5$[6]. As figure 1.2 illustrates, there are at least three distinct phases present in this range of oxidation states[5,7]. Allowing for the possibility of surface phases and phase boundaries, almost any combination of $V^{+4}$ and $V^{+5}$ on the surface could be active for catalysis. The bulk structures of the higher oxidation state phases are related[8,9,10,11]. Vanadium pentoxide, $V_2O_5$, is comprised of zig-zag chains of asymmetric, edge-linked VO$_6$ octahedra which are corner linked to adjacent chains to form sheets. The sheets are corner linked to create the layered structure shown in figure 1.3 [12]. As oxygen is removed from these oxides,
anion vacancies (the principle form of defect) order over long ranges. Even at low defect concentrations, the structure collapses along shear planes to eliminate oxygen vacancies, making double and quadruple zig-zag chains of edge sharing VO$_6$ octahedra[13]. A similar relation is seen in the structure of titanium and molybdenum oxides[14]. The structure of V$_6$O$_{13}$ is very similar to that of V$_2$O$_5$ and V$_6$O$_{13}$ will grow topotactically on a V$_2$O$_5$ (010) surface. V$_6$O$_{13}$ is often assigned as the active phase in vanadium oxide catalysts[9]. The structure of other vanadium oxide compounds, including amorphous V$_2$O$_5$, is also based on zig-zag chains of VO$_6$ octahedra[15]. The “octahedra” are asymmetric with one short V=O bond opposite an often uncoordinated site, and four shorter V-O bonds (see figure 1.3).

The vanadyl oxygen (V=O) is believed to be the active site for nucleophilic hydrogen abstraction in catalytic reactions, and its reactivity depends on what is coordinated to the other five sites on the vanadium ion[16]. Hydroxyl groups and other metal cations in the structure can change the local octahedral structure substantially. Good examples of this can be seen in the structures of vanadium oxyhydroxides, vanadium bronzes, and mixed V + Mo oxides[17,18,19,20].

Figure 1.2 shows which bulk vanadium oxide phases can exist in a working catalyst. A pressure-temperature phase diagram, as shown in figure 1.4, or a free energy diagram, relates the stability of these oxide phases to the temperature and oxygen pressure over the oxide[7,21,22]. This type of phase diagram is useful in determining the suitability of oxide phases for study in UHV. Such diagrams, however have their limitations. It will become evident in the following chapters that the reduction of vanadium oxides, especially in the presence of carbon and hydrogen, proceeds more rapidly than oxidation and that equilibrium conditions are seldom met[23]. A poor understanding of the kinetics of gas-surface reactions has hindered previous research studying the equilibrium pressure of oxygen over vanadium oxide and the kinetics of oxygen diffusion in various vanadium oxide phases[24,25,26,27]. Both types of information are necessary to understand the interrelation of vanadium oxide bulk and surface chemistry in catalysis.
Figure 1.3: Structural models of $V_2O_5$: a.) ball and stick b.) space filling c.) $VO_6$ octahedron. [12]
Figure 1.4: Pressure-temperature phase diagram for Vanadium-Oxygen[7].
CHAPTER 1. INTRODUCTION

<table>
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<th>Reactant</th>
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<td>V₂O₅ + MoO₃</td>
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<td>nd</td>
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<td>o-Xylene</td>
<td>Phthalic Anhydride</td>
<td>V₂O₅/SiC</td>
<td>460</td>
<td>nd</td>
<td>[6]</td>
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</tr>
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<td>10⁻²-10⁻⁴</td>
<td>[34]</td>
</tr>
</tbody>
</table>

Table 1.1: Partial listing of reactions catalyzed by vanadium oxide. nd = not determined.

1.3 Catalytic Properties of Vanadium Oxide

Vanadium oxide based catalysts are used to selectively oxidize alcohols, olefins, and aromatics. Table 1.1 shows a partial listing of reactions catalyzed by vanadium oxide. Typical turnover rates are relatively low (10⁻²–10⁻⁴ molec site⁻¹s⁻¹). The high selectivity of the catalyst for specific reactions is of primary importance. Often H₂O is added as a reactant to improve the reaction selectivity by helping partial oxidation products desorb. The high selectivity of vanadium oxide surfaces, in addition to the coupling of surface and bulk reactions at elevated reaction temperatures, presents the surface scientist with a variety of questions.

Vanadium oxides are very anisotropic, with many different vanadium and oxygen sites, so that a simple consideration of periodic trends, without considering oxide structure are not very useful in explaining reaction mechanisms. Activity in vanadium oxide based catalysts correlates with V⁴⁺ concentration in o-xylene oxidation[35] and V=O concentration in furan and butane oxidation[36,37]. V₂O₅
and V$_2$O$_4$ are generally considered to be inactive with the active catalyst phase falling somewhere between the two[38]. However, average oxidation states are misleading. Visual color changes (from orange to blue-green), as well as x-ray diffraction show that the bulk oxidation state of a fixed catalyst bed changes across the length of reactor[6]. This suggests that the same surface structure may exist for a range of bulk phases. Many reaction mechanisms propose shearing mechanisms which rearrange and stabilize the vanadium oxide surface after lattice oxygen removal. This mechanism is consistent with the solid state chemistry of mixed valent vanadium oxides. UHV studies on well characterized surfaces can shed some light on the exact nature and location of the active sites (V$^{+4}$ or V=O) on vanadium oxide catalysts, and the surface rearrangements accompanying catalytic reactions.

The presence of structure sensitivity in a catalytic reaction is an indication that the active site for a reaction lies on a particular crystal face of the catalyst. The structures of crystalline vanadium oxides are very anisotropic, with different crystal faces displaying very different oxygen species. However, both crystalline and supported V$_2$O$_5$ exhibit similar reactivity for some reactions[39]. Since only a limited number of surface structures are shared by crystalline and supported vanadium oxide, the proven presence or absence of structure sensitivity in a chemical reaction would aid greatly in the understanding of specific active sites or ensembles for that reaction.

Our initial interest in the surface chemistry of vanadium oxide arose from its ability to partially oxidize alkanes. Reactivity for these reactions was too low for UHV studies on low surface area samples to be performed. However, the partial oxidation products of alkane oxidation, alcohols, are also oxidized by V$_2$O$_5$ catalysts. The selective oxidation of alcohols to aldehydes and carboxylic acids occurs much faster than the oxidation of alkanes. Ethanol partial oxidation was studied in detail in this research.
1.4 Summary and Questions to be Addressed

The distinction between the bulk and the surface chemistries of vanadium oxide is difficult to make. The oxidation state and structure of the surface is clearly related to both the catalytic reactions occurring over the surface and the solid state reactions occurring in the bulk. The structures of \( \text{V}_2\text{O}_5 \) and oxides derived through its reduction are anisotropic, and both the number of V=O species and the number of \( V^{+4} \) ions correlate with catalytic activity. An active site common to both crystalline and supported \( \text{V}_2\text{O}_5 \) catalysts is probable. Reduction of \( \text{V}_2\text{O}_5 \) occurs much more readily than gas phase oxidation; however, this does not prohibit reoxidation of the surface via oxygen segregation from the bulk.

With these guidelines in mind it is clear that oxidation of reduced vanadium oxide is difficult at best and that samples may be easier to prepare by reduction of \( \text{V}_2\text{O}_5 \) rather than by oxidation of metallic vanadium. However, reoxidation of vanadium oxide is only one step in catalytic reactions, a step which can be omitted for short periods of time allowing other reactions to be studied.

My research has addressed the following questions:

- Chapter 3: Can vanadium single crystals be used as substrates on which to grow clean, ordered vanadium oxide films?

- Chapter 4: Can clean, ordered films of vanadium oxide be grown on Au(111)? What is their structure? What is their composition? How do they react with hydrogen, ethanol, and ethylene?

- Chapter 5: Is \( \text{V}_2\text{O}_5 \) supported on gold foil stable in UHV? What is its structure? What is its surface composition? How does it react with hydrogen, ethanol, and ethylene?

- Chapter 6: What are the kinetics of methane partial oxidation over \( \text{SiO}_2\text{-V}_2\text{O}_5 \)? How can the active surface area of supported \( \text{V}_2\text{O}_5 \) be measured? Is the partial oxidation of ethanol over \( \text{SiO}_2\text{-V}_2\text{O}_5 \) structure sensitive?
By carefully preparing and characterizing vanadium oxide surfaces and by isolating single steps in the reactions of ethanol and other organic molecules with a $\text{V}_2\text{O}_5$ surfaces, I have attempted to answer these questions.
Chapter 2
Experimental

2.1 Introduction

Since meaningful interpretation of data requires an understanding of the operation of instruments used to collect it, this chapter will present the correct operation of a UHV chamber and accompanying instruments. Detailed data interpretation will be presented in the following chapters. Additional theoretical information concerning experimental techniques is best obtained from other sources. [40,41,42]

The tools of a surface scientist are techniques involving electrons, ions and molecules. Regardless of how they are produced, all of these particles interact with, or originate in, only the top few atomic layers of a sample. Low Energy Electron Diffraction (LEED) utilizes low energy (0–300 eV) electrons diffracted by the periodicity of an ordered surface. Auger Electron Spectroscopy (AES), analyzes Auger electrons in the 0–2000 eV range excited by either 1.5–3 kV electrons or x-rays. X-ray Photoelectron Spectroscopy (XPS or ESCA) and Ultra-Violet Photoelectron Spectroscopy (UPS) analyze photoelectrons, in the same energy range as Auger electrons, which have been emitted by a sample after excitation using photons. Ions can be used to clean the surface, as in Argon Ion Sputtering (Ar\(^+\) with 500–2000 eV energy), or can be analyzed spectroscopically, as in Ion Scattering Spectroscopy (ISS or LEIS) to yield information about the elemental composition of a surface. Additionally, molecular fragments sputtered from a sur-
face can be detected with mass spectrometry (MS) to yield information on surface composition and bonding as in Secondary Ion Mass Spectroscopy (SIMS). In Temperature Programmed Desorption (TPD) molecules can be adsorbed, reacted, and desorbed from surfaces using MS detection.

The universal curve depicted in figure 2.1 shows the approximate escape depths for electrons in the energy range normally studied. Electrons emitted from the sample after any type of excitation will originate in the top 3 to 5 atomic layers of a sample. This is what gives electron spectroscopy its surface sensitivity. The universal curve is a result of the high cross section for interaction between the electrons used for spectroscopy and electrons with similar energy in the sample. Electrons with energies much lower or much higher than the electrons of sample atoms will have a low cross section for interaction, hence a large escape depth.

In order for electrons and ions to have a long enough mean free path to reach the spectrometer after leaving the sample, a high vacuum ($10^{-7}$ Torr) or ultra-high vacuum (UHV) environment ($10^{-8}$ to $10^{-11}$ Torr) is required. The experimental requirement for a UHV environment can be advantageous since a vacuum is an inherently clean environment. The kinetic theory of gases provides the standard unit of gas exposure in UHV experiments, the Langmuir (L):

$$Flux = 3.52 \times 10^{22} Pressure(Mass \times Temperature)^{-1/2}$$

(2.1)

Simply put, if each atom or molecule of gas striking a surface adsorbs (a sticking probability of 1), then a one second exposure at $10^{-6}$ Torr and room temperature (300 K) will cover the surface ($\sim 10^{15}$ atoms/cm$^2$) with 1 monolayer (ML) of adsorbed gas[41]. If experiments are performed at $10^{-10}$ Torr, 10,000 seconds are necessary for the surface to become contaminated from the residual gas in the UHV chamber. If experiments were performed in an inert gas atmosphere rather than in vacuum, a gas purity of 0.00013 ppb would be required for the same degree of cleanliness as a UHV chamber operated at $10^{-10}$ Torr.

If reactive surfaces are being studied, a UHV environment is ideal since the surface can be kept clean throughout the course of an experiment. If less reactive
Figure 2.1: Universal curve for the escape depth of electrons in Å as a function of electron energy (eV) with a vanadium on gold Auger spectrum included for reference.
surfaces are being studied, UHV may not be ideal. Note that equation 2.1 assumes that molecules are at room temperature. Unless the entire chamber were heated to reaction temperature, or a molecular beam source is used, molecules impinging on the sample are at room temperature. If an adsorption process is activated, and has a very low sticking probability, the low temperature and low flux of impinging molecules, even at $10^{-4}$ Torr (the highest operating pressure of a UHV chamber) make prohibitively long gas exposures necessary.

Appendix A gives a detailed discussion of the pumping system and UHV chamber used for the majority of this research. The book by O'Hanlon is also a good reference on other types of pumping systems and UHV in general[43].

2.2 General

2.2.1 Materials Preparation

The surface of any sample which has been exposed to air will be covered with a layer of oxide and adsorbed water and organic molecules. A combination of heating in vacuum, Ar$^+$ sputtering, and chemical cleaning is required to produce a clean, ordered surface. The review by Musket et. al. provides convenient cleaning procedures for different metal surfaces[44].

All materials to be introduced into the UHV chamber; samples, instruments, and gases, undergo stringent cleaning procedures to prevent contamination of the UHV environment.

Solid materials typically undergo a series of cleaning steps:

1. Rough cleaning: bead blasting of ceramics, electropolishing or acid etch of metal parts, degreasing in trichloroethylene.

2. distilled water rinse using ultrasonic cleaning.

3. acetone rinse using ultrasonic cleaning.
CHAPTER 2. EXPERIMENTAL

4. methanol rinse using ultrasonic cleaning.

5. drying with heat gun or in a vacuum oven.

Some laboratories use Freon for a final rinse. However, we have observed some chlorine contamination after using Freon. The final drying procedure decreases outgassing of solvent soaked parts in vacuum. After cleaning, all parts and tools are handled only with latex gloves that have been wiped clean of talc residue.

Once vacuum is reestablished, outgassing rates, particularly of water, are increased by a bake-out: heating the entire chamber to 150°C using an infrared lamp, heating tapes or an oven-like shroud. After 12–36 hours of bake-out, pressures of $\leq 1 \times 10^{-8}$ Torr are common. Upon cooling back to room temperature, outgassing rates are low enough that pressures $\leq 10^{-9}$ can be maintained.

Liquid samples were freeze-pump-thawed 3 to 10 times to remove dissolved gases. The liquids are stored in vials with Teflon valves, often with 13 Å sieve to trap water. The vials can be connected to the gas manifold with Ultra-Torr fittings. The vapor pressure of most liquids is sufficient to fill gas lines for dosing.

Gases to be introduced into vacuum were typically passed through a $\text{N}_2$ cooled copper coil containing 13 Å molecular sieve to remove water contamination. Regulators are all adapted for vacuum service and all copper tube is flamed with a torch while passing oxygen through it to burn out oil contamination. Gas lines are filled and pumped several times.

Gas dosing, whether for cleaning purposes or reaction studies, is accomplished by admitting gas from the gas handling manifold (see Appendix A.1) at a controlled rate into the UHV chamber. Gas can be admitted directly into the chamber or can be directed at the sample via a 1/8 inch O.D. stainless steel tube with or without a capillary array. Gas movement at low pressures ($\leq 10^{-4}$ Torr) is limited by conductance (classical collisional bouncing). Since UHV chambers are geometrically complex, the pressure of gas at one point (the ion gauge) may not be the same as that at another point (the sample). Additionally, the ion gauge is not equally sensitive to all gases. Without careful calibration for each gas used,
Langmuir exposures are relative and are chamber-unique. For this work, no directional dosing of gases was used. The UHV chamber was backfilled with gas to a given pressure for a given amount of time. Langmuir exposures are not corrected for ionization gauge sensitivity.

2.2.2 Sample Mounting

Samples used in UHV studies can be mounted in many ways. Figure 2.2 shows three of these. Mount A was used for electron beam heating. The sample is mounted in front of a 3/8 inch I.D. ceramic cup containing a filament similar to those used in electron guns (see section 2.2.3). The sample is normally grounded and the filament is kept at a high negative voltage, however the reverse arrangement can also be used. The insulating ceramic cup directs emitted electrons toward the sample making the heating more efficient. In fact, even a small hairpin shaped filament can space-charge limit under normal operating conditions. Very even and fast heating rates can be obtained with electron beam heating. Since this method of heating involves electron emission it is only useful within a high vacuum environment. Mounts B and C were used for resistive heating. This method involves passing an electric current through the sample or through a backing plate on which the sample is mounted. Unless the cross sectional area of the sample is small (i.e. 0.001–0.002 inch thickness) the main component of heating is conduction from hot support wires or from high resistance spot welds. Care must be taken to avoid uneven heating. In addition, support wires with melting points above the melting point of the sample are recommended. Nonmetallic samples such as Si or single crystal $V_2O_5$ can be heated using either method by attaching them to a metal backing such as 0.002–0.003 inch thick Au or Ta foil. They can be attached mechanically, with ceramic cement (Aremco) with graphite or copper powder mixed in to make it electrically conductive, or with indium (below 400°C only). Powdered samples can be mechanically pressed into gold mesh and backed with gold foil. If using either of these configurations, care must be taken that heating rates
Figure 2.2: Methods of mounting samples.
are low enough for the sample temperature to equilibrate with the backing plate temperature since the thermocouple is often sandwiched between the two.

2.2.3 Electron, Ion and X-Ray Formation

Surface sensitive spectroscopies are derived from some combination of excitation by, and detection of, electrons, ions, and photons. A brief description of the formation, energy, and detection of each of these species will aid in the understanding of specific techniques as well as pinpoint experimental optimization procedures.

Electrons

The electron source for surface science spectroscopies was either a cathode ray gun from an oscilloscope or an electron gun coaxial with the CMA. Figure 2.3 illustrates the parts of an electron gun.

The beam voltage (energy of emitted electrons) will be a distribution centered
on the voltage of the filament \((V_{F1} - V_{F2})/2\) minus the work function of the filament. Since the width of the beam energy distribution increases with filament temperature, special filaments which emit electrons at low temperatures are normally used for experiments requiring a monoenergetic electron source. The focus \((V_2)\) and deflection \((V_{X1}, V_{X2}, V_{Y1}, V_{Y2})\) voltages are normally measured as a variable percentage of the beam voltage. For convenience, the experimental measurement of gun voltages is normally performed at the gun end of the cable with the beam voltage set at a low value (100 eV) for safety. Unless the gun has an off-axis or indirect filament, yellow to white light should be emitted from the gun during operation. Common filament materials are tungsten (emission temp = 1600–2100 °C) and thoriated iridium (emission temp = 1300–1500 °C). If geometry allows, an optical pyrometer can be used to measure filament temperature. A 0.007 inch diameter wire or 0.002 inch \(\times\) 0.010 inch ribbon used as a filament normally operates at 1.5 to 4 amps. Typically the bend of the filament is etched slightly in 1:1 HNO\(_3\):HF so that it is thinner than the rest of the filament[45]. This allows electron emission from this section without having to heat up the entire filament. If current is being passed and no light is visible, the filament connections (F1 and F2) may be shorted internally. A good indicator of internal shorting is an operating voltage less than normal (\(~2\) V) for a desired filament current. The emission current is often \(~10\) mA when the gun is operating. This is the total current loss from the filament. Most of the emitted electrons hit the extractor \((V1)\), and actual beam currents (electrons impinging on the sample) are in the range of 0.1–30 \(\mu\)A. The placement of the filament with respect to the hole in the extractor is critical for high beam current and small spot size.

Once the filament is hot and voltages are correct an electron beam should be present. A blue fluorescence can be seen when the electron beam hits stainless steel, molybdenum, ceramics, or fiberglass thermocouple insulation. A simple phosphor screen fashioned by coating a glass slide or metal foil with P11 phosphor bound with potassium silicate allows electron, ion, and x-ray beams to be easily observed[46]. This screen can be mounted in place of the sample to check alignment.
or a section of the sample manipulator itself can be phosphor coated. A visual check of a gun's deflection and focus (at or near the sample position) can be a useful way of aligning the sample and electron beam at the focal point of an electron energy analyzer.

If at all possible, the sample should be mounted so that it is electrically isolated and attached through an external feedthrough to allow measurement of beam current and sample biasing (see figure 2.4). When the sample is grounded, the measured current is the difference between the primary beam current and the secondary electron emission current. Depending on the angle at which the primary electron beam strikes the surface, the energy of the primary electron beam, and the secondary emission characteristics of the surface the secondary emission current can be less than, equal to, or larger than the primary beam currents. Even at very high primary beam currents, the measured current to ground can be deceptively low.

Since the majority of the electrons emitted from a sample are at low energies, positively biasing the sample with a 300 V battery traps the majority of emitted secondary electrons so that the primary beam current can be measured. Comparison of the primary beam current with the current measured when the sample is grounded allows the secondary emission current to be calculated. Often, the secondary emission current from a sample is more sensitive to adsorbates in the monolayer regime than is AES.

Ions

Ions are formed as a result of collisions between high energy electrons and gas molecules. Figure 2.5 illustrates the basic geometry and voltage ranges for an ionizer. Basically, the electronic fields within the ionizer keep electrons flying around the grid until they hit a gas molecule or one of the cage wires.

If the relative voltages are kept the same and a center wire at ground is added
Figure 2.4: a.) Circuit for measuring primary electron beam current (battery in series with ammeter) and the difference between the primary beam current and the secondary emission current (no battery) b.) Energy distribution of electrons leaving a surface after excitation with an electron beam with energy $E_p$. 

Primary Electron Beam
(1-3 kV, 1-20 uA)
to collect the ions, we have a Bayard-Alpert ion gauge. If the emission current from the filaments is kept constant (usually 4 mA) the ion current can be used to determine gas pressures. If the relative ionizer voltages are kept positive (+) relative to an adjacent plate with a hole in it, ions can be extracted through the hole and mass analyzed as in a mass spectrometer or accelerated and focussed as in a sputter ion gun.

At very low gas pressures ($\leq 10^{-11}$ Torr) so few gas molecules are ionized that the ion current is no longer proportional to gas pressure. At high gas pressures ($\geq 10^{-4}$ Torr) ions collide with neutral gas molecules and again, the ion current is no longer proportional to gas pressure.

In order to get the pressure without differential pumping, a gas leak line was added to the ion (sputter) gun. Gas introduced at the base of the gun is directed through a hole in the gun’s shielding adjacent to the ionizer by a metal “skirt” around the gun. Figure 2.6 shows a schematic diagram of the gun/doser assembly and a comparison of ion current as a function of Ar pressure with argon backfill and direct gas introduction. Both curves show a maximum beam current at $10^{-4} - 10^{-5}$ Torr argon but the direct gas introduction yields higher beam currents for a
Figure 2.6: a.) Ion gun modification b.) measured beam currents as a function of Ar pressure with and without the modification.
CHAPTER 2. EXPERIMENTAL

given chamber pressure.

X-rays

X-rays were used for X-ray photoelectron spectroscopy (XPS or ESCA). Aluminum or magnesium anodes are used to produce Kα x-rays of 1486 eV and 1253.6 eV respectively. X-rays with these energies produce photoelectrons in the proper energy range for surface analysis. X-rays are produced by bombarding the anode with high energy electrons (10-20 kV). This produces considerable heat and anodes are designed with coaxial cooling. Electrons are produced from a hot filament and accelerated by keeping the anode at high positive potential and the filaments at ground or the anode at ground and the filaments at high negative potential. Although the former requires low conductivity cooling water, the electronics for this configuration are simpler and more robust than the floating filament power supply required for the latter configuration.

The entire filament-anode assembly is covered with a shield and a very thin (2µ) aluminum window is used to keep stray electrons from escaping. However, photoelectrons from the window itself will impinge on the sample. The X-rays are emitted in all directions so the flux reaching the sample drops with distance from the source. The X-ray source and CMA are at right angles and the end of each is angled so that the source can be as close to the sample as possible.

2.2.4 Energy and Mass Selection

The electron energy analyzers used in this work are the Retarding Field Analyzer (RFA) and the Cylindrical Mirror Analyzer (CMA). The RFA consists of four hemispherical screen grids and a hemispherical collector encompassing a solid angle of 120°. The sample is positioned at the focal point of the grids and excited electrons are produced with an electron gun protruding from the center of the
Figure 2.7: Retarding field analyzer showing potentials for LEED and AES.

The first and fourth grids are always grounded to shield electric fields originating from the second and third grids, which are biased. The RFA acts as a high pass filter allowing only those electrons with energy higher than the potential on grids 2 and 3 to pass. The hemispherical collector is biased (90–300 V for AES and 5,000–7,000 V for LEED) to accelerate and collect the energy-analyzed electrons.

For LEED, grids 2 and 3 act as the suppressor and are biased almost at the potential of the electron beam being diffracted so that only the elastically scattered electrons are allowed to pass. In LEED, the diffracted electrons are accelerated by the potential on the collector which is coated with phosphor. On impact the electrons cause the phosphor to glow. Without the suppression, inelastically scattered background electrons (which number more than the diffracted electrons) would also reach the collector and obscure the diffraction pattern. In AES, grids 2 and 3 are ramped in potential from 0 to 2,000 V and Auger electrons over this entire energy are analyzed. Because the RFA signal is so noisy, it is differentiated electronically by modulating the signal and using a lock-in amplifier. Although signal modulation is normally obtained by modulating the filtering potentials (grids 2
and 3), a modulation of the sample potential or excitation beam potential can also be used[47].

The CMA acts as a band-pass filter (see figure 2.8). Whereas the RFA filters out only electrons with energy less than those desired, the CMA filters out electrons with both higher and lower energies. Electrons (or ion trajectories) must be just right for the particle to pass through the analyzer. The potential difference between the two cylinders determines the trajectories of charged particles. The CMA, whether single pass (with one filtering stage) or double pass (as shown), is an imaging analyzer and accepts electrons from a small spot on the sample. Although ideal for AES which employs small spot excitation, this type of detector is not ideal for XPS using an unfocussed source[48]. The very small focal spot of the CMA can make alignment difficult. However, placing the sample in the light from the coaxial electron gun and defocusing the electron beam somewhat will usually allow a spectrum to be obtained. From there, sample and electron beam positions can be optimized.

The energy resolution of a CMA depends on the energy of the electrons being passed through the CMA.

\[ \frac{\Delta E}{E} = 0.3 - 0.7\% \] (2.2)

In the Auger mode, the inner cylinder (IC) and the retarding grid are grounded and the potential of the outer cylinder (OC) is ramped so that electrons with progressively higher energies reach the detector. In this mode the OC potential is normally modulated, the channeltron is used in the analog mode, and lock-in detection is used. For XPS, the CMA is run in the retarding mode. The retarding grid and IC are ramped so that all electrons to be detected have a constant energy after passing the retarding grid. For low energy electrons, actual acceleration, with the retarding grid potential more positive (+) than ground, is required. As the retarding potential is ramped, the OC follows. A constant pass energy for all electrons over the range of energies analyzed means that the resolution of the spectrometer is constant. XPS signals are usually so low that the channeltron is
CHAPTER 2. EXPERIMENTAL

Auger Mode

XPS (Retarding Mode)

Figure 2.8: Double pass cylindrical mirror analyzer showing electrical potentials for Auger and retarding modes.
used in pulse-counting mode.

Ions can also be energy analyzed with either an RFA or CMA using positive (+) potentials. Ion scattering spectroscopy (ISS) is easily performed with a CMA by inverting voltages and closing off part of the entrance for a better angular resolution[49].

2.2.5 Electron and Ion Detection

With the exception of an RFA/AES apparatus, ion and electron currents after energy analysis are so small that actual detection is done with an electron multiplier. Electron multipliers can be either copper-beryllium based or lead doped glass. Electron multipliers work on the principle that secondary electrons produced by the initial collision of an electron, ion, or photon, with the detector, are accelerated into the detector and collide with its walls. Each collision produces many secondary electrons which are accelerated further into the detector before they collide with the walls, producing still more secondary electrons. Gains of $10^6$ (i.e. each signal electron produces $10^6$ electrons at the collector end of the multiplier) are common. The gain of these devices is very sensitive to surface contamination. Operation below $10^{-6}$ Torr, slow initial voltage conditioning, and a 2–3 hour break-in period at low signal levels is recommended.

Copper-beryllium multipliers are used in the mass spectrometer where very high ion currents are detected (the throughput of a quadrupole mass spectrometer is much higher than a CMA operated to filter ions.) These are more robust than channeltrons and have the added feature of a Faraday cup. The Faraday cup is the first dynode of the multiplier, the place of first impact of an ion or electron. At high ion current levels (high gas pressures) the signal can be measured at the Faraday cup without any multiplication. During operation the bias potential on the multiplier must be increased slowly to keep a constant gain. After a year or so of operation, any multiplier reaches a level of degradation where the highest operating potential (usually 3000 V) across the multiplier will no longer produce
Electrons, Ions, or Photons

Figure 2.9: Channeltron showing electrical connections for analog and pulse counting[51].

enough gain. Unlike leaded glass channel electron multipliers (channeltrons), Cu-Be multipliers can be effectively regenerated and reused [50].

Channeltrons were used for their high gain, low noise characteristics. Additionally a channeltron can be used in analog mode for high signal levels or a pulse counting mode for low signal levels. Channeltrons can be obtained in all shapes and sizes and can be optimized for different applications. A schematic diagram of the Galileo 4731 channeltron is shown in figure 2.9. This model is not optimized for the current (analog) mode or pulse counting (digital) mode but may be used in either.

Within a CMA, the entrance of the channeltron (−) is slightly positive with respect to the filtering section of the CMA (slightly negative in the case of ion detection), and the collector of the channeltron (Coll) is at a high positive voltage, slightly higher than the (+) end of the channeltron. Remember that net movement of electrons is from (−) to (+). The high voltage power supply must put out a bias current to maintain the voltages on the channeltron. For the 4731, this current is approximately 1 μA/100 V bias. To maintain linearity in the analog mode, and
not degrade the device, the output signal from the channeltron should not exceed 10% of the bias current. For the 4713 operating at 800 V this means that the output signal should not exceed 0.8 μA. One way to check this value is to use an oscillating reference signal (from a lock-in amplifier in series with a 1 MΩ resistor) to generate a signal, mimicking the output of the channeltron, to calibrate the electronics. In the pulse counting mode, higher potentials are used so that each impinging electron saturates the detector producing a uniform pulse. If a plot of signal vs. bias potential is made, a plateau will be seen at high potentials. Ideal operating bias potential is just at the beginning of the plateau.

2.3 Utilization of Specific UHV Techniques

2.3.1 LEED

Low energy electrons are easily deflected by stray magnetic or electric fields in a UHV chamber. Hence, for normal usage, without elaborate shielding, a LEED pattern below 70 eV was impossible to obtain. Degassing instruments and removing ceramic insulators and fiberglass tubing (which can build up an electric charge) from the vicinity of the sample is helpful. Caution not to deposit metal on the phosphor collector or screens via evaporation or sputtering is also important. Deposited metals can oxidize and become insulating or simply obscure the phosphor. Such considerations also apply to a CMA since low energy Auger and photoelectrons are also susceptible to deflection.

Normal electron beam currents for LEED range from 0.1 μA at 50 eV to 5 μA at 300 eV. Somewhere within this energy range a LEED pattern exhibiting one unit cell should be obtainable from a clean, ordered surface. The intensity of spots varies with beam voltage and will vary from spot to non-symmetry equivalent spot. Minor adjustments of beam voltage and several photographs may be necessary to observe all spots. Screen voltage should be high enough to see spots, but not so high that field omission occurs. The suppressor should be used to filter out as
much background as possible. Initially, sample position and beam voltage can be optimized with the suppressor low.

2.3.2 Auger Electron Spectroscopy

Procedures for finding and aligning electron beams have already been discussed as has channeltron optimization. Operating parameters to consider for AES are the energy of the primary beam, the beam current, the size of the modulation voltage, the time constant of the lock-in amplifier, and the scan rate. Figure 2.10 indicates that the Auger electron signal is relatively unaffected by beam potential as long as that potential is well above the energy of the Auger electrons being analyzed. The signal is proportional to the beam current with currents of $10^{-20}$ $\mu$A being typical for a double pass CMA or RFA and $0.1-1.0\mu$A for a single pass CMA. Increasing the modulation voltage increases signal at the expense of resolution. As the modulation becomes much larger than the peak width, peaks are distorted. The signal magnitude is determined by the modulation voltage and acceptable beam currents. Both of these factors depend on sample composition. The signal to noise ratio determines the time constant necessary for satisfactory spectra. The time constants and peak widths determine the allowable scan rates as follows:

For $\leq 1\%$ peak attenuation:

$$\tau r/w \leq 0.045$$  \hspace{1cm} (2.3)

For $\leq 0.1$ eV peak shift:

$$\tau r/w \leq 0.1$$  \hspace{1cm} (2.4)

where $\tau$ is the time constant; $r$, the scan rate; and $w$, the peak width measured between positive and negative maxima[53]. If the instrument is not optimized for the narrowest peaks of a spectrum problems will result. Figure 2.11 shows how important proper operating parameters are for obtaining reliable spectra. The variation in the vanadium 473 eV peak-to-peak height is a direct result of scanning...
Figure 2.10: Effect of operating parameters on Auger peak heights[52].
Figure 2.11: Effects of scan rate and time constant on relative Auger peak heights of the vanadium 437, 473, 512 eV triplet: a.) $\tau = 1$ sec, $r = 10$ eV/sec b.) $\tau = 1$ ms, $r = 10$ eV/sec (the energy scales for the two spectra are different.)
the spectrum faster than the time constant of the lock-in amplifier allows. The 473 eV peak, because it is the narrowest of the Auger triplet, is the most drastically affected.

The primary function of AES is to monitor the elemental composition of the surface. The uptake curves of deposited vanadium were established by monitoring the 69 eV gold peak and the 437 eV vanadium peak. The carbon peaks overlap with some of the higher energy gold peaks as seen in figure 2.1. Typical operating parameters were 20 μA with 2.0 kV beams, 4 V peak-to-peak modulation, and 10 eV/sec scan rates.

Auger spectroscopy is also used to monitor the oxidation state of vanadium. Figure 2.12 shows Auger spectra for clean vanadium and V₂O₅. The assignments of the Auger peaks explain the changes in the AES spectrum accompanying the oxidation of vanadium. Transitions involving d-electrons (473 eV, 514 eV) decrease in intensity as d-electrons are removed during oxidation. The increase of the 514 eV peak corresponds to an increase in oxygen content. The oxygen and vanadium peaks overlap at 514 eV. In addition the 437 eV peak shifts to lower energy as vanadium is oxidized. Figure 2.13 plots changes in peak height relative to 437 eV and peak shifts obtained from a number of sources. Comparing an Auger spectrum of vanadium oxide with this plot, an oxidation state ± 1 can be obtained. With this spectrometer, very small changes in oxidation state cannot be observed.

2.3.3 XPS

Most of the aspects of XPS have been discussed previously. The X-ray source is run at 40 MA and 12 kV. The source is positioned as close to the focal point of the CMA as possible (~1 cm) and aligned visually with a phosphor coated foil. For XPS, the CMA is run in the retarding mode with pulse counting and signal averaging. For full scan surveys a pass energy of 100 eV is used. For high resolution scans a pass energy of 5 or 10 eV may be used. A compromise between resolution and collection time must be made.
Figure 2.12: Changes in the Auger electron spectra accompanying the oxidation of vanadium: a.) Metallic vanadium b.) $\text{V}_2\text{O}_3$ on Au(111).
Figure 2.13: Plot of Auger electron spectra changes as a function of oxidation state.
CHAPTER 2. EXPERIMENTAL

2.3.4 Ion Scattering Spectroscopy

Ion scattering spectroscopy (ISS) is a technique used for obtaining the elemental composition of the topmost layer of a surface. Using an ion sputter gun, low energy ions are directed at a surface. Ions are inelastically scattered with energies dependent on their primary energy \(E_0\), their mass \(M_1\), the scattering angle \(\theta\), and the mass of the surface atom \(M_2\) they strike.

\[
E = E_0 \left[ \frac{1}{1 + \frac{M_2}{M_1}} \right] \left[ \cos \theta \pm \sqrt{\frac{M_2}{M_1}} - \sin^2 \theta \right]^2 \quad (2.5)
\]

Since He\(^+\) has such a low mass, little actual momentum transfers to the surface and minimal sputtering occurs. The numbers and energies of scattered He\(^+\) ions can be measured with either a modified CMA or a MS. [54] ISS was performed with 500 eV He\(^+\) ions using the double pass CMA with all but the quarter of the entrance closest to the ion gun covered, with a pass energy of +300 eV, in pulse counting mode[49].

2.3.5 Temperature Programmed Desorption

Temperature programmed desorption (TPD) experiments were performed by adsorbing a gas on the sample followed by ramping the sample temperature linearly while observing desorbing species with a mass spectrometer. Heating typically was performed with a constant current or feedback-controlled power supply for resistively heating the sample. Both methods produce reasonably linear temperature ramps in the range of 10–30 K/sec. The sample was positioned 1–2 mm from the end of a tube (approx 1/2 the size of the sample) leading through a shield to the mass spectrometer (see figure 2.14). No pumping problems were encountered with this arrangement and the shielding eliminated most of the desorption signal from the sample mount.

Table 2.1 shows sensitivity factors for various cracking fragments of molecules studies in this thesis. Since most TPD experiments show oxygen desorption, sen-
Table 2.1: Molar sensitivity factors for mass spectrometer signal relative to \( \text{O}_2 \), 32 amu.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mass amu</th>
<th>Sensitivity (relative to ( \text{O}_2 ), 32 amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>32</td>
<td>1.0</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>0.24</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>44</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>2.2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>18</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>28</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>2.1</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5\text{OH} )</td>
<td>46</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Figure 2.14: Aperature and shield surrounding quadrupole mass spectrometer.
CHAPTER 2. EXPERIMENTAL

sivities are shown relative to oxygen. With the exception of the hydrogen ad-
sorption experiments and experiments with V(110) all TPD spectra show data
corrected for molar sensitivity.

Most experiments were performed with very long gas exposures at \( \sim 10^{-5} \) Torr. Such exposures tended to degrade the vacuum and a wait of an hour or more
before desorption was common. TPD was used to monitor the desorption of
products from the surface. Temperature ramps of 20 K/s were obtained with
a programmable power supply.

Desorption energies were estimated from the TPD spectra assuming first order
desorption kinetics. The following equation was solved iteratively\[55\]:

\[
\left[ \frac{\nu_1}{\beta} \right] \exp\left[ -\frac{E_d}{RT_p} \right] = \frac{E_d}{RT_p^2}
\]

(2.6)

Uncertainties were estimated by assuming \( \nu_1 = 10^{12} - 10^{14} \) and heating rates of 15-25
k/s. Changing these values changed the calculated desorption energies by \( \pm 4 \) kcal
mol\(^{-1}\). Second order kinetics were not used since in no case could the coverage of
the desorbing species be determined.

2.4 Preparation and Characterization of Gold-Supported V\(_2\)O\(_5\)

2.4.1 Epitaxial V\(_2\)O\(_3\) on Au(111)

In UHV, vanadium oxide was grown on Au(111) by depositing metallic vanad-
dium and oxidizing it at low pressures. Metallic vanadium was deposited by
wrapping a tungsten wire with vanadium foil. The tungsten wire was heated
to melt and vaporize the vanadium allowing it to be deposited. Some metal com-
binations react, making this method inappropriate. This was not the case with
vanadium/tungsten.

Vanadium films were oxidized at room temperature at \( \mathrm{O}_2 \) pressures of \( 1 \times 10^{-7} \)
to \( 1 \times 10^{-5} \) Torr. Pressures above \( 5 \times 10^{-6} \) Torr were optimal. Once oxidized, the
samples were annealed at 500–700°C to order the vanadium oxide films. This method produced epitaxial $V_2O_3$ on Au(111)

2.4.2 $V_2O_5$ on Au Foil

Polycrystalline $V_2O_5$ was deposited on Au foil outside of the UHV chamber by direct deposition of $V_2O_5$. The samples were prepared by vapor depositing $\sim$1000 Å of amorphous $V_2O_5$ onto gold foil and annealing at 500°C in air for several days. The gold foil was cleaned in aqua regia before introduction into the high vacuum chamber. The $V_2O_5$ deposition was performed in a small high vacuum chamber ($10^{-3}$–$10^{-6}$ Torr) by electron beam evaporation of $V_2O_5$ in a tungsten boat. Resistive heating of a 0.001 inch thick platinum crucible to 850°C was also used. For simplicity and optimal heat transfer the resistively heated platinum crucible worked best. For use in a UHV chamber where small amounts of randomly deposited metal or metal oxide can greatly upset the operation of various instruments, a shield around the source with a moveable shutter is highly recommended.

Depending on their thickness, the films appeared yellow or red, but turned green after several hours of exposure to moisture from the air. After annealing, the films were hazy and did not appear to be moisture sensitive. X-ray diffraction (XRD) was used to verify the presence of crystalline $V_2O_5$. XPS (figure 2.16) was used to determine the surface oxidation state of the samples, and Raman spectroscopy was used to characterize the bonding in both the amorphous and crystalline phases. The Raman spectra (see figure 2.17) and physical properties of the amorphous films are similar to films prepared by Sanchez et al. which crystallize at 400°C [15].

After several experiments in UHV, an oxidized surface could no longer be maintained. In situ reoxidation at high pressures of dry oxygen ($\geq 10$ Torr) at 500°C was used to reoxidize the samples without carbon or water contamination.
Figure 2.15: Scanning electron micrograph of $V_2O_5$ crystallites supported on gold foil.
Figure 2.16: XPS spectra of 1000 Å V₂O₅ on gold foil: a.) amorphous, after standing in air for several weeks b.) crystalline, after annealing at 500 °C in air for two days and standing in air for several weeks c.) crystalline, after 2 minutes of sputtering in UHV.
Figure 2.17: Laser Raman spectra of a.) 1000 Å amorphous $\text{V}_2\text{O}_5$ on gold foil b.) $\text{V}_2\text{O}_5$ on gold foil after annealing at 500 °C for two days in air c.) single crystal $\text{V}_2\text{O}_5$[56].
High pressure reoxidation could also be performed in a high pressure cell attached to the sample introduction apparatus. Oxidation in flowing \( \text{O}_2 \) at 350–500\(^\circ\text{C} \) for several minutes could be followed by evacuation and introduction into UHV or evacuation and exposure to reaction gases.

2.5 Preparation and Characterization of High Surface Area Catalysts

2.5.1 Catalyst Preparation

The catalyst for the methane oxidation experiments, 2.0\% \( \text{V}_2\text{O}_5\)-\( \text{SiO}_2 \), was prepared by addition of the silica support to a basic (\( \text{pH} = 10.5 \)) solution of ammonium metavanadate to form a gel, followed by drying under a heat lamp, grinding, and calcining overnight in air at 825 K. The support, Cab-O-Sil HS-5 fumed silica, had a reported surface area of 350±25 m\(^2\) g\(^{-1} \). The finished catalyst was pressed and sifted to 30–60 mesh particles. The final surface area, as determined by BET measurement, was found to be 230±10 m\(^2\) g\(^{-1} \). The active vanadium oxide surface area was not determined.

For the active surface area determination and ethanol oxidation experiments, unsupported \( \text{V}_2\text{O}_5 \) powder (Aldrich 99.999\%) was used as received. It had a surface area of 2.2 m\(^2\) g\(^{-1} \). The 0.3\% \( \text{V}_2\text{O}_5/\text{SiO}_2 \) catalyst for ethanol oxidation experiments was prepared by mixing a heated slurry of 0.331 mmol of \( \text{NH}_4\text{VO}_3 \) (Aldrich 99.99\%) and a heated solution of 0.662 mmol of oxalic acid (Aldrich 99+\%). The mixture was kept at \( \sim 350 \) K and stirred until the \( \text{NH}_4\text{VO}_3 \) dissolved and reacted completely. The resulting solution of vanadyl oxalate was diluted with distilled water to a volume of 16 cm\(^3\), cooled, and used to impregnate 10 g of \( \text{SiO}_2 \) (Cabosil L90 99.8\%) to incipient wetness. The solid was dried for 2 h at 573 K and calcined for 12 h at 773 K. Similar procedures were employed to prepare the other supported catalysts. As described elsewhere[57], the catalyst particle size for the ethanol oxidation experiments was carefully tested for mass and heat transfer.
2.5.2 Apparatus and Methods

Surface area measurements were carried out with a flow system (Figure 2.18a.) equipped with a thermal conductivity detector, TCD (Hewlett-Packard 19302-60530). Samples (0.2–0.6 g) were loaded into pyrex or quartz cells and held with calcined glass wool plugs. A six-way valve allowed switching between a pretreatment gas and a carrier gas without disconnecting the sample cells. Prior to O$_2$ (Linde Specialty Grade 99.99%) chemisorption, samples were pretreated by heating them in flowing H$_2$ (Linde High Grade 99.995%) (45 cm$^3$ min$^{-1}$) for 1 h at various temperatures. Oxygen uptakes were measured at both the reduction temperature and room temperature. Prior to total surface area measurements using the BET method, samples were heated in flowing He (Linde High Purity Grade 99.995%) (45 cm$^3$ min$^{-1}$) for 1 h at $\sim$390 K.

Irreversible oxygen chemisorption was measured by dosing small amounts (17.2 $\mu$mol) of O$_2$ through a sampling valve into a He carrier gas stream passing over a heated sample. Doses were repeated every 60 seconds until the the sample no longer adsorbed all the oxygen and the pulses reached the TCD. Dosing was continued until peaks of constant area were observed. (Figure 2.18b.). The difference between the area of these peaks and that of earlier peaks is due to the irreversible uptake of O$_2$ by the sample(Figure 2.18c.).

Total surface areas were measured using a single point BET measurement. A 30% N$_2$/He (Linde Custom Grade 99.995%) gas stream was passed over a sample maintained at liquid nitrogen temperatures. After 600 seconds the sample was flashed to desorb the physisorbed N$_2$. The quantity of nitrogen adsorbed was determined from the calibrated TCD signal. Reproducibility in measured surface areas was $\pm$ 5%.

Temperature Programmed Reduction of bulk samples was performed by flowing a 10% H$_2$-N$_2$ mixture over the sample and ramping the temperature at 15 K/min.
Figure 2.18: The flow adsorption measurement technique: a.) Schematic diagram of the apparatus b.) Thermal conductivity detector signal showing pulses of gas c.) Uptake curve.
Reduction was monitored by detecting the reduction product (H₂O) with a thermal conductivity detector (TCD).

Powder x-ray diffraction measurements were carried out with a Norelco 12206/7 spectrometer using Ni filtered Cu Kα radiation generated at 35 kV and 14 mA.

The fixed-bed reactor and the gas manifold used in this study are schematically represented in figure 2.19. The flow of reactant and carrier gases was regulated by needle valves and monitored by rotometers. Steam was introduced into the gas stream by passing the reaction gases through a heated-water reservoir (methane experiments) or by using a syringe pump to inject water into a tightly packed plug of glass wool through which the reaction gases were flowing (ethanol experiments). The mixed gas stream was led through a Valco six-port switching valve before and after passing through the reactor to allow for pre and post-reaction GC analyses. The entire reaction manifold was kept at 120°C to prevent condensation of the water vapor.

The fused-silica reactor measured 35 cm in length and 2.2 cm in diameter (methane) or 1.5 cm in diameter (ethanol). The catalyst bed, supported between pads of silica wool, was usually 2 cm thick. The temperature was monitored by a quartz-shielded thermocouple probe embedded in the catalyst bed. The reactor exit was narrow (2 mm I.D.) so that product gases were rapidly removed from the hot zone of the reactor and quenched. A valve assembly was placed at the exit in order to direct the exit-gas stream either through a cold trap, where water and soluble products could be condensed out, or through the six-port valve. The catalyst bed and quartz chips for gas preheating were centered in the hot zone of a tube furnace, the temperature of which could be maintained within 1°C over the entire reaction zone. The radial temperature gradient was usually less than 2°C. The reaction was initiated by heating the catalyst to the maximum temperature reached during reaction in flowing oxygen, steam, and helium and introducing the reaction mixture. One to two hours were allowed for the system to reach a steady-state condition before product analysis was initiated. Typical reaction mixtures of 0.1 CH₄ + 0.35 N₂O + 0.35 H₂O + 0.2 He and flows of 80 cm³min⁻¹ were used.
Figure 2.19: Continuous-flow apparatus for partial oxidation of methane and ethanol.
during methane oxidation. Typical reaction mixtures of $0.016 \text{CH}_3\text{OH} + 0.28 \text{O}_2$
$+ 0.10 \text{H}_2\text{O} + 0.61 \text{He}$ and gas flows of $110 \text{cm}^3\text{min}^{-1}$ were used during ethanol oxidation.

A Hewlett-Packard Model 5793A dual-column gas chromatograph, equipped with a thermal conductivity and a flame ionization detector, was used for all analytical purposes. A 10-port Valco injection valve was installed in line to the reactant gas flow for sample analysis utilizing both the thermal conductivity and the flame ionization detectors. Separation and detection of $\text{N}_2$, $\text{CO}$, $\text{CO}_2$, and $\text{H}_2\text{O}$ were accomplished with a Carbosieve S-II (methane) or carbosphere (ethanol) column and a thermal conductivity detector. For hydrocarbons a Poropack-QS column and a flame ionization detector were used. For quantitative analysis the measured peak areas were corrected for the molar response factors of the various components as determined by Dietz[58]. Since gas-phase concentrations were so low during methane partial oxidation, the concentrations of $\text{CH}_3\text{OH}$ and $\text{HCHO}$ were determined by injecting quantitatively $1.00$ to $2.00 \mu\text{l}$ of the solution collected in the cold trap into the GC and matching the FID signal with calibration curves prepared from a series of aqueous standards. High conversions in the ethanol oxidation eliminated the need for the cold traps.

2.5.3 Raman Spectroscopy

Powdered samples were pressed at 7–14 MPa into $13 \text{mm} \times 1\text{mm}$ wafers. These were spun in the excitation beam. With the use of an evacuable quartz cell around the sample holder, in situ experiments up to $873 \text{K}$ could be monitored with the apparatus.

Raman spectra were taken with the 488.0 nm and 514.5 nm lines of an argon laser (Spectra Physics, Model 165). The beam (5–100 mW) was focussed to an ellipse on the sample. The scattered light was collected by a camera lens (Nikon, F/1.2, f/50 mm) and focussed onto a double monochrometer (Spex, Model 1403) equipped with ruled gratings (Bausch and Lomb, 300 gr/mm). Additional re-
CHAPTER 2. EXPERIMENTAL

Injection of the laser line was provided by bandpass filters (Omega Optical). The dispersed light was detected by an optical multichannel analyzer (Tracor Northern, Model 6122) using a cooled, intensified photodiode array. Multiple scans were collected and averaged on a computer (Digital, LSI 11-23). Total acquisition times over the range $200 \text{ cm}^{-1}$ to $1200 \text{ cm}^{-1}$ with a resolution of $6 \text{ cm}^{-1}$ ranged from 10 to 5000 seconds depending on sample and laser intensity[56].
Chapter 3

The Surface Chemistry of Vanadium Metal

3.1 Introduction

One approach to obtaining oxide surfaces for UHV studies is to grow an oxide on a metallic substrate. Initial research on vanadium oxide surfaces employed metallic vanadium as a substrate for the growth of vanadium oxide films in UHV. It was expected that a clean vanadium surface could be readily oxidized to yield a stable vanadium (IV or V) oxide overlayer analogous to the oxide overlayers grown on molybdenum surfaces[59,60]. The possibility of growing ordered overlayers was examined by using single crystals and recrystallized foils as substrates. Additionally, TPD experiments examining the reactivity of metallic vanadium surfaces were performed for comparison to similar experiments on vanadium oxide surfaces.

Published literature on vanadium surfaces is sparse; the majority is devoted to periodic trends in LEED [61,62,63,64,65,66,67,68] or to the reactivity of metal surfaces as a function of d-orbital filling [69,70,71]. Both theory and experiments indicate that clean vanadium surfaces are extremely reactive and difficult to clean. Removal of surface contaminants requires Ar⁺ sputtering. Annealing is required after sputtering to reorder the surface. Unfortunately, annealing also allows facile segregation of bulk contaminants to the surface. In the literature, two approaches
are used to study vanadium surfaces; static and dynamic. Static experiments such as LEED and TPD are performed by cleaning the sample, exposing it to a reactant and examining the surface at various temperatures. Dynamic experiments employ continuous sputtering to remove surface contaminants during the course of the experiment[72,73]. The static approach was used in this work.

Low index, (110) and (100), crystal faces of vanadium were chosen as substrates for these studies. Figure 3.1 illustrates the structure of these surfaces. These are the closest-packed surfaces of vanadium and should be less reactive and more easily prepared than more corrugated crystal faces. Nevertheless, the intrinsic reactivity of vanadium may far outweigh differences between close-packed and more open surfaces. Additionally, these surfaces have been the subject of earlier research[61,62,63,64,65,66,67,68,69,70,71].

Experiments were performed in three areas: sample cleaning, LEED, and TPD. Cleaning involved both bulk purification with H₂ treatments and surface cleaning. The surface cleaning required an understanding of the temperature dependent surface segregation of various contaminants in an effort to optimize cleaning efficiency. Cleaning experiments utilized AES to monitor surface contamination. However, the surface segregation of oxygen was studied in more detail with LEED. Finally, the reactivity of the vanadium surfaces was studied with TPD. Previous research found Br₂ and Na to be the only adsorbates that could be adsorbed and desorbed reversibly from vanadium[65,74]. Our studies involve H₂ and K, both of which are associated with vanadium oxide catalysts (as a reactant and a promoter respectively). These experiments yielded information on the relative strength of oxygen binding to hydrogen, potassium, and vanadium. The reaction of vanadium surfaces with low pressures of oxygen was also studied.

Throughout the course of all these experiments the suitability of vanadium metal as a substrate for vanadium oxide growth was evaluated. In general, the temperatures required for working with metallic vanadium substrates were well above those at which vanadium oxide overlayers were stable.
CHAPTER 3. THE SURFACE CHEMISTRY OF VANADIUM METAL

3.2 Results

3.2.1 Sample Cleaning: Hydrogen Treatment and Contaminant Segregation

Vanadium forms very stable oxides, carbides, sulfides, and hydrides. Consequently, it is difficult to obtain in its pure state. Zone refining and vacuum gettering are the most effective forms of bulk purification[76,77,78]. Preliminary UHV experiments in this laboratory indicated that sulfur was the most persistent contaminant in the vanadium samples and that it was extremely difficult to remove from the surface using UHV cleaning procedures.

Hydrogen pretreatment is a method used to remove sulfur from iron single crystals[54]. Vanadium forms at least two hydrides below 240°C, and low temperature hydrogen treatment will destroy a vanadium single crystal. However, upon examination of the isobar for hydrogen and vanadium (figure 3.2) it is evident

Figure 3.1: Schematic diagrams of the (110) and (100) surfaces of BCC vanadium[75].
that treatment at high temperatures (1000–1200°C ) should keep hydrogen from dissolving in the bulk vanadium. For these experiments, a brew furnace used for metallurgy was employed. Care was taken that the introduction and removal of hydrogen from the furnace did not change the treatment temperature. Although hydrogen pretreatment removed sulfur from the samples, it embrittled all but one sample (a foil). Additionally, the surface finish of the polished crystals became hazy.

The surface of a vanadium single crystal newly introduced to UHV was coated with an oxide layer, carbon oxides, and water. Its bulk contained significant quantities of carbon, oxygen, sulfur, and hydrogen (even without H₂ pretreatment). Enough hydrogen was present in the bulk that high temperature outgassing was required. Without the outgassing, the room temperature hydrogen loss from a sample would seriously impair the vacuum for days. At this point, heating the sample to 1300°C reduced the surface oxide via desorption of CO, CO₂, and H₂O, and removed hydrogen from the bulk of the crystal. This, as any heat treatment, caused sulfur to migrate to the surface. Extended sputtering at elevated temperatures was then necessary to remove enough sulfur from the subsurface region of the crystal to perform even short experiments. The UHV chamber used for these experiments was ion pumped and sputtering required Ar backfilling and subsequent evacuation. During evacuation, carbon and oxygen from the residual gas adsorbed on the surface. The carbon could be removed through post-sputtering annealing ≥800°C . Oxygen, the subject of our experiments, migrated into the bulk at high temperatures and segregated to the surface at low temperatures.

Experiments were performed to investigate the segregation behavior of different contaminants on V(110) as a function of temperature. Figure 3.3 shows a plot of surface concentrations of contaminants after annealing the sample for 1 minute at various temperatures. High temperatures clearly favor the surface segregation of sulfur and the bulk segregation of carbon. Both these processes are irreversible. Oxygen shows a tendency to diffuse into the bulk at high temperatures. However, the overlap of vanadium and oxygen Auger peaks makes quantification of small
Figure 3.2: The Vanadium-Hydrogen phase diagram showing a 1 atm. H$_2$ isobar. Vanadium hydrides are unstable above 240°C [79,80].
Figure 3.3: The effect of annealing temperature on the surface concentration of impurities on V(110). Auger peak heights are plotted after annealing at specified temperatures for 1 minute.

amounts of surface oxygen uncertain.

Using the information derived from figure 3.3, and published literature, a cleaning procedure was developed[44,63]. V(110) single crystals were cleaned with cycles of high temperature Ar$^+$ sputtering ($\geq$800°C) to remove sulfur, low temperature Ar$^+$ sputtering (400–500°C) to remove carbon and oxygen, and annealing (1300–1500°C) to reorder the surface. Although 400°C is too high a temperature for optimal surface concentrations of carbon and oxygen, it is the lowest temperature at which facile contaminant diffusion to the surface occurs. The same procedure was used for V(100) and vanadium foil samples. A perfectly clean, ordered vanadium surface was never obtained. Slight oxygen contamination could be detected more easily with LEED than with AES. For our experiments, the presence or ab-
sence of new LEED structures was used to monitor the presence of small amounts of oxygen on the surface.

### 3.2.2 LEED

Both the V(110) and V(100) surfaces show complex LEED structures in the presence of small amounts of surface impurities, especially oxygen. Owing to the difficulty in cleaning vanadium surfaces and detecting small quantities of surface oxygen, questions arose concerning whether or not clean vanadium surfaces reconstruct. Hence, the large percentage of published literature on vanadium surfaces which deals with LEED structures.

Figure 3.4 shows a sequence of LEED photos taken of an apparently clean V(110) single crystal surface. After sputtering, four spots from a very disordered (1x1) pattern with a high background intensity can be seen. As the surface is heated to 400°C streaking along the [001] direction becomes evident. (The crystallographic orientation of the sample was determined when it was cut from the single crystal boule.) At higher temperature (800°C) this streaking disappears revealing a sharp (1x1) pattern. Upon cooling, first streaking, then two mirrored domains of a sharp c(6x2) pattern become evident. The temperature dependence of this LEED data is consistent with the surface segregation behavior of oxygen discussed in the previous section. These LEED structures are very reproducible from sample to sample and reversible with temperature cycling.

Although the V(100) crystal was too contaminated for use, the recrystallized vanadium foil was comprised of large grains (0.5–1 mm diameter) with a V(100) orientation. Figure 3.5 shows a photograph of the foil and a LEED photo from one of the grains. Translation of such a foil across the LEED beam (0.1 mm diameter) revealed that all the grains are oriented with their (100) faces in the plane of the foil, but that they are rotationally disordered. The foil proved to be free of sulfur, carbon, and oxygen, and no reconstruction of the (100) surfaces was observed after temperature cycling and oxidation experiments.
Figure 3.4: LEED photos showing the evolution of the V(110)-o C(6×2) surface structure as a function of sample annealing a.) After room temperature sputtering, 89 eV b.) At 400°C, 99 eV c.) During cooling after annealing at 800°C, 86 eV d.) Room temperature after annealing at 800°C, 97 eV.
Figure 3.5: a.) Optical micrograph, the bar is 1 mm, and b.) LEED pattern from a recrystallized vanadium foil, 84 eV.
In contrast to clean V(110), the ordered V(110)-o c(6×2) overlayer, estimated from Auger data at 0.2 ML oxygen[63], is quite unreactive. No CO or CO₂ from the residual gas in the UHV chamber adsorbs on this surface, even over a period of several days. (This can be monitored easily by observing the carbon region of the Auger spectrum.)

### 3.2.3 Reactivity, TPD and Oxidation Experiments

Once an unchanging level of contamination was achieved, several reaction studies employing Temperature Programmed Desorption (TPD) were undertaken. Of the adsorbates relating to vanadium oxide-based catalysis, only H₂ and K could be reversibly adsorbed and desorbed. Other molecules (CO, CO₂, ethanol, and H₂O) dissociate and irreversibly adsorb and can only be removed by Ar⁺ sputtering or heating close to the melting point of vanadium (1890°C). Low to medium temperature desorption of CO, CO₂, and H₂O only occurs from the thick oxide contamination on samples newly introduced to UHV.

Experiments were performed with monolayer exposures of H₂ and D₂ at room temperature on "clean", oxygen covered, and sulfur contaminated V(110) surfaces. After exposure, only H₂, HD, and D₂ desorbed. Figure 3.6 shows the desorption spectra of H₂, HD, and D₂ after exposure to 7.2 L D₂. D₂ desorbs at 363 K and 663 K. HD desorbs at 663 K and higher. H₂ desorbs without distinct peaks above 500 K. Desorption energies (assuming first-order desorption and ν=10¹³) of 21±4 and 40±4 kcal mol⁻¹ were calculated for the 363 K and 663 K peaks respectively. Since no H₂ was initially adsorbed, any hydrogen desorbing (as HD or H₂) must originate from the bulk of the sample. No experiments were performed to test for desorption from the tantalum sample mounts. However, the sample was positioned directly in front of the entrance aperture of the mass spectrometer (see figure 2.14) so that only species desorbing from the central portion of the sample were observed. No surface cleaning via H₂O or H₂S desorption was observed.

The desorption of potassium was also examined (figure 3.7). After a ~0.2 L
Figure 3.6: Temperature programmed desorption of D₂ on V(110) after exposure for 1 minute at 1.2×10⁻⁷ Torr D₂ at room temperature. Temperature ramp ~20K/s.
dose of potassium (estimated from AES spectra), desorption (39 amu) at 644 K, 793 K, and 1300 K was observed. Some CO desorption (28 amu) accompanies both low temperature peaks. The high temperature (≥1200 K) signal is attributed to a rising background rather than a desorption of potassium since the residual gas pressure of the UHV chamber increased appreciably at high temperatures. First order desorption energies of 39±4 and 48±4 kcal mol⁻¹ were calculated (assuming ν=10¹³) for the 644 K and 795 K peaks respectively. No desorption of mixed potassium-oxygen species was seen. This is a measure of the relative strengths of the V-O, V-K, and K-O bonds.

Low pressure oxidation was explored as a means of removing sulfur from vanadium surfaces (as SO₂) and of growing an oxide layer. Although sulfur removal was unsuccessful, oxidation of V(110) for 20 minutes in 1×10⁻⁶ Torr O₂ at 350°C produced an oxidized surface. Figure 3.8 shows the Auger spectra of the oxidized surface and the same surface after heating to 1200°C. During the heating to 1200°C, H₂O, CO, and CO₂ desorbed and the surface returned to its pre-oxidation
CHAPTER 3. THE SURFACE CHEMISTRY OF VANADIUM METAL

Figure 3.8: Auger electron spectrum a) after oxidation of V(110) for 20 minutes in $1 \times 10^{-6}$ Torr $O_2$ at 350°C. b) after heating to 1200°C.

The exact composition of the oxide layer could not be determined from the Auger spectra. Obviously the oxide layer was not stable at 1200°C, however no experiments were performed to determine its maximum stable temperature.

As with the V(110) oxidation experiments, oxidation at $1 \times 10^{-6}$ Torr $O_2$ and 300°C for 20 minutes oxidized the vanadium foil. After oxidation, the surface of the foil showed only a diffuse background in LEED. However, flashing to 800°C restored the clean surface and the (1×1) LEED pattern.

Besides the reversible oxygen adsorption-oxidation exhibited in the LEED and low pressure oxidation experiments, the V(110) samples showed evidence of irreversible oxide formation. The areas of the crystal that were the hottest; the center of electron beam heated samples and the edge of resistively heated samples (see figure 2.2) became hazy after a few heating cycles. The haze could not be removed by either annealing at very high temperatures or extended Ar$^+$ sputtering. Scanning Electron Microscopy (SEM) shows the hazy area to be comprised of platelets of a precipitate (figure 3.9). Presumably these platelets are vanadium oxide since
CHAPTER 3. THE SURFACE CHEMISTRY OF VANADIUM METAL

the hazy areas could be observed in the absence of other impurities. The lack of spatial resolution of the spectrometer and the overlap of vanadium and oxygen Auger peaks preclude determination of the exact composition of the precipitate.

3.3 Discussion

The difficulties in cleaning vanadium surfaces, the segregation behavior of impurities, and the LEED structures of oxygen on V(110) and V(100) have all been discussed in the literature. To this body of knowledge, the present work has added: crystal preparation using hydrogen pretreatment, methods of obtaining V(100) grains in foils, reactivity of hydrogen and potassium on V(110), and evidence of higher oxides nucleating on the V(110) surface during temperature cycling.

This work corroborates previous research concerning the surface segregation behavior of contaminants. The different surface segregation temperatures for S, C, and O pose an interesting problem for surface cleaning. It is clear from figure 3.3 that high temperature sputtering removes sulfur, but drives carbon and oxygen into bulk. In fact, if a sulfur-free sample can be obtained, a vanadium surface will be free of contamination at high temperatures. Low temperature sputtering favors carbon and oxygen removal, but decreases the rate of contaminant diffusion to the surface. A method consisting of room temperature sputtering to remove gross contamination followed by 800°C and 400–500°C sputtering to remove S and C, O respectively is the only effective means of cleaning the surface in UHV[63]. Once in the vacuum chamber, very low pressures are required to maintain a contamination-free vanadium surface. This is only possible if a dynamic sputtering procedure, rather than a static, back-fill method such as that used for this research, is used. With the lower pressures and fast pumpdown times accompanying dynamic sputtering, a freshly sputtered surface should remain clean after the argon is pumped out.

For experiments on the surface chemistry of metallic vanadium, sample prepa-
Figure 3.9: Scanning electron micrograph of oxide precipitates on a V(110) surface.
RATION is critical. Sulfur-free, very high purity samples are absolutely necessary. If V(100) is to be studied, recrystallized foils are recommended. (Work induced grain orientation is well known in metallurgy.) Although not consistently successful, the high temperature hydrogen pretreatment of samples may provide a method for bulk cleaning of vanadium. We found the cleanliness of the pretreated vanadium foil outstanding. The embrittlement of the samples pretreated in this study was probably due to trace H$_2$O contamination in the H$_2$ and subsequent bulk suboxide formation. The use of ultra-pure H$_2$ and careful temperature control should alleviate the problems encountered with this pretreatment method.

An interesting aspect of the surface segregation of oxygen, but one not pursued in this work, is the presence of ordered oxygen overlayers on both the V(110) and V(100) surfaces. The stability of these overlayers may affect the segregation behavior of oxygen. The V(110)-o c(6×2) structure resembles a face of the V$_9$O suboxide structure in several ways. The streaking along the [001] direction and the presence of mirrored domains are common to both[81,82]. Vanadium possesses at least three suboxide phases V$_9$O, V$_4$O, and V$_2$O [81,82,83,84,85,86,87,88,89,90]. Careful study of vanadium containing various amounts of oxygen might yield more ordered oxygen surface structures related to the structures of the suboxides.

The surface segregation of oxygen is an interesting problem and one uniquely suited to UHV studies. Since oxygen does not readily desorb from vanadium surfaces, and in UHV very little oxygen adsorbs, the sample is a closed system and oxygen reversibly segregates to vanadium surfaces as a function of temperature. This can be readily observed with LEED as shown in figure 3.4. After sputtering, the surface is disordered and only a diffuse (1×1) pattern is seen. As the sample is heated, oxygen diffuses to the surface producing streaking. At high temperatures, the driving force for surface segregation diminishes and a clean (1×1) pattern is seen again. As the sample cools, oxygen again diffuses to the surface and orders to produce the V(110)-o c(6×2) structure. A heat of segregation of $\Delta H^\circ = 117 \pm 4$ kJ/mol has been determined for a thin vanadium foil using SIMS[73]. From what we know of the recrystallization of vanadium foil, this represents the value
for the V(100) surface. It is conceivable that the value for V(110) is different. The vanadium foil appeared to have less surface oxygen than V(110) samples, even after oxidation experiments. Unless the foil was substantially cleaner than the single crystal V(110) due to hydrogen pretreatment, it is probable that surface oxygen on the vanadium foil preferentially segregates to grain boundaries. This behavior indicates that different crystal faces may have different heats of segregation. Oxygen may also segregate preferentially to oxide precipitates on the V(110) surface.

It was observed that temperature cycling during the cleaning procedure caused oxide precipitation on V(110) surfaces, perhaps nucleating at pits left over from polishing. Other researchers have reported hazy areas thick enough to appear yellowish[91]. Slow cooling of samples while sputtering rather than abrupt temperature cycling might keep surface oxygen concentrations low enough to inhibit oxide nucleation on the surface. However, a small amount of nucleated oxide might help to keep the rest of the surface oxygen-free by gettering surface oxygen. A similar phenomenon is used in the silicon industry to keep silicon devices oxygen free.

The hydrogen and deuterium TPD experiments give an indication of the relative strengths of the V-O, V-S, V-H, H-O, and H-S bonds. Hydrogen is unable to abstract oxygen or sulfur from the surface and hydrogen itself is only weakly bound to vanadium at elevated temperature (as evident from the V-H phase diagram). The D<sub>2</sub> desorption peak at 363 K is due to surface deuterium. The desorption peaks for D<sub>2</sub> and HD at 663 K are attributed to subsurface deuterium and hydrogen. HD and H<sub>2</sub> can only originate from the recombination of dissolved hydrogen with itself or deuterium which has diffused into the bulk either upon adsorption or during the temperature ramp. Similar effects are seen in the TPD of H<sub>2</sub> from Pd[92]. The hydrogen outgassing observed with vanadium samples newly introduced into UHV is consistent with a diffusion controlled desorption of hydrogen at low temperatures. The calculated desorption energies for both peaks (21±4 and 40±4 kcal mol<sup>-1</sup>) are much higher than the heat of solution of deuterium in
vanadium or the heat of formation of $\alpha$-vanadium deuteride ($\sim 3.0$ kcal mol$^{-1}$)$^{[93]}$.

As with deuterium adsorption, no oxygen abstraction from the surface was observed with potassium desorption. Potassium TPD shows two distinct desorption peaks at 370 K and 793 K. The calculated desorption energies of $39 \pm 4$ and $48 \pm 4$ kcal mol$^{-1}$ are slightly higher than those reported previously for sodium on V(110)$^{[65]}$. Two peaks are seen in the sodium experiments, the first peak is due to surface potassium, and the second peak is due to subsurface potassium. However, the presence of oxygen on the surface has been shown to stabilize surface sodium to higher temperatures. In the present work, a low coverage of potassium ($\sim 0.2$ ML) was used and CO desorbed coincident with both potassium peaks. The major contribution to this TPD spectrum is probably due to K-O$_{ads}$ interactions rather than subsurface potassium. The presence of two desorption peaks may indicate two types of surface sites, perhaps with differing numbers of adjacent oxygen species. No desorption (sublimation) of multilayer potassium was observed.

The interaction of the surface and subsurface regions of the sample is seen with oxygen as well as deuterium and potassium. In its natural state vanadium is rarely found with an oxidation state below +3. However, with the exception of the oxide precipitates found after temperature cycling, UHV prepared samples do not seem to oxidize substantially even at $10^{-6}$ Torr O$_2$. This observation is consistent with the passivating effect of very low oxygen coverages. Low oxygen coverages inhibit further adsorption and oxidation. This is certainly the case for CO, and CO$_2$ adsorption on V(110). At low pressure, the high temperatures required for further adsorption of O$_2$ favor diffusion of oxygen into the bulk rather than formation of a surface oxide.

### 3.4 Conclusions and Recommendations

Due to the extreme reactivity of vanadium, and the difficulty in obtaining clean, ordered surfaces, vanadium is not a suitable substrate for growing vana-
vanadium oxide films for study in UHV. The oxide overlayers are not stable at the high temperatures required for preparing the vanadium surfaces. Even at the temperatures required to desorb CO, CO₂, and H₂O from oxide covered samples, oxygen tends to migrate into the bulk of the sample and sulfur tends to migrate to the surface. By way of qualification, the samples studied in this work were never oxidized in such a way that the precipitated oxide phase covered the entire surface. This phase appears to be thermally stable although it is not known if it presents a barrier to surface segregation of bulk sulfur. Conceivably a surface completely covered with the precipitated phase might be suitable for UHV studies.

Experiments worth pursuing are the heats of segregation and ordered overlayer structures of oxygen on different vanadium crystal faces. Overlayer structures and stability may be related to the various suboxide phases of vanadium. Any studies of the adsorption of molecules on vanadium surfaces would be best performed with a dynamic approach involving continuous sputtering.

The major problems encountered in growing films of vanadium oxide on a metallic vanadium substrate were contaminants in the vanadium and the tendency for oxygen to diffuse into the bulk of the sample upon heating. Evaporation of metallic vanadium may prove to be a method for depositing very clean films of vanadium. If the vanadium is deposited on an inert metal substrate that does not have a tendency to dissolve oxygen, the oxygen diffusion problem should also be solved. The following two chapters will discuss the preparation and properties of vanadium oxide films grown on gold substrates.
Chapter 4

Vanadium Oxide on Au(111)

4.1 Introduction

Ordered transition metal oxide surfaces can be obtained by growing oxide films on a metallic substrate. This method is often easier and inherently cleaner than bulk crystal growth. This chapter describes the growth of thin films of vanadium oxide on Au(111) single crystal surfaces. The growth mechanism, structure, composition, and reactivity of the oxide surfaces are discussed.

Ordered native oxide films can be grown on the transition metal of interest. Previous research has shown this to be true for molybdenum single crystal surfaces[60,59]. However, the high reactivity and inherent lack of cleanliness of vanadium single crystal substrates makes them unsuitable substrates for the growth of vanadium oxide. This has been shown in the previous chapter and in published literature[63,62,67]. Even if clean vanadium crystal surfaces were obtained, the diffusion of surface oxygen into the bulk of the sample inhibits the growth of thick oxide films.

Pure vanadium can be evaporated from a hot filament onto an inert Au(111) substrate and oxidized to produce clean, ordered vanadium oxide films. These films, can then be used to study the surface chemistry of vanadium oxide. The growth mechanism, composition, and structure of these films provide information about the strength of V-O and V-Au bonding relative to that of bulk vanadium oxide. The reactivity of the oxide surface towards adsorbed molecules provides
information about the relative reactivity of different oxidation states of vanadium.

The adsorbates studied; hydrogen, ethanol, and ethylene; relate to the partial oxidation of ethanol over vanadium oxide catalysts. Although the net oxidation state of a working catalyst is rarely less than +4, localized V$^{+3}$ ions may be produced in the course of the ethanol partial oxidation reaction. A mixture of +3, +4, and +5 oxidation states is difficult to characterize spectroscopically. The desorption energies of various molecules provide a more sensitive measure of surface oxidation states.

4.2 Methodology

Vanadium oxide films were grown on inert Au(111) substrates. The Au(111) single crystal was mounted on Ta wires and heated resistively. The high thermal conductivity of gold insured even sample heating even during temperature ramps of 20 K/s. Before vanadium deposition, the crystal was cleaned in UHV with alternating cycles of 500–2000 eV Ar$^+$ bombardment and annealing at 1000 K. Occasionally, annealing at 800–1000 K in 1 x 10$^{-5}$ torr O$_2$ was used to segregate contaminants to the surface prior to Ar$^+$ bombardment.

Vanadium was deposited from a resistively heated 15 Mil Tungsten filament wrapped with Marz grade vanadium wire. The filament was surrounded with a Ta shield to limit deposition to a small area in which the Au(111) sample could be placed. Typically the evaporator was degassed at ~1400 K for 1 hour prior to actual deposition. Deposition could be accomplished at 5x10$^{-9}$ Torr after outgassing of the source. Judging from the O(514 eV)/V(437 eV) Auger peak ratio of 0.22, the evaporated vanadium was cleaner than any of the bulk vanadium samples previously studied.

After deposition in small amounts onto the Au(111) surface, the vanadium was oxidized in 1x10$^{-7}$ Torr O$_2$. The film was ordered by annealing at 800–1000 K. Figure 4.1 illustrates the procedure for growing the V$_2$O$_3$ films on Au(111). Normally the second and third steps were combined, annealing in 1x10$^{-7}$ Torr O$_2$. 
Figure 4.1: Procedure for growing vanadium oxide films on Au(111).
4.3 Results

4.3.1 Vanadium Deposition and Oxidation

Films of metallic vanadium and vanadium oxide on Au(111) differ in thermal stability and reactivity. Metallic vanadium readily diffuses into Au(111) and is very reactive towards adsorbed molecules. Vanadium oxide is stable on the Au(111) surface and is relatively inert. The presence of oxygen along with the vanadium changes the films' properties dramatically.

Before oxidation, the clean vanadium deposited on Au(111) is not thermally
stable. Even at 450 K, the vanadium irreversibly diffuses into the bulk of the gold crystal. Figure 4.2 shows the decrease in vanadium (437 eV) Auger electron signal after annealing the sample at various temperatures for one minute. Using the decrease in Auger electron signal as an estimate of the diffusion rate as a function of temperature an activation energy for dissolution of 3 kcal/mole is obtained. If oxygen is present on the surface, this behavior changes drastically.

Even at room temperature the deposited vanadium oxidizes readily. Some pressure/exposure dependence of the oxidation rate is observed. The oxidation is slow at pressures below \(5 \times 10^{-6}\) Torr \(O_2\), but above this pressure there is rapid uptake of oxygen by the vanadium. Accompanying oxidation is a sharp attenuation of the Auger signal from the gold substrate. Some coverage dependence was observed in the oxidation behavior of vanadium on Au(111). Smaller quantities of vanadium on the surface oxidized under milder conditions than thicker deposits.

In the presence of oxygen, vanadium is stable on the Au(111) surface to \(\geq 800\) K. This is true whether the vanadium was initially deposited on the surface or was dissolved in the gold. Between experiments, a cleaning procedure which involved annealing the Au(111) crystal at 800–1000 K in \(1 \times 10^{-5}\) Torr \(O_2\) was used. This treatment caused vanadium which had dissolved in the gold to segregate to the surface and form a vanadium oxide film.

4.3.2 Film Growth Mechanism and Coverage Determination

Auger Electron Spectroscopy and secondary electron emission were used to monitor the growth of vanadium oxide on Au(111). Spectra were taken as a function of deposition time. Each point was taken after vanadium deposition, oxidation, and annealing. Due to the thermal stability of the oxide films on Au(111), the films could be annealed and ordered between depositions. Figure 4.3 shows the increase in V (437 eV) Auger signal and decrease in Au (69 eV) signal as increasing amounts of vanadium oxide were deposited on the Au(111) surface. No distinct breaks, which could distinguish a particular growth mechanism, are observed. The
CHAPTER 4. VANADIUM OXIDE ON AU(111)

Figure 4.3: Increase in V (437 eV) Auger signal and decrease in Au (69 eV) Auger signal as vanadium oxide is deposited on the Au(111) surface.
change in secondary electron emission accompanying vanadium oxide deposition are also shown. The secondary electron emission (determined from the sample current to ground) is very sensitive to the deposited vanadium oxide, but again, no distinct breaks in the uptake curves are observed.

4.3.3 Composition of Vanadium Oxide on Au(111)

The composition of the vanadium oxide overlayer was determined by AES. The O(514 eV)/V(437 eV) AES peak-to-peak ratio, the V(473 eV)/V(437 eV) peak-to-peak ratio and the chemical shift of the V(437 eV) peak were used to follow changes in the oxidation state of the vanadium. Immediately following deposition vanadium had O/V and V/V peak ratios of 0.3 and 1.5 respectively. The annealed, ordered overlayer had O/V and V/V peak ratios of 2.2 and 0.9 respectively. If the films were further oxidized at 20 Torr O₂ the O/V and V/V peak ratios became 2.5 and 0.8 respectively. After any combination of vanadium and oxygen was annealed at 800–1000 K in UHV, the values for the annealed, ordered vanadium oxide overlayer were always observed. This corresponds to V₂O₃.

4.3.4 Structure of Vanadium Oxide on Au(111)

After several cleaning cycles, the room temperature LEED pattern characteristic of the Au(111) (1 x 1) surface structure was obtained (figure 4.4 a.). Although not very sharp, this pattern exhibits the 3-fold symmetry characteristic of hcp(111) surfaces. No reconstruction of the clean Au(111) surface was observed.

After deposition, the vanadium film was oxidized in 5×10⁻⁵ to 5×10⁻⁶ Torr O₂. A (\(\sqrt{3}\times\sqrt{3}\))R30° pattern is observed (figure 4.4 b.) after annealing the oxidized film at 800–1000 K. This pattern is coincident with the substrate lattice. The overlayer pattern could be seen at all coverages of vanadium oxide, from trace coverages (\(<1\) ML) to coverages at which no gold signal was observed with AES. The overlayer spots were of much lower intensity at low coverages, and all spots were of equal intensity at high coverages.
Figure 4.4: Room temperature LEED patterns of: a.) clean Au(111), 77 eV
b.)~1 ML vanadium oxide on Au(111), 96 eV.
CHAPTER 4. VANADIUM OXIDE ON AU(111)

The \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure is stable and reproducible. Oxidation of the vanadium at 20 Torr \(O_2\), either through intentional oxidation or removal of a vanadium covered Au(111) from UHV, resulted in a diffuse background with no LEED pattern. However, annealing of such samples at 800 K in vacuum for several minutes restored the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure. This same structure was also obtained when dissolved vanadium segregated to the Au(111) surface after annealing in \(O_2\).

Occasionally, especially after extreme oxidation treatments, there was evidence of other incommensurate surface structures. However, these were too poorly characterized to obtain any structural information.

4.3.5 Chemisorption of Hydrogen, Ethanol, and Ethylene

The chemisorption of hydrogen, ethanol, and ethylene on the vanadium oxide surface was studied. In UHV, the Au(111) substrate is inert to these molecules so that only chemisorption due to the oxide is observed.

Molecular \(H_2\) did not adsorb on the vanadium oxide surface. However, predissociated hydrogen did interact. Following adsorption, the hydrogen abstracted an oxygen, and desorbed as \(H_2O\). Figure 4.5 shows a series of experiments with increasing doses of hydrogen. The desorption of \(H_2O\) after the initial 3000 L dose of hydrogen occurred at 550 K (a desorption energy of 33±4 kcal mole\(^{-1}\)). Subsequent, larger doses of hydrogen did not produce larger amounts of \(H_2O\) desorption. Rather, subsequent hydrogen doses produced smaller and smaller \(H_2O\) desorption peaks. Low pressure reoxidation of the vanadium oxide was required in order to obtain the original quantity of desorbed \(H_2O\). There appears to be a limited quantity of removable oxygen in the vanadium oxide film.

TPD after ethanol adsorption produces only CO and \(CO_2\) desorption at 800 K (a desorption energy of 48±4 kcal mole\(^{-1}\)). Figure 4.6 shows desorption spectra after two different exposures of ethanol. Larger exposures of ethanol produce more CO and \(CO_2\). No clear desorption of \(H_2O\) was observed.
Figure 4.5: TPD spectra of H$_2$O desorption from vanadium oxide on Au(111) a.) after exposure to 3000 L molecular H$_2$ b.) after exposure to 3000 L predissociated hydrogen c.) after subsequent exposure to 6000 L predissociated hydrogen d.) after subsequent exposure to 9000 L predissociated hydrogen e.) after low pressure reoxidation and exposure to 3000 L predissociated hydrogen. No correction is made for actual hydrogen dose.
Figure 4.6: Desorption of reaction products after adsorption of a.) 3000 L ethanol b.) 8000 L ethanol on vanadium oxide on Au(111).
Figure 4.7: Desorption of reaction products after adsorption of 30,000 L ethylene on vanadium oxide on Au(111)
Ethylene, a possible decomposition product of ethanol, was also adsorbed (see figure 4.7). As with ethanol adsorption, a mass 28 amu (CO or C\textsubscript{2}H\textsubscript{4}) peak was observed, this time at 750 K (a desorption energy of 45±4 kcal mole\textsuperscript{-1}). A mass 30 amu peak at 750 K was also observed, which may arise from the platinum supports for the Au(111) crystal. No distinct desorption of H\textsubscript{2}O at 550 K or any other temperature was observed.

4.4 Discussion

4.4.1 Vanadium Deposition and Oxidation

The use of evaporated vanadium to grow oxide films on a gold single crystal produces a very clean vanadium oxide film. The use of a Au(111) substrate eliminates the tendency for the oxygen to diffuse into the bulk of the sample. However, metallic vanadium diffused into the Au(111). Gold and vanadium can form several intermetallic compounds[94]. Since metallic vanadium is much more reactive than gold and probably has a higher surface free energy, the thermodynamic driving force was directed towards vanadium dissolution into the bulk of the gold.

The presence of oxygen on the surface reversed the driving force so that vanadium segregated to the surface. The ordered vanadium oxide film on Au(111) is a thermodynamically stable phase. If a film with excess vanadium is heated in UHV, some vanadium dissolves in the Au(111). If a film with excess oxygen is heated in UHV, excess oxygen desorbs. When heated to 800–1000 K in UHV, any combination of vanadium and oxygen on Au(111) will produce the same ordered phase.

4.4.2 Film Growth Mechanism and Coverage Determination

The uptake curves (Auger electron signal as a function of deposition time) do not show any features which would distinguish a particular growth mechanism. The exponential change in the curves is typical of some type of 2D growth, as opposed
to 3D island growth[95]. This is consistent with the observed loss of substrate AES signal during the oxidation of deposited vanadium. If 3D islands were forming, the substrate should be seen in AES. If 2D growth is occurring the volume increase accompanying oxidation would hasten the attenuation of the substrate signal.

The presence of an ordered LEED pattern at all coverages of vanadium oxide is consistent with the formation of 2D islands. Similar studies of FeO on Pt(111) [96] and TiO$_2$ on Rh(111)[97] show that the oxides grow in a layer-by-layer manner on these metal substrates. Gold is less reactive than either Pt or Rh, and should interact less than either Pt or Rh. However, it is probable that the growth mechanism for vanadium oxide on Au(111) is also layer-by-layer.

4.4.3 Composition of Vanadium Oxide on Au(111)

The Auger spectrum of the ordered vanadium oxide film on Au(111) is consistent with V$_2$O$_3$. Due to the possibility of chemisorbed oxygen, the O(514 eV)/V(437 eV) peak-to-peak ratio is not as reliable as other measurements of oxide stoichiometry. However the O(514 eV)/V(437 eV) peak-to-peak ratio of 2.2 observed for the annealed overlayer is consistent with a 1.4 ratio of oxygen to vanadium. The V(473 eV)/V(437 eV) peak-to-peak ratio of 0.9 is close to that reported by Rao et. al. for V$_2$O$_3$[98]. The assignment of V$_2$O$_3$ for vanadium oxide films annealed in UHV is further substantiated by experiments showing that V$_2$O$_3$ is the last congruently vaporizing oxide of vanadium in vacuum[99]. Upon heating in vacuum, either vanadium or oxygen is lost until the V$_2$O$_3$ stoichiometry is reached. The vanadium oxide film on Au(111) is stable to temperatures above those at which oxygen from higher oxides should desorb, and it is probable that excess vanadium from lower oxides dissolves in the gold substrate.

4.4.4 Structure of Vanadium Oxide on Au(111)

The structure of the vanadium oxide film we observed matches that of the (0001) face of corundum-structure V$_2$O$_3$. The lattice parameter of V$_2$O$_3$ is identical to that of the ($\sqrt{3} \times \sqrt{3}$)R30° structure observed on Au(111). The lattice parameters
of V₂O₃ (5.1 Å) and √3 Au(111) (2.88 Å) differ by only 2%. The amount of lattice mismatch may vary slightly depending on the amount of non-stoichiometry in the V₂O₃. Whereas FeO on Pt(111) has a large mismatch [96] and forms different LEED patterns at ≤1 ML and >1 ML coverages, V₂O₃ on Au(111) shows the same LEED pattern at all coverages. This indicates that monolayers and multilayers of vanadium oxide on Au(111) have the same structure. Any incommensurate structures of vanadium oxide on Au(111) were observed following extreme oxidation conditions and were probably due to higher oxides.

The (0001) face of V₂O₃ consists of alternating layers of oxygen anions and vanadium cations. This is different from the (047) face exhibited by cleaved V₂O₃ crystals[100], which always exposes a mixture of both vanadium and oxygen ions. The (0001) face offers the possibility of exposing either all oxygen anions or an ordered array of smaller vanadium cations on top of a layer of close packed oxygen anions. The activity of the surface towards adsorption of molecules should be different depending on whether or not vanadium ions are accessible.

### 4.4.5 Chemisorption of Hydrogen, Ethanol, and Ethylene

V₂O₃ is the lowest oxide typically observed after stoichiometric reduction of V₂O₅ during temperature programmed reduction (TPR). Working vanadium oxide catalysts have average oxidation states between +4 and +5. However, some surface V³⁺ ions are likely to be present during the course of a reaction. The TPD of hydrogen and hydrocarbons shows that the ease of oxygen abstraction from vanadium oxide decreases as the oxide is reduced.

The activated adsorption of molecular H₂ is to be expected. In general, oxide surfaces lack the ability to dissociate diatomic molecules[101]. The predissociation of hydrogen allows the abstraction of oxygen as H₂O to be studied. The desorption of H₂O occurs at 550 K until such a level of reduction is reached that no more oxygen abstraction occurs. The desorption temperature of 550 K for H₂O is very close to that found for reduced V₂O₃ surfaces. If large amounts of hydrogen are adsorbed, the amount of H₂O desorbed is limited by the film stoichiometry rather
than by the adsorbed hydrogen. Since no other hydrogen containing species were observed, excess hydrogen probably recombines and desorbs at room temperature. Low pressure oxidation will replenish the abstracted lattice oxygen. The quantity of oxygen which can be removed as H2O may be related to the degree of non-stoichiometry in the V2O3 film necessary for its lattice parameters to match those of the Au(111) substrate.

Ethanol and ethylene adsorption occur readily on V2O3/Au(111) with complete oxidation to CO and CO2 occurring. Since no distinct H2O desorption is observed the desorption of H2O is probably reaction limited. Since CO and CO2 desorption occurs at roughly the same temperature after adsorption of all molecules, their desorption is probably desorption limited. There were indications of a more tightly bound carbon which required oxidation to remove; however, this was only observed after extreme reducing treatments and may be due to carbide formation.

4.5 Summary

The growth of vanadium oxide films on an inert Au(111) substrate is an ideal method of preparing vanadium oxide surfaces for surface science studies. The evaporation produces much cleaner metallic vanadium than do other preparation methods. Similarly the use of a gold support eliminates the tendency for oxygen to diffuse into the bulk of the sample. Although metallic vanadium readily dissolves in gold, once oxidized, it remains stable on the surface. An ordered vanadium oxide film can be reproducibly obtained on the surface by heating any coverage of vanadium and oxygen on Au(111) to 800-1000 K in UHV. The composition of this film is V2O3 and it appears to grow via a layer-by-layer mechanism. A small quantity of oxygen can be abstracted from the film at 550 K as H2O after adsorption of predissociated hydrogen. Adsorption of ethanol and ethylene produce primarily CO and CO2. The occasional appearance of non coincident surface structures suggests that higher vanadium oxides can be grown if more extreme oxidation treatments can be performed.
These experiments with $V_2O_3$ on Au(111) provide information on the surface chemistry of $V_2O_3$. The desorption energies of $H_2O$, CO, and $CO_2$ on $V_2O_3$ should be compared to those from $V_2O_5$ discussed in the next chapter. The growth of vanadium oxide layers on gold is an ideal method for obtaining clean vanadium oxide surface. The major drawback of the preparation in UHV is the inability to obtain films with oxidation states higher than +3. The next chapter discusses the preparation of polycrystalline $V_2O_5$ supported on gold foil. Theses samples have a large bulk to surface ratio, and reoxidation of the surface can occur through the surface segregation of lattice oxygen rather than through oxidation from the gas phase.
Chapter 5

V$_2$O$_5$ on Gold Foil

5.1 Introduction

Chemisorption studies on oxide surfaces in UHV can be quite difficult. Often mounted as pressed pellets or powders, oxides are difficult to heat evenly and to characterize using surface science techniques. Single crystal samples, in addition to being difficult to mount, can be plagued by low reactivity. However, well characterized samples, with surface areas appreciably higher than that of single crystals, can be obtained by growing crystallites of V$_2$O$_5$ on a gold foil. The gold is chemically inert, and its thermal properties make it heat very evenly. These samples are used to model supported V$_2$O$_5$ catalysts. The V$_2$O$_5$ crystallites on gold foil (see figure 2.15) are similar in appearance to those formed on SiO$_2$ supported catalysts[102] and present three faces for reaction, the (010) cleavage plane, the (100) cleavage plane, and the less well formed (001) growth plane (see figure 1.3). Additionally, the crystallites (1$\mu$ x 1$\mu$ x 10$\mu$) have a large bulk to surface ratio so that an oxidized surface can be maintained over the course of several experiments via segregation of bulk oxygen before extreme reoxidation at higher pressures is necessary.

A series of experiments were performed to investigate the stability of V$_2$O$_5$/Au foil in UHV, and the strength of the V-O bond. The P-T diagram for vanadium oxide (see figure 1.4) shows that V$_2$O$_3$ or V$_2$O$_4$ should be the stable phase in UHV[7]. However, research from other laboratories indicates that clean V$_2$O$_5$ is
stable in UHV even at elevated temperatures[1,103,3]. In addition to characterizing \( \text{V}_2\text{O}_5/\text{Au} \) foil with respect to homogeneous \( \text{O}_2 \) loss, Temperature Programmed Reduction (TPR) was used to characterize the stability of the oxide with respect to \( \text{H}_2\text{O} \) loss. TPR has traditionally been used to characterize the oxygen bonding of oxide catalysts. Figure 6.4 shows a TPR of bulk \( \text{V}_2\text{O}_5 \) powder. A single step reduction to \( \text{V}_2\text{O}_3 \) occurs at 930 K. However, other researchers have reported stepwise reduction of \( \text{V}_2\text{O}_5 \) using TPR[104], indicating that TPR in UHV might be a method for preparing partially reduced \( \text{V}_2\text{O}_5-x \) surfaces for chemisorption experiments. The desorption temperature of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) was more sensitive to surface oxidation state than was Auger Electron Spectroscopy.

In conjunction with spectroscopic and reduction-reoxidation experiments, the adsorption of ammonia, ethanol, and molecules relating to ethanol partial oxidation was studied. All adsorption experiments were performed at room temperature or above and investigated the chemisorption rather than physisorption of molecules. Ammonia was used to probe Lewis acid sites (oxygen vacancies) on the surface. Ethanol, \( \text{H}_2\text{O}, \text{C}_2\text{H}_4, \text{CO} \) and \( \text{CO}_2 \) were adsorbed to investigate reaction pathways involved in the partial oxidation of ethanol over \( \text{V}_2\text{O}_5-\text{SiO}_2 \) catalysts. (\( \text{SiO}_2 \) is an inert support used for \( \text{V}_2\text{O}_5 \) catalysts.) To cope with the difficulties of low reactivity encountered at low pressures (\( \leq 10^{-4} \) Torr), an apparatus allowing high pressure reoxidation of the sample as well as exposure of the sample to high pressures (\( \geq 10 \) Torr) of ethanol, followed by introduction into UHV, was also used.

### 5.2 Experimental

The preparation of \( \text{V}_2\text{O}_5/\text{Au} \) foil samples is discussed in Chapter 2 (Subsection 2.4.2). Upon introduction into UHV these samples were slightly contaminated with carbon and water. This contamination was easily removed by raising the sample temperature linearly at 20 K/s to 650 K. This treatment results in a clean \( \text{V}_2\text{O}_5 \) surface. The contaminants desorbed as \( \text{CO}, \text{CO}_2 \), and \( \text{H}_2\text{O} \). Occasionally, with badly contaminated samples, low temperature \( \text{O}_2 \) desorption was seen in
addition to the other species. After several experiments, an oxidized surface could no longer be maintained. In situ reoxidation at 770 K in high pressures of dry oxygen (≥10 Torr) was used to reoxidize the samples without carbon or water contamination.

High pressure reoxidation was also performed in a high pressure cell attached to the sample introduction apparatus. Oxidation for several minutes in flowing O\textsubscript{2} at 350–500°C was followed by evacuation and introduction into UHV or by evacuation and exposure to ethanol vapor for 5–10 minutes at room temperature. Most experiments were performed with very long gas exposures at ~10^{-5} Torr. Such exposures tended to degrade the vacuum and a wait of an hour or more before desorption was common. Temperature Programmed Desorption (TPD) was used to monitor the desorption of products from the surface. Temperature ramps of 20 K/s were obtained with a programmable power supply. TPD spectra, with the exception of the H\textsubscript{2}O desorption after hydrogen dosing, are corrected for the molar sensitivity factors listed in table 2.2.

5.3 Results

5.3.1 Temperature Programmed Decomposition

The thermal stability of clean V\textsubscript{2}O\textsubscript{5}/Au foil in UHV was tested by raising the temperature of the sample and observing the desorption of O\textsubscript{2}. No other species desorbed from clean samples. Figure 5.1 shows the 32 amu mass spectrometer signal for a series of temperature ramps. The first time the sample is heated in vacuum, oxygen loss starts at 725 K. During consecutive temperature ramps the desorption temperature for oxygen increases to 800–850 K and the quantity of oxygen desorbed decreases. These peaks correspond to desorption energies of 43±4 and 48–51±4 kcal mole\textsuperscript{-1} respectively. After 10–15 temperature ramps, no oxygen is lost below 875 K.
Figure 5.1: Consecutive TPD experiments monitoring the O$_2$ loss (32 amu) from a V$_2$O$_5$/Au foil sample in UHV.
5.3.2 Temperature Programmed Reduction

Attempts to perform a TPR experiment at \(\leq 10^{-4}\) Torr \(\text{H}_2\) were unsuccessful. However, small quantities of water desorbing after dry \(\text{H}_2\) exposure in the presence of hot filaments was observed. Predissociation of the \(\text{H}_2\), exposing the sample to \(\text{H}_2\) in the presence (1 cm away) of a coiled tungsten filament, was attempted. The predissociated hydrogen adsorbed and yielded two water desorption peaks at 425 K and 500 K as shown in figure 5.2. \(\text{H}_2\text{O}\) desorption after \(\text{H}_2\) exposure without the hot filament is shown for reference. Consecutive hydrogen exposures (no correction is made for actual atomic hydrogen dose) and temperature ramps to 700 K yield only the second peak which increases in size with longer exposures, and increases in temperature with each consecutive experiment up to \(\sim 613\) K. These desorption peaks correspond to desorption energies of \(24\pm4\) and \(30-36\pm4\) kcal mole\(^{-1}\). However, if the temperature is raised to 750 K or the sample is annealed at 750 K for a few minutes between TPD experiments (no \(\text{O}_2\) desorption is observed), the 425 K peak is seen each time, and the high temperature peak remains at \(\sim 500\) K.

AES spectra were taken before and after hydrogen adsorption and TPD experiments. Figure 5.3 shows AES spectra taken before and after a 30,000 L hydrogen dose and after the TPD. Adsorption of atomic hydrogen should reduce the surface, however this is not observed in these spectra. The desorption temperature of the \(\text{H}_2\text{O}\) is more sensitive to the state of the surface than is AES.

It was observed that \(\text{H}_2\text{O}\) will not readsort at room temperature after the desorption of \(\text{H}_2\text{O}\) from \(\text{V}_2\text{O}_5/\text{Au}\) foil. Adsorption of ammonia was used to probe for defects and exposed vanadium ions (Lewis acid sites) which may have been left on the surface when water desorbed. Ammonia adsorption was also tried after sputtering the to remove surface oxygen. No room temperature adsorption of ammonia occurred after any of these treatments.
CHAPTER 5. $\text{V}_2\text{O}_5$ ON GOLD FOIL

Figure 5.2: Water (18 amu) desorption from $\text{V}_2\text{O}_5$/Au foil after dosing atomic hydrogen: a.) 30,000 L dose no predissociation b.) and c.) 15,000 L doses d.) 30,000 L dose e.) 45,000 L dose. Exposures are not corrected for actual atomic hydrogen dose.
Figure 5.3: AES spectra taken: a.) after reoxidation of $V_2O_5$ Au foil b.) after dosing 30,000 L hydrogen c.) after TPD.
5.3.3 Adsorption of Ethanol and Related Molecules

At low pressures ($5 \times 10^{-5}$ Torr), long exposures (10 min, 30,000 L) were required to observe adsorption of ethanol. Ethanol decomposes either upon adsorption or during the temperature ramp and only decomposition products are seen in the desorption spectrum. Figure 5.4 shows the TPD spectrum after adsorption of 10,000 L of D6-ethanol at room temperature. Mass 28 and 44 desorption peaks (CO and CO$_2$ respectively) are observed at 700 K ($42 \pm 4$ kcal mole$^{-1}$) and mass 32 (O$_2$ and C$_2$D$_4$) desorption peaks are observed at 410 K, 725 K and $\geq$ 800 K ($24 \pm 4$, $43 \pm 4$, and $\geq 48 \pm 4$ kcal mole$^{-1}$ respectively). The 32 amu desorption $\geq$800 K is attributed to O$_2$ from V$_2$O$_5$ decomposition, and two lower temperature peaks are attributed to C$_2$D$_4$. The 410 K peak was seen intermittently and may be arising from platinum wires used to support the Au(111). The assignment of the high and low temperature regions of the mass 32 amu desorption spectrum to O$_2$ and C$_2$D$_4$ respectively is based on the spectra of lower cracking fragments and similar experiments with H6-ethanol. No distinct desorption of D$_2$O (20 amu) was observed.

To determine whether the desorption of oxidation products following ethanol adsorption was reaction or desorption limited, the TPD of the reaction products of ethanol partial oxidation was also investigated. Water does not adsorb. CO and CO$_2$ do not absorb either. However, ethylene did adsorb, although inconsistently. Figure 5.5 shows the desorption spectra obtained intermittently during TPD experiments after adsorption of C$_2$H$_4$. Ethylene desorbs at 700 K ($42 \pm 4$ kcal mole$^{-1}$ desorption energy). Blank experiments with Au foil indicate that no desorption of any species arises from the gold.

Exposure of the sample to ethanol vapor in the high pressure cell was used to obtain saturation coverages of ethanol on V$_2$O$_5$/Au foil. After exposure to ethanol vapor, a saturation coverages of $\sim$ 1 ML ethanol (as estimated from the 40% attenuation of the vanadium 437 eV Auger peak) was obtained. The use of the high pressure cell allows large exposures without degradation of the vacuum
Figure 5.4: TPD spectrum monitoring the desorption of reaction products after a 10,000 L exposure of D6-ethanol at room temperature. 20 K/s temperature ramp.
Figure 5.5: TPD spectra after 45,000 L exposure of C\textsubscript{2}H\textsubscript{4} at room temperature.

in the main UHV chamber. The TPD spectrum after high pressure exposure to ethanol is shown in figure 5.6. The desorption of CO, CO\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4} is similar to that seen for low pressure experiments. Additionally there is evidence for small quantities of acetaldehyde (39 amu) desorption.

It is worth noting that the desorption temperatures for CO and CO\textsubscript{2} from any source are always the same. Surface carbon is easily removed from V\textsubscript{2}O\textsubscript{5}/Au foil, and samples are always carbon free after TPD experiments.

5.4 Discussion

The low reactivity of V\textsubscript{2}O\textsubscript{5}/Au foil in UHV is not surprising given the low turnover numbers (10\textsuperscript{-2}-10\textsuperscript{-4} molec site \textsuperscript{-1} s \textsuperscript{-1}) for V\textsubscript{2}O\textsubscript{5} catalysts even at atmospheric pressure. The adsorption sites for molecules aren’t known. However, the fact that ammonia would not adsorb even after reduction treatments suggests that all surface vanadium cations are well shielded by neighboring oxygen anions. Chemisorption on sputtered or otherwise reduced V\textsubscript{2}O\textsubscript{5} does not differ significantly from that on oxidized V\textsubscript{2}O\textsubscript{5}. Since H\textsubscript{2}O will not readsorb at room temperature after desorption of H\textsubscript{2}O or after sputtering, a rearrangement of the V\textsubscript{2}O\textsubscript{5} surface must
Figure 5.6: TPD spectrum after exposure to ethanol at 10 Torr for ten minutes.
accompany the removal of surface oxygen. Low concentrations of defects are consistent with the solid state chemistry of vanadium oxide. However, the low levels of adsorption are probably due to an activation barrier for chemisorption rather than a lack of adsorption sites (defects). The ability to achieve saturation coverages after high pressure adsorption at room temperature supports this view. Low temperature physisorption experiments could be used to probe defects. However, high temperature experiments are most useful when investigating chemical reactions occurring at the surface.

The vacuum decomposition experiments correlate well with similar experiments on powdered samples in flowing helium. The 720 K and ≥ 800 K desorption temperatures correspond to the lattice oxygen loss from V_2O_5 and V_6O_13 respectively as reported by Dziembaj[105,24]. It is noteworthy that, when contaminated, bulk powders show low temperature O_2 loss in addition to H_2O, CO, and CO_2 losses at intermediate temperatures. Dziembaj observes a correlation between the cleanliness of the sample and the absence of the low temperature oxygen peak. Conceivably, a weakly bound state of molecular oxygen exists which is only associated with badly contaminated vanadium oxide surfaces. TPD experiments show that the V_2O_5 surface behaves very differently in the presence of carbon and hydrogen than when clean. Since carbon and hydrogen are present during catalytic reactions, UHV experiments aimed at understanding catalysis should focus on the behavior of carbon and hydrogen contaminated surfaces rather than “clean” vanadium oxide surfaces.

The hydrogen TPD experiments are consistent with the view that traditional TPR experiments are adsorption limited. The lack of H_2 adsorption in UHV is probably due to an activated adsorption process. Also, the UHV experiments show that both lattice oxygen diffusion and H_2O desorption occur well below the peak reduction temperature in TPR (930 K). The 425 K desorption peak observed during the initial TPD experiment, or after heating the sample to 750 K indicates that this peak arises from a surface oxygen species that is depleted after one TPD experiment to 700 K. This species is replenished through diffusion of lattice oxygen.
to the surface upon heating to 750 K. The assignment of 750 K as the temperature above which facile lattice oxygen diffusion occurs is consistent with other research on single crystal V$_2$O$_5$[1]. The high temperature H$_2$O desorption probably arises from subsurface oxygen since it does not disappear, but increases in temperature as the subsurface region of the crystallites become more reduced. After several experiments the temperature of this second desorption peak rises above that found on V$_2$O$_3$ samples. This would be consistent with reduction of the surface region to an oxidation state $\leq$+3. Although the peak desorption temperatures for O$_2$ and H$_2$O change substantially with surface oxidation state, no changes were observed in the Auger electron spectra over the course of these experiments.

The addition of atomic hydrogen via predissociation, hydrogen spillover, and electrochemical methods has been used to synthesize a number of hydrogen vanadium bronzes H$_X$V$_2$O$_5$ (0 $\leq$ X $\leq$ 3.77)[106,107,108]. Several phases have been produced with V-H bonds being present at the higher loadings. Exposure of V$_2$O$_5$ surfaces to predissociated hydrogen presumably forms a hydroxylated surface similar in structure to the bronzes or vanadium oxide minerals. Most of the hydrogen bronze experiments have used hydrogen spillover from platinum, so reverse spillover and desorption of H$_2$ is favored over H$_2$O desorption as the decomposition pathway. No TPD from hydrogen vanadium bronzes or the hydroxyl-containing vanadium oxide minerals is available for comparison with our TPD results.

The activation barrier for reduction of V$_2$O$_5$/Au foil varies considerably. If carbon or hydrogen can be adsorbed, reduction via oxygen removal as H$_2$O, CO, and CO$_2$ occurs much more readily (24–42 kcal mole$^{-1}$) than O$_2$ loss (43–48 kcal mole$^{-1}$). In fact, O$_2$ desorption occurs at temperatures well into the region of rapid lattice oxygen diffusion. The high activation energy for O$_2$ desorption and the low rate of reoxidation with O$_2$ may be related. The site left after O$_2$ desorption may be the same one necessary for O$_2$ adsorption. Given the tendency for oxygen vacancies in V$_2$O$_5$ to order over large distances, an adsorption site comprised of adjacent vacancies formed upon O$_2$ desorption would be unstable and would not exist in large numbers on the surface.
It is interesting to note the resemblance between the desorption product distribution in ethanol TPD and the high conversion product distribution for catalytic ethanol oxidation (figure 6.12). Although small amounts of acetaldehyde (39 amu) and ethylene (27 amu) are also seen, the desorption spectrum after adsorption of ethanol is comprised primarily of CO and CO$_2$. H$_2$O is also seen, but without distinct desorption peaks. This is true after both low pressure and high pressure exposures of ethanol. In catalytic experiments a similar relationship is observed for ethanol partial oxidation over Nb$_2$O$_5$-based catalysts. The lack of partial oxidation products in the TPD of these catalysts in flowing He, and at high conversions during catalytic reactions, is attributed to a lack of gas phase ethanol which is required to induce the desorption of partial oxidation products$^{[109]}$. The lack of distinct H$_2$O desorption peaks in our TPD experiments is consistent with this interpretation. The ethanol is decomposing either upon adsorption or during the temperature ramp. After ethanol adsorption, H$_2$O does not desorb at 425 K or 500 K, where it does after room temperature hydrogen adsorption. During the TPD experiment, it is probable that H$_2$O is desorbed continuously at temperatures above 425 K as intermediates from the ethanol adsorption (ethoxy ?) decompose. If the intermediates were decomposing at low temperatures, H$_2$O should desorb as a distinct peak between 425K and 500K. The lack of partially oxidized desorption products in UHV is probably due to the lack of gas phase ethanol and water required to induce the desorption of acetaldehyde and acetic acid. The adsorption of CO, CO$_2$, H$_2$O, and C$_2$H$_4$ at higher pressures has not been pursued.

Little can be said about the adsorption of other molecules except that all CO and CO$_2$ species appear to desorb with a desorption energy of 42±4 kcal mole$^{-1}$.

5.5 Conclusions

A consistent picture of surface reactions on V$_2$O$_5$ arises from these experiments. The adsorption of most molecules is activated so that V$_2$O$_5$ surfaces are relatively inert. V$_2$O$_5$ itself is thermally stable in UHV up to 700 K. However, if carbon
or hydrogen can be adsorbed by some means, the surface reduces at much lower temperatures. Although reduction with molecular \( \text{H}_2 \) occurs at too high a temperature to selectively reduce the surface, reduction with predissociated hydrogen appears to be a viable approach to obtaining reduced surfaces. However, as the ammonia and \( \text{H}_2\text{O} \) adsorption experiments indicate, active adsorption sites do not exist on the surface even after low temperature reduction. These observations are all consistent with a mechanism for stabilizing the surface after oxygen removal, perhaps a reconstruction of the surface.

The hydrogen TPD experiments on \( \text{V}_2\text{O}_5/\text{Au} \) foil and \( \text{V}_2\text{O}_3/\text{Au}(111) \) (see chapter 4) provide some insight into reactions occurring on vanadium oxide catalysts. The desorption energies for \( \text{H}_2\text{O}, \text{CO}, \text{and CO}_2 \) all increase with decreasing oxidation state. Increasing desorption energies would slow down the desorption of oxygen containing molecules from the surface. If the rate of surface reoxidation stays constant or increases with decreasing oxidation state, the oxidation state of the surface would remain at some steady state value. The UHV experiments with \( \text{V}_2\text{O}_5/\text{Au} \) foil show that facile diffusion of lattice oxygen occurs \( \sim 750 \text{ K} \). Many catalytic reactions are performed above this temperature. There must be substantial interaction between the bulk and the surface of the catalyst during the catalytic reaction. As mentioned in the previous chapter, kinetic experiments with samples of varying thickness (1–10 ML) might provide information on bulk-like rearrangements accompanying surface reactions at temperatures above 750K. Not only is there interaction between surface and bulk during most reactions, the ethanol adsorption experiments suggest an important surface-gas phase interaction necessary for the desorption of partially oxidized products from \( \text{V}_2\text{O}_5/\text{Au} \) foil. This implies a need for TPR experiments on well characterized samples in high pressures of gas.

The Au-supported \( \text{V}_2\text{O}_5 \) samples appear to be ideal samples to model \( \text{V}_2\text{O}_5\)-SiO\(_2\) catalysts. They are easy to work with and perform reactions expected from the real catalysts. Since the low and high pressure adsorption experiments yield similar results, it is apparent that reactions on vanadium oxide can be studied
in UHV. However, to adsorb large amounts reactants on the surface, experiments using the high pressure cell are necessary.
Chapter 6
Catalysis over $V_2O_5$-$SiO_2$

6.1 Introduction

Supported vanadium pentoxide (vanadia) based catalysts are used extensively for a variety of oxidation reactions. The ability to selectively catalyze specific reactions is a characteristic of vanadia catalysts which we studied with both kinetic experiments using model $V_2O_5$-$SiO_2$ catalysts and UHV experiments using gold-supported $V_2O_5$ (chapter 5). Silica ($SiO_2$) was chosen as a support for the catalytic experiments since it is the most inert high surface area support used for vanadia catalysts[39,110]. The partial oxidation of methane and ethanol were investigated in catalytic experiments. The partial oxidation of methane with nitrous oxide over $V_2O_5$-$SiO_2$ catalysts was initiated by similar studies over molybdenum trioxide based catalysts[111,112,113,114]. The partial oxidation of methane produces methanol (which can also be oxidized by vanadia). Ethanol, rather than methanol, was chosen as the reactant for alcohol partial oxidation experiments because of the possibility of producing acetaldehyde and acetic acid. The partial oxidation of ethanol results discussed in this chapter can be compared with the adsorption of ethanol on $V_2O_5$/$Au$ foil in UHV.

The energetics of the methane (or any other organic molecule) oxidation favor fully oxidized products, especially if water is formed as a byproduct. As figure 6.1 indicates, the oxidation of $C_1$ compounds to $CO_2$ is thermodynamically favorable. In addition, methane is much less reactive than other $C_1$ molecules so that reaction
conditions favoring its oxidation will favor the oxidation of the desired products to an even greater extent. The energetics for methane partial oxidation with \( \text{N}_2\text{O} \) are shown, since partial oxidation of methane was only accomplished using \( \text{N}_2\text{O} \) as an oxidant. The ethanol partial oxidation experiments were run using \( \text{O}_2 \) as an oxidant.

Although \( \text{V}_2\text{O}_5\text{-SiO}_2 \) has slightly higher activity than \( \text{MoO}_3\text{-SiO}_2 \) for methane partial oxidation it's activity is too low to warrant studies in UHV. Also, the use of nitrous oxide as an oxidant is expensive and impractical. Additionally, it has been shown that oxygen radicals are involved in the reaction of methane and \( \text{N}_2\text{O} \)[113,114] so it is not obvious that the surface properties of vanadia for anything other than oxygen radical formation are important in this reaction. The partial oxidation of ethanol using \( \text{O}_2 \) over vanadia is a more suitable reaction for parallel UHV and catalytic studies. The higher activity for this reaction makes studies with low surface area samples possible. Although different oxidants are used, several aspects of the methane oxidation reaction will apply to ethanol oxidation. In particular, the high dispersion of low loadings of \( \text{V}_2\text{O}_5 \) on \( \text{SiO}_2 \) and the use of
steam to inhibit total oxidation reactions are common to both reactions.

Previous research has suggested that the different crystal faces of $\text{V}_2\text{O}_5$ are active for different reactions\cite{102}. A catalytic reaction can be characterized as either structure insensitive or structure sensitive. The presence of structure sensitivity can aid in the understanding of reaction mechanisms on surfaces. Vanadia catalysts have been classified both ways\cite{115,116,117}. The structural anisotropy of vanadium oxide and the very different nature of various crystal faces lend themselves to discussions of structure sensitivity, yet several very good studies have concluded that reactions over vanadia catalysts are structure insensitive\cite{57}.

Since structure sensitivity in the partial oxidation of ethanol over $\text{V}_2\text{O}_5$-SiO$_2$ catalysts directly influences the appropriateness of the samples used in the UHV studies (chapters 3–5), it was necessary to test for its presence or absence. If structure sensitivity exists, then experiments should be continued with single crystal samples. If structure sensitivity does not exist, then polycrystalline samples are appropriate.

A traditional method to test for the structure sensitivity of a catalytic reaction is to vary the particle size of a catalyst in the range of 10 to 100 Å. This will vary the dispersion (surface to bulk ratio of catalyst atoms) and the ratio of different crystal faces exposed for reaction. This type of experiment is difficult to verify unless the surface area of the active catalyst can be measured and compared to the value expected if all of the atoms of the supported catalyst are surface atoms. The active surface of a supported metal catalyst can be measured using a molecule such as $\text{H}_2$ or CO (which selectively adsorbs only on the metal surface) to titrate the surface\cite{118}. Determining the active surface area of a $\text{V}_2\text{O}_5$-SiO$_2$ catalyst is not straightforward. Molecules which selectively chemisorb on $\text{V}_2\text{O}_5$ but not on SiO$_2$ are unknown. Previous research has used the selective reaction of the $\text{V}_2\text{O}_5$ surface with pulses of $\text{NH}_3 + \text{NO}$ \cite{119,120} or the selective reduction of the $\text{V}_2\text{O}_5$ surface followed by irreversible oxygen chemisorption\cite{121,122,123} to determine the active surface area of $\text{V}_2\text{O}_5$-SiO$_2$ catalysts. The oxygen chemisorption method was chosen for this work. This method can be evaluated in light of studies of
Once the dispersion of a series of catalysts is known, kinetic data can be evaluated for structure sensitivity. If the specific activity or product distribution of the catalyst varies with dispersion the reaction is structure sensitive. If no variation is found the reaction is structure insensitive. In addition, if the preferred shape of the catalytic compound is known, the reactivity of different crystal faces can be theorized[115,116,124,125,126]. A series of V₂O₅-SiO₂ catalysts were prepared and used to test for structure sensitivity in the partial oxidation of ethanol.

The kinetics parameters for both reactions are necessary to help elucidate the reaction mechanism. Activation energies and rate laws for the methane oxidation reaction are discussed. The structure sensitivity and temperature dependent product distribution for ethanol oxidation are also discussed.

### 6.1.1 Methane Partial Oxidation with N₂O over V₂O₅-SiO₂

Methane partial oxidation under a variety of reaction conditions was investigated. Table 6.1 illustrates the effects of changing contact times and reaction temperature on the conversion and selectivity of the methane partial oxidation reaction with N₂O over 2.2% V₂O₅-SiO₂. Increasing the temperature of the reaction in the range 733–773 K increases conversion but favors carbon monoxide and carbon dioxide production. Increasing contact time from 1.2 seconds to 4.6 seconds also increases conversion at the expense of selectivity. The highest selectivity to partial oxidation products (including a large proportion of formaldehyde) with N₂O is achieved at 0.1% conversion. The use of oxygen as the sole oxidant under these reaction conditions yields 80% selectivity to carbon oxides. However, the addition of 2% oxygen to the N₂O increases conversions to ~1% without substantially decreasing the selectivity[33]. The turnover rates shown in table 6.1 were calculated assuming that each vanadium ion in the catalyst is a surface ion. Turnover rates are in the range of 0.1 to 1.0 × 10⁻⁴ molecules/site⁻¹ s⁻¹.

Figure 6.2 shows Arrhenius plots for the formation of each product. Activation energies for methanol, formaldehyde, and carbon monoxide formation are 40±4,
CHAPTER 6. CATALYSIS OVER V$_2$O$_5$-SIO$_2$

<table>
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<tr>
<th>Temp K</th>
<th>Contact Time (S)</th>
<th>Turnover Rate $\times 10^4$ (molec.s$^{-1}$ atom$^{-1}$)</th>
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Table 6.1: Conversion and turnover rates at various temperatures and contact times: Reactant composition: 0.15 CH$_4$ + 0.30 N$_2$O + 0.40 H$_2$O + 0.13 He + 0.02 O$_2$. Total flow 80 cm$^3$min$^{-1}$.

22±2, and 47±4 respectively. Logarithmic plots of reaction rates as a function of mole percentage of reactant were used to determine reaction orders and rate laws. Figure 6.3 shows the plot for the pressure dependence of water at 773 K. Water (steam) in the reaction is required to inhibit total oxidation. Lower pressures of methane were required for this set of experiments to prevent the cracking of the methane at low steam pressures. Similar studies were performed to determine the pressure dependence of methane, nitrous oxide, and oxygen. The following rate laws were obtained:

\[
\frac{d(CH_3OH)}{dt} \propto [CH_4]^{1/2}[N_2O]^{1/2}[H_2O]^{1/2}
\]

\[
\frac{d(HCHO)}{dt} \propto [CH_4]^{1/2}[N_2O]^{1/3}[H_2O]^0
\]

\[
\frac{d(CO)}{dt} \propto [CH_4]^{1/2}[N_2O]^{1}[H_2O]^{-1}
\]

The large scatter in this data is due to problems with obtaining reliable steam pressures using the hot water reservoir assembly. This problem was corrected in ethanol oxidation experiments.
Figure 6.2: Arrhenius plots for formation of CH$_3$OH, HCHO and CO. Reactant gas: 80 cm$^3$ min$^{-1}$ flow of 0.15 CH$_4$ + 0.30 N$_2$O + 0.40 H$_2$O = 0.15 He, contact time of 1.2 sec.
Figure 6.3: The effect of changing the steam concentration of the reactant feed on turnover rates at 773 K. Composition (mole percent): H₂O = 14–31, CH₄ = 4, N₂O = 2S, O₂ = 1.6 and balance He.
6.1.2 **O₂ Chemisorption: Determination of the Active Surface area of V₂O₅**

Figure 6.4 shows a Temperature Programmed Reduction (TPR) spectrum of V₂O₅ powder. A variation on this experiment, reduction in flowing hydrogen followed by oxygen chemisorption at either room temperature or at the reduction temperature, was used to develop a procedure for the determination of the active surface area of unsupported V₂O₅ powders. Figure 6.5 shows the oxygen uptake curves for V₂O₅ powder reduced at various temperatures. Oxygen uptake is measured at the reduction temperature. The higher the reduction temperature, the higher the oxygen uptake.

Figure 6.6 plots the oxygen uptake data as a function of reduction temperature. Total BET surface area is also plotted. For comparison, the room temperature oxygen uptake after high temperature reduction is shown at the bottom of the plot.
Figure 6.5: The oxygen uptake curves of V$_2$O$_5$ after reduction at various temperatures.
Elevated temperatures are required for both reduction and appreciable oxygen uptake. In addition, although oxygen uptake changes drastically with reduction temperature, the total surface area of the samples does not. Three regions of oxygen uptake are observed in figure 6.6. Below 500 K, no appreciable chemisorption occurs. This is also the case for low temperature chemisorption following high temperature reduction. Between 500 K and 600 K oxygen uptake increases slowly with reduction temperature. Above 640 K, oxygen uptake increases drastically with increasing reduction temperature. XRD spectra taken after reduction, but before oxygen chemisorption (Figure 6.7), show the appearance of new peaks, attributed to lower vanadium oxides when the samples are reduced above 650 K. A reduction-oxygen chemisorption temperature of 641 K was chosen for active surface area measurements. The surface area calculated from oxygen uptake after reduction at 641 K (assuming 1 oxygen atom per surface vanadium) for V$_2$O$_5$ powder is 90% of the theoretical area calculated for ideal crystallites of V$_2$O$_5$.

6.1.3 Determination of the Dispersion of V$_2$O$_5$-SiO$_2$

Following the procedure described in the previous section, a series of V$_2$O$_5$-SiO$_2$ catalysts were evaluated. Weight loadings of 0.3% V$_2$O$_5$ to 9.8% V$_2$O$_5$ were studied. Oxygen uptake curves for these catalysts are shown in Figure 6.8. Plotting the oxygen uptake as a function of V$_2$O$_5$ loading, the dispersion curve shown in Figure 6.9 is obtained. As V$_2$O$_5$ loadings are increased, the oxygen uptake relative to vanadium content decreases. Whereas on the 0.3% and 1.4% catalysts nearly every vanadium ion is a surface ion, (90-100% dispersion) on the 9.8% catalyst only a fraction of the vanadium ions are on the surface (50% dispersion).

6.1.4 The Partial Oxidation of Ethanol with O$_2$ over V$_2$O$_5$-SiO$_2$

A summary of the conversion and selectivity of ethanol oxidation over 9.8% V$_2$O$_5$-SiO$_2$ is shown in Figure 6.10. At low conversions, selective oxidation products, acetaldehyde and acetic acid, are favored. As temperature and conversion are
Figure 6.6: Oxygen atom density and total surface area after reduction at various temperatures: a.) oxygen uptake at the same temperature as reduction (left scale) b.) B.E.T. surface area (right scale) c.) oxygen uptake at 298 K after reduction.
Figure 6.7: X-Ray Diffraction Pattern of Unsupported V$_2$O$_5$ Samples. a.) Reduced at 643 K. b.) Reduced at 658 K. c.) Reduced at 691 K.
Figure 6.8: Oxygen uptake curves for silica-supported $V_2O_5$ catalysts.
Figure 6.9: Dispersion curve for V$_2$O$_5$-SiO$_2$ catalysts plotted as $\mu$mol O$_2$ g$^{-1}$ catalyst as a function of catalyst loading.
CHAPTER 6. CATALYSIS OVER $V_2O_5-SiO_2$

Figure 6.10: Conversion and selectivities for ethanol oxidation over 9.8% $V_2O_5-SiO_2$.

Increased, decomposition products, ethylene, CO, and CO$_2$, are favored.

Activation energies for ethanol oxidation for the series of silica-supported vanadia catalysts with loadings from 1.4%-9.8% were determined to test for structure sensitivity. As figure 6.11 illustrates, the specific activities and activation energies for each of the catalysts are very close. Ethanol partial oxidation over $V_2O_5-SiO_2$ catalysts is structure insensitive.
CHAPTER 6. CATALYSIS OVER V$_2$O$_5$-SiO$_2$

Figure 6.11: Activation energies for product formation in ethanol partial oxidation with O$_2$ over 9.8% V$_2$O$_5$-SiO$_2$. 
6.1.5 Raman Spectroscopy of V₂O₅-SiO₂

It is possible that other vanadium oxide species besides crystalline V₂O₅ exist on V₂O₅-SiO₂ catalysts. Laser Raman spectroscopy was used to monitor the changes in the bonding of V₂O₅-SiO₂ catalysts as the catalyst loading and dispersion was changed. Raman spectroscopy was chosen to probe the vibrations of VOₓ species on the surface of these catalysts. Figure 6.12 shows Raman spectra for the series of V₂O₅-SiO₂ catalysts used for ethanol oxidation. The spectrum for the 9.8% catalyst is nearly identical to that of crystalline V₂O₅ (see figure 2.17). The 1040 cm⁻¹ vibration is characteristic of the vanadyl bond at the surface of V₂O₅-SiO₂[57]. As Figure 6.13 shows this stretch rapidly decreases in intensity with exposure of the catalyst to ethanol. This is expected if the vanadyl species is reacting with the ethanol. As the loading of the catalysts is decreased, the Raman spectra becomes more and more like the spectrum for amorphous V₂O₅[15,13]. Low signals and poorly resolved spectra preclude exact determination of surface species on the highly dispersed catalysts.

6.2 Discussion

Catalytic data can provide useful information concerning the surface chemistry of oxides. Active surface area measurements provide information concerning adsorption and oxygen diffusion energetics. Methane partial oxidation experiments provide information on radical-based reaction mechanisms. Dispersion measurements provide an estimate of V₂O₃ crystallite size. Ethanol partial oxidation provides information concerning secondary reactions in methane oxidation as well as lower temperature oxygen based reactions.

Comparison of the TPR spectrum of V₂O₅ with experiments in UHV suggest that the reduction of V₂O₅ with H₂ is an adsorption limited reaction. The peak reduction temperature of 930 K is well above the temperature necessary for facile lattice oxygen diffusion (750 K) and the maximum temperature for H₂O desorption from both V₂O₃ (550K) and V₂O₅ (613 K). occurs. These findings agree with
Figure 6.12: Laser Raman spectra of silica supported $V_2O_5$ catalysts[56].
Figure 6.13: Laser Raman spectra of 1.4% $V_2O_5$-$SiO_2$ exposed to ethanol[56].
other research[102,104]. When performed using molecular H₂, the TPR experiment monitors both bulk and surface reduction. If the experiment were performed with predissociated hydrogen, only surface reduction would be observed below 750 K. If the surface is to be reduced below 750 K, using H₂, longer reduction times will be necessary. The one hour reduction times at 641 K were found to reduce just the surface of the V₂O₅.

The reoxidation of vanadium oxide is also activated[127]. Figure 6.6 shows that oxygen adsorption on V₂O₅ is negligible at room temperature adsorption of oxygen. This means that V₂O₅ samples that have been reduced can be removed from the controlled environment of the reactor to other analytical instruments without altering their surfaces. The XRD spectra of samples reduced at various temperatures corroborates the conclusion based on oxygen uptake experiments that the sharp rise in oxygen uptake above 650 K is due to bulk as well as surface reduction and reoxidation.

Different methods were used to prepare the catalysts for the methane and ethanol experiments. However, other researchers suggest that the resulting catalysts should be the same[39,128,129]. The basic solutions used in the methane work favor monomeric vanadate species and compounds with more hydroxyl ligands, while the acidic solution used in the ethanol experiments favor large condensed species[18,130]. Regardless of preparation method, low loadings of V₂O₅-SiO₂ favor highly dispersed catalysts, whereas higher loadings favor condensation of the V₂O₅ into crystallites[39]. The dispersion experiments performed in conjunction with the ethanol oxidation studies show that the 2.2% V₂O₅-SiO₂ used for the methane oxidation studies is nearly 100% dispersed, as was assumed.

Other research has shown that methane oxidation with N₂O involves a radical mechanism[113,114]. Research on methane partial oxidation in other groups has moved away from vanadium and molybdenum oxide catalysts to catalysts such a Li⁺ promoted MgO[131], which are more efficient at producing oxygen radicals and require O₂ rather than N₂O. Using MgO catalysts, the gas phase combinations of methyl radicals after hydrogen extraction is the primary reaction path[131]. The
structure sensitivity of the methane partial oxidation reaction is not known. Conceivably the different activation energies for methanol, formaldehyde, and carbon monoxide formation reflect the adsorption of methyl radicals at different active sites on the catalyst. The rate laws indicate that water in the reactant feed favors methanol formation and inhibits carbon monoxide formation. The activation energy for CO formation in the methane oxidation experiments (47±4 kcal mo\text{-1}) is very close to that found for CO desorption from V\textsubscript{2}O\textsubscript{3}/Au(111) (45-48±4 kcal mo\text{-1}). This suggests that the surface of the working V\textsubscript{2}O\textsubscript{5}-SiO\textsubscript{2} catalyst may be reduced to V\textsubscript{2}O\textsubscript{3} and that the formation of CO may be desorption limited. Without spectroscopic evidence, exact reaction mechanisms are difficult to determine. The mechanism for ethanol oxidation may involve dissociative adsorption followed by hydrolysis or dehydrogenation of the adsorbed ethoxy group. Studies on Nb\textsubscript{2}O\textsubscript{5} catalysts have led to a proposed mechanism in which gas phase water helps partial oxidation products to desorb\cite{109}. The product distribution for ethanol partial oxidation is also consistent with the Nb\textsubscript{2}O\textsubscript{5} work and UHV work on gold-supported V\textsubscript{2}O\textsubscript{5} which shows only fully oxidized products and ethylene in the absence of gas phase ethanol or water.

The results of the ethanol partial oxidation show similar reactivity for all loadings of V\textsubscript{2}O\textsubscript{5}-SiO\textsubscript{2}. The structure insensitivity for the partial oxidation of ethanol over V\textsubscript{2}O\textsubscript{5}-SiO\textsubscript{2} catalysts is surprising given the structure of V\textsubscript{2}O\textsubscript{5} crystallites. Other species may exist on silica-supported catalysts. The active site for catalysis may be similar on both crystalline V\textsubscript{2}O\textsubscript{5} and dispersed V\textsubscript{2}O\textsubscript{5}. Many types of dispersed phases have been proposed. Some of these species are tetrahedral, similar to those proposed by Goddard for MoO\textsubscript{3} catalysts\cite{132}. Most involve pairs of vanadyl bonds or paired hydroxyl and vandyl bonds\cite{128,129}. NMR favors such species\cite{133} and their presence is compatible with the poorly resolved Raman spectra.

Dispersion measurements and Raman spectroscopy of V\textsubscript{2}O\textsubscript{5}-SiO\textsubscript{2} catalysts are consistent with the presence of a highly dispersed surface phase in addition to crystalline V\textsubscript{2}O\textsubscript{5}. However, such a phase is not necessarily monomeric. Vanadium
oxide tends form chains of octahedra. Even in its amorphous form, V₂O₅ is composed of tangled chains of octahedra. One can speculate that the dispersed phase of V₂O₅ on SiO₂ is similar in structure to amorphous V₂O₅.

6.3 Conclusions

Several observations from this work on V₂O₅-SiO₂ catalysts are consistent with observations from the work in UHV on gold-supported vanadium oxide. The selective surface reduction and subsequent oxygen uptake show that both reduction and oxidation are activated and that surface specific reactions occur below ~650 K. The UHV studies also encountered activated adsorption of H₂ and O₂ and found facile oxygen diffusion on a much shorter time scale at a slightly higher temperature (≥700 K). The possibility that the TPR of V₂O₅ in H₂ is adsorption limited is also consistent with the TPD of H₂O performed in UHV. Both methane and ethanol partial oxidation require the presence of gas phase water for partially oxidized products to be obtained. In the UHV experiments the primary desorption products after ethanol adsorption are CO, CO₂, and C₂H₄. The lack of gas phase water or ethanol in UHV has been suggested as the reason that partially oxidized desorption products are not observed.

Gold-supported V₂O₅ crystallites and silica supported crystallites (and a dispersed phase) exhibit similar behavior. An active site or ensemble may be common to both. If this site is not unique to specific crystal faces of V₂O₅, the structure insensitivity of the ethanol partial oxidation would be explained. Experiments on well characterized V₂O₅ samples at higher pressures will be necessary to elucidate the exact nature of the ethanol-V₂O₅ interaction.
Chapter 7

Conclusions

In this research, I set out to understand how molecules react with vanadium oxide surfaces. The methods I chose to use were primarily UHV surface science methods designed to monitor changes in the structure or composition of the surface accompanying reactions. A large part of my research dealt with preparing well characterized samples and studying their surface properties in UHV. This was necessary in order to determine whether or not the vanadium oxide surfaces behave the same in UHV as they do at higher pressures. Finally, the energetics of the stoichiometric reactions of hydrogen, ethanol, and ethylene were studied and compared with kinetic data obtained from catalytic studies.

The oxide growth on vanadium metal, although unsuccessful, provided insight into the chemical behavior of metallic vanadium. The affinity of vanadium for oxygen and other contaminants was obvious. Clean vanadium surfaces were impossible to obtain. However, the reaction of the surface with even small amounts of adsorbates (principally CO and O₂) passivated the surface towards further adsorption. Hydrogen was the only molecule that could adsorb on such a passivated surface. The high temperatures necessary to adsorb large amounts of oxygen tended to drive surface oxygen into the bulk of the sample. Upon cooling, some of this dissolved oxygen would segregate to the surface to form an inert, low coverage c(6×2) surface structure while other oxygen precipitated out into small platelets of some oxide phase. This precipitate was the closest thing to an oxide film obtained on vanadium substrates. Had research been continued on metallic vanadium sub-
strates, the use of high temperature hydrogen treatments and oriented foil samples would have been pursued. The subject of the experiments would have been the relationship of ordered surface structures to vanadium suboxide phases. However, this type of study more closely relates to metallurgy than to catalysis.

To answer the first question posed in chapter 1: Vanadium single crystals are not suitable substrates for the growth of vanadium oxide films for surface studies. Vanadium oxide film growth on other substrates was pursued.

Depositing vanadium from an outgassed evaporation source proved to be an easy method for obtaining clean films of vanadium. A Au(111) single crystal provided an ordered, yet inert, substrate. Although metallic vanadium has an affinity for gold, vanadium oxide does not. Annealing the thermally stable vanadium oxide films produced ordered V$_2$O$_3$ films which apparently grew via a layer-by-layer growth mechanism. The lattice parameter for Au(111) and V$_2$O$_3$ (0001) are nearly identical. The (0001) face is not the crystal face normally exposed when V$_2$O$_3$ single crystals are cleaved, but is the face exposed by the epitaxial V$_2$O$_3$ films. Only under extreme conditions could the V$_2$O$_3$ layers be oxidized further. V$_3$O$_3$ should be the most stable oxide phase in UHV at temperatures used to anneal the films.

TPD experiments with the V$_2$O$_3$ surface yield approximate desorption energies of 48±4 and 33±4 kcal mole$^{-1}$ for carbon oxides and water respectively. Carbon oxides desorbed at the same temperature after exposure to any source of carbon: ethanol, ethylene, or residual gas. However, water only desorbed at a distinct temperature after adsorption of predissociated hydrogen. (Unlike metallic vanadium, V$_2$O$_3$ cannot dissociate H$_2$.) Even when predissociated hydrogen was adsorbed, there appeared to be a limited amount of oxygen which could be abstracted from the V$_2$O$_3$ and desorbed as H$_2$O. The desorption of CO and CO$_2$ is probably desorption limited since it always occurs at the same temperature. The lack of distinct desorption peaks for water suggests that after ethanol or ethylene is adsorbed, hydrogen desorption as H$_2$O is reaction limited and occurs continuously as adsorbed intermediates decompose during the temperature ramp. The interpretation of TPD spectra is difficult owing to the extremely large gas exposures
required (>1000 L) for adsorption. Low reactivity of oxide surfaces is commonly observed. The use of predissociated hydrogen to study the binding strength of oxygen on the surface was a new method of probing oxide surfaces. The desorption energies for H₂O, CO, and CO₂ can be compared to the desorption energies obtained from V₂O₅ surface to see if they explain why the oxidation state of active vanadium oxide catalysts is between +4 and +5 rather than +3 (especially since it appears to be easier to reduce vanadium oxide than to oxidize it).

To answer the second set of questions posed in chapter 1: Clean, ordered vanadium oxide films can be grown on Au(111) in UHV. The films grow layer-by-layer and have the structure and composition of V₂O₅. These films react with hydrogen to desorb H₂O and ethanol and ethylene to desorb CO and CO₂. The desorption energies of H₂O, CO, and CO₂ can be compared to their desorption energies from V₂O₅. The oxidation from the gas phase oxidation states higher than +3 was a problem so samples with a large bulk to surface ratio were required. Polycrystalline V₂O₅ on gold foil was pursued.

In order to study V₂O₅ surfaces, samples with a large bulk to surface ratio were required. These were samples composed of crystallites (exposing three crystal faces) supported on gold foil. As with vanadium metal, oxygen segregates to the surface of vanadium oxide. This behavior was used to obtain a fully oxidized surfaces in UHV. Reoxidation from the gas phase requires high pressures (~10 Torr) of oxygen. Molecular oxygen can be desorbed from V₂O₅ with a desorption energy ranging from 43 to 48±4 kcal mole⁻¹. TPD experiments with predissociated hydrogen show a weakly bound surface oxygen which desorbs as water with a desorption energy of 24±4 kcal mole⁻¹ can be reproducibly obtained if the sample is annealed at 750 K between experiments. At 750 K bulk oxygen readily segregates to the surface. If temperatures lower than 750 K are used, the weakly bound oxygen disappears and another oxygen species appears. This species desorbs (as H₂O) with an energy which increases from 30±4 to 36±4 kcal mole⁻¹ as more oxygen is removed. The high end of this desorption energy range is above that observed for H₂O desorption from V₂O₃.
As with the $V_2O_3$, CO and CO$_2$ from any source desorbed with the same energy: this time $42\pm4$ kcal mole$^{-1}$. It appears that it is easier to remove oxygen as O$_2$, H$_2$O, CO, or CO$_2$ from $V_2O_5$ than to remove oxygen from $V_2O_3$. A self-leveling behavior in which a +3 oxide is less reactive toward reduction (desorption of oxygen containing products) than a +5 oxide, might explain why active catalysts have oxidation states closer to +5 than to +3. As with $V_2O_3$, the $V_2O_5$ surface is relatively inert. Exposure to ethanol vapor at high pressures using a new pretreatment chamber solved the problem of low reactivity. This method of gas exposure yielded monolayer coverages of ethanol. However, even with high coverages, the primary desorption products were total oxidation products (CO, CO$_2$, and C$_2$H$_4$) rather than partial oxidation products (acetaldehyde and acetic acid). Other researchers suggest that gas phase ethanol and water, which are present in catalytic reaction mixtures, are required to induce the desorption of partially oxidized products. TPR of the same samples in flowing gas mixtures rather and in UHV will be necessary to test this hypothesis.

To answer the third set of questions posed in chapter 1: $V_2O_5$ crystallites on gold foil are stable in UHV to $\sim775$ K. However the presence of carbon and hydrogen makes reduction of the surface (via H$_2$O, CO, and CO$_2$ desorption) much easier than reduction via O$_2$ loss. If the sample is heated to 750 K the surface segregation of lattice oxygen reoxidizes the surface. Ethanol decomposes on $V_2O_5$/Au foil and CO, CO$_2$, and C$_2$H$_4$ desorb. Very few partially oxidized products are seen even after high pressure adsorption of ethanol. The desorption temperatures for H$_2$O, CO, and CO$_2$ are generally lower for $V_2O_5$ than $V_2O_3$. For both oxides, after adsorption of ethanol, the desorption of H$_2$O appears to be reaction limited and the desorption of carbon oxides appears to be desorption limited. These results are consistent with the kinetic data from $V_2O_5$-SiO$_2$ catalysts.

Catalytic experiments were also performed. Just as an inert, low surface area support (gold) was used for the UHV experiments, an inert high surface area support (SiO$_2$) was used for the $V_2O_5$ catalysts. Much of the work was directed at determining a method for measuring the surface area of the $V_2O_5$ in the cata-
lyst. This value was necessary to evaluate kinetic data. A method of reducing the surface of the supported V$_2$O$_5$ in H$_2$ at 641 K and measuring oxygen uptake at the same temperature was derived. Both reduction with H$_2$ and oxygen adsorption/oxidation are activated and require high temperatures. Activated adsorption of H$_2$ and O$_2$ is consistent with the reactivity of V$_2$O$_5$ observed in the UHV experiments. The UHV experiments also show that facile diffusion of bulk oxygen to the surface only occurs at ~750 K. Allowing for the different time scales of the UHV and catalytic experiments (seconds and minutes respectively) reduction and oxygen uptake should be restricted to the surface of the V$_2$O$_5$ at 641 K.

The catalytic reactions studied with these catalysts were methane partial oxidation with N$_2$O and ethanol partial oxidation with O$_2$. The activity of V$_2$O$_5$-SiO$_2$ for methane partial oxidation was too low for continued studies. Other catalysts are much more active than V$_2$O$_5$-SiO$_2$ for partial methane oxidation. The secondary reaction of partial oxidation products (methanol) had plagued the methane partial oxidation experiments. Alcohol partial oxidation over V$_2$O$_5$-SiO$_2$ occurs readily. Interest in acetic acid prompted studies with ethanol rather than methanol. The problem of determining structure sensitivity was chosen. The presence structure sensitivity was explored by performing experiments with a series of V$_2$O$_5$-SiO$_2$ catalysts having different dispersions. No structure sensitivity was found. This implies that the polycrystalline V$_2$O$_5$ sample used in the UHV experiments was an appropriate model of vanadium oxide catalysts. The conversion of the ethanol partial oxidation reaction increased with temperature. However total oxidation products were favored at higher temperatures. High conversions decrease the amount of gas phase ethanol in the reaction mixture and, if the UHV experiments are any indication, favor the desorption of fully rather than partially oxidized products.

Supported V$_2$O$_5$-SiO$_2$ catalysts are less well characterized than V$_2$O$_5$ on gold. Raman spectroscopy is being continued in order to determine what vanadium oxide species, other than crystalline V$_2$O$_5$, exist in the supported catalysts. If reactivity to moisture in the air is an indication, these species more closely resemble amor-
phous V$_2$O$_5$ than crystalline V$_2$O$_5$. However, both forms of V$_2$O$_5$ (and some lower vanadium oxides as well) have very similar microscopic structures based on VO$_6$ octahedra. For a structure insensitive reaction such as ethanol partial oxidation, the microscopic structure is probably much more important than long range structure. Raman experiments with supported V$_2$O$_5$ catalysts and monolayer samples prepared and characterized in UHV should be able to determine what microscopic structure participates in ethanol partial oxidation.

To answer the last set of questions posed in chapter 1: Methane partial oxidation does not proceed very rapidly over V$_2$O$_5$-SiO$_2$ catalysts. The active surface area of V$_2$O$_5$-SiO$_2$ catalysts can be measured by reducing the catalyst at 641 K for 1 hour and measuring irreversible oxygen chemisorption at than same temperature. Ethanol partial oxidation over V$_2$O$_5$-SiO$_2$ catalysts in structure insensitive. Both the oxygen chemisorption and ethanol partial oxidation results are consistent with observations from UHV experiments on vanadium oxide surface.

The preparation of samples for the UHV experiments employed methods new to surface studies of oxides. The growth of vanadium oxide on gold was a good choice. Although other metal substrates might aid in the oxidation of the films through O$_2$ dissociation and spillover, they might also participate in the surface chemistry. The use of a high pressure pretreatment cell should alleviate problems with oxidation rates and activated adsorption of molecules. If the cell is coupled with GC or MS detection, high pressure TPR experiments on carefully prepared samples should be possible. The interaction of the bulk and the surface of vanadium oxide at elevated temperatures is well documented. Experiments with monolayer and multilayer oxide films grown by evaporation in UHV might determine how many layers are involved in catalytic reactions. If shearing mechanisms are important to stabilize the surface during the desorption step of a reaction (as many people would like to think), then several layers may be necessary.

This thesis research has uncovered much basic vanadium oxide surface chemistry; oxygen diffusion, the growth of films of vanadium oxide on gold, predissociated hydrogen adsorption and H$_2$O desorption, and the lack of partial oxidation
products desorbing from vanadium oxide surfaces, upon which further research can be based.
Appendix A

Chamber Design

Ultra High Vacuum (UHV) chambers are typically designed with one or two types of experiments in mind. The complexity of the apparatus and the difficulty in keeping all components working at the same time discourage too complex a chamber design. The choice of a particular chamber design is a compromise between the types of samples to be studied, the experiments to be performed, the budget, and the availability of parts. In an academic research environment the assembly time, the cost, the availability of found parts, and adaptability of the instrument for future experiments are all equally important considerations. Since it would be impossible to list all the factors leading to the design of a UHV chamber, I will describe in detail and point out major design considerations for the chamber used in this thesis work. Additionally, this description will list the sources of important components for future reference.

A.1 Pumping and Bell Jar

Ignoring the fact that all components of the UHV chamber are considered together during the design stage, the easiest place to start a description of a UHV chamber is its pumping and the format of the bell jar. Figure A.1 shows a stylized schematic diagram of the system.

The bell jar containing all the surface analytical instruments is a custom built 12 in. O.D. chamber from MDC Manufacturing, Inc. (Hayward, CA) with 27
Figure A.1: Schematic diagram of the pumping and gas manifold for the UHV chamber.
ports of various sizes and geometry. Custom building is not as extravagant as it seems since the cost of the bell jar is a very small percentage of the total cost of the UHV chamber and 12 week delivery times are standard. Prices range from $5,000 up depending on the number, size, and sealing mechanism of ports and the accuracy of focal point alignment.

Primary pumping for the UHV chamber is accomplished with a Varian VHS-6 diffusion pump backed with a Duo-Seal 1397 two-stage mechanical pump. To achieve UHV \((2 \times 10^{-10} \text{ Torr})\) pressures, several modifications were necessary. A "mexican hat" cold cap was installed on the pumping stack of the diffusion pump, a liquid nitrogen cryotrap (Varian) was installed directly above the diffusion pump, and Sanovac 5 diffusion pump oil was used. The cryotrap was kept filled using a Nelberg Cryogenic Instruments (Albany, CA) LN-C controller to activate a solenoid valve (ASCO, Florham Park, NJ) on a fill line connected to an LS-160 liquid nitrogen dewar.

For safety as well as to prevent contamination of the bell jar in the event of an accident, a 10 in. pneumatic gate valve (High Vacuum Apparatus Mfg. Inc., Hayward, CA) and a pneumatic foreline valve with solenoid valve operation (Airco Temescal, Santa Clara, CA) is installed above and below the diffusion pump. A lab-built interlock (7S2402-1) is interfaced with a Varian temperature sensor, a cooling water flow sensor (Proteus Industries, Mountain View, CA), and Varian thermocouple pressure gauges (type 0531, model 810) both before and after the foreline valve. The pneumatic valves are set will close and the power to the diffusion pump power will turn off automatically in case of emergency. The pneumatic valves operate from a cylinder of compressed air and all solenoid valves are set in the normally closed position so that utility failure will not prevent shutdown. The pressure gauge in the foreline of the diffusion pump before the pneumatic foreline valve is particularly important to prevent inadvertent start-up of the diffusion pump at too high a pressure.

The diffusion pump system just described has the advantages of high pumping speed for most gases as compared to an ion pumped system, and few moving parts
as compared to a turbo-pumped system. Its major disadvantages are contamination from pump oil, the need for an interlock, high electric power drain, high cooling water consumption (~2 gal/min), and high liquid nitrogen consumption (~200 liter/week). Cooling water, electrical power, and liquid nitrogen are readily available in our lab and the VHS-6, cryotrap, and backing pump were available from an obsolete system. Many new systems currently use a combination of turbo and ion pumping. O'Hanlon is a good reference on the relative merits of various pumping systems.

All vacuum tight seals are made with con-flat (or Del-seal) flanges and copper gaskets. Since copper gaskets are expensive, Viton O-rings (Parker O-ring), which fit the flanges, are used during initial testing of new components. Metal seals are also important for the bonnet of the gate valve. The foreline of the pumping system and the actual seals of the gate valves are exceptions. These use Viton O-ring seals. Unless exposure of the sealing mechanism on the back side of the valve to high gas pressures poses a problem, valves are normally oriented so that a pressure difference across them aids in their sealing.

The roughing valve between the bell jar and the gas manifold is a 1 1/2" all metal valve (Varian) which seals with a copper disk and can withstand high bakeout temperatures. (Viton seals which are baked under load vulcanize and become brittle.) This valve is located above the gate valve to enable the bell jar to be brought up to atmosphere for maintenance without shutting down the diffusion pump. The gas manifold, like the bell jar is fashioned from 304 (sulfur free) stainless steel and connections are either welded, VHS, or Swagelock (Oakland Valve and Fitting Co. Oakland, CA). Valves for gas lines are of the Nupro SS-B series with a bellows sealed valve stem and a Kel-F gasket sealing mechanism.

Rough pumping is accomplished with two sorption pumps operating in tandem. These are filled with a 5Å molecular sieve and cooled with liquid nitrogen. (4Å sieve will not pump nitrogen and 13Å sieve is only used to remove water.) Using one pump as a rough pump and the other for fine pumping decreases the frequency of regeneration and also helps pump noble gases.
Varian variable leak valves operating with a copper gasket sealing on an optically flat sapphire disk are used to admit controlled amounts of gas into the vacuum chamber. Gas lines are all copper (flamed) or stainless steel tubing, and gas regulators are adapted for vacuum service to allow pumpout and purging of gas lines.

A.2 Analytical Instrumentation

Figure A.2 shows a diagram and photograph of the UHV chamber used for the majority of this thesis research. The split level chamber allows auxiliary pumping with a titanium sublimation pump (TSP), leak valves, roughing valve, and bakeout lamp (G.E.) to be incorporated below the surface analysis instruments. A 10-mesh 304 stainless steel screen is used to prevent debris from falling into the diffusion pump. (The pump is located directly below the bell jar to increase pumping speed.)

The chamber geometry consists of opposing 8 inch ports for the LEED optics and viewport and at 72°, opposing 8 inch ports for the CMA and mass spectrometer. The remaining circumference is taken by a 6 inch port currently used for a sample entry assembly and two ports normal to the CMA at its focal point for X-ray and UV sources. All ports are as close to the bell jar as possible and adapters are made for each instrument. The cost of adapters is small considering the technical support for our research group and the added adaptability provided by large ports close to the chamber wall may be useful in the future. The unconventional bell jar geometry allows better use of space and an easier incorporation of both LEED (requiring opposing ports) and XPS (requiring two perpendicular ports) than conventional chamber designs with four large ports at right angles. However, new rear-view LEED optics may alleviate some of the problems. The ports for LEED and CMA are oriented in such a way that by shifting the sample manipulator one bolt hole on its flange, the x-y motion of the manipulator can be oriented with respect to either instrument.
Figure A.2: Schematic diagram and photograph of the UHV designed and built for this thesis research.
APPENDIX A. CHAMBER DESIGN

All flanges are through-drilled. Although this requires that all bolts use nuts, it diminishes the risks of breaking a bolt off in a tapped flange hole and subsequent redrilling. Also, all 2.75 inch flanges in the instrument section of the bell jar have 1.75 inch O.D. rather than 1.5 inch O.D. tubing so that a sputter gun can fit through them.

A home-built double pass cylindrical mirror analyzer (CMA) is used as an electron energy analyzer for AES and XPS[134]. It is a replica of a Perkin-Elmer CMA. The ceramic field terminating plates were purchased from Perkin-Elmer, mu-metal shielding from Mushield Company (Malden, MA), and channeltron electron multiplier from Detector Technology Inc. (Brookfield, MA). Operating electronics are a mixture of home-built and Perkin-Elmer power supplies controlled with a Commodore PET computer [135].

At the focal point of the CMA are directed a sputter gun, x-ray source, moveable shield, viewport and one empty port. The sputter gun (Varian) is modified as to allow direct leakage of gases into the ionizer of the gun. Argon is used for sputter cleaning samples and helium for ion scattering spectroscopy (ISS). For ISS the moveable shield is used to block out 3/4 of the entrance of the CMA and the CMA is converted to positive potentials and 300 eV pass energy to energy analyze scattered ions[49].

The X-ray source is a home-built device based on a design by Ganschow [136]. The first version was used by T. Rucker[137]. The gun has a positively (+) biased anode and grounded filaments. Low conductivity cooling water must be used to cool the anode. A deionizing bed, 5μ filter and water cooler/circulator (Continental Water Systems, Hayward, CA) are run in a closed loop and a Thornton series 200 conductivity cell is used to monitor water purity. No UV sterilizer is used and bacterial contamination is a problem. A Spellman (Plain View, NY) 20 kV, 100 MA power supply is used to bias the anode. Universal Voltronics makes similar power supplies. Any current source can power the filaments. The high voltage power supply is interlocked with the UHV chamber interlock, cooling water flow sensor, cooling water purity sensor, and high voltage electronics rack...
APPENDIX A. CHAMBER DESIGN

door. If tripped, the HV power supply is automatically grounded through a series of diodes and resistors. This interlock and the use of a high frequency switching HV supply, rather than one with storage capacitors, decreases the risk of improper use and injury.

The 20 KV ceramic feedthrough for the x-ray gun as well as other UHV ceramic feedthroughs is made by Ceramaseal (New Lebanon Center, NY). Insulator Seal Inc. makes similar feedthroughs. A gimbal type mount incorporating a welded bellows similar to those used in sample manipulators (Metal Flex Welded Bellows, Inc., Derby Line, VT) is used to position the x-ray gun. Since this is an non-focused x-ray gun, positioning the source as close to the sample as possible is imperative. No x-rays should escape the bell jar.

Standard Varian LEED optics and a UTI 100-C mass spectrometer with a directional entrance aperture are used. The MS can be adapted for ISS. [54] An additional electron gun of the type used in oscilloscopes is sometimes used. Evaporation sources and gas dosers are discussed in the experimental section.

A.3 Sample Manipulation

Traditionally a question of on-axis or off-axis sample manipulation has centered on the ease of sample cooling and high pressure containment for on-axis and ease of reaching all instruments for off-axis manipulation. The advent of differentially pumped piston seals and high pressure cells suitable for off-axis use have eliminated this distinction [137]. A manipulator that offsets the sample 2.5 inches was chosen so that all instruments, CMA, LEED, MS, etc can be reached simply by rotating the manipulator rather than by moving bellows-mounted instruments in and out hydraulically to a focal point at the center of the chamber. (A 2.75 inch flange-mounted instrument is the largest size which can be moved manually against the atmosphere-vacuum pressure differential.)

A varian manipulator with X, Y, Z, θ, and a coaxial push-rod is the basis of the manipulator. The X, Y, Z movement of the manipulator is allowed through the
use of welded bellows and the push-rod is used for a vertical axis flip of the sample to allow both LEED (sample normal to the instrument axis) and XPS (sample 45° from the CMA axis) to be performed. Cooling is accomplished by connecting two electrically isolated liquid nitrogen cold fingers to either side of the sample with 3/8 inch copper braid (from shielded high voltage cable) insulated with woven glass tubing (Thermo 1200 Fr-1, Markel, Morristown, PA). Resistive heating is accomplished by attaching heating leads to each cold finger and using the copper braid to carry current to and from the sample. Sample temperature is measured by spotwelding 0.005 inch diameter thermocouple (Omega), also insulated with woven glass tubing, to the sample.

The manipulator holds a Macor (Corning Glass Works, Corning, NY) block mount containing four slit tube plugs; two molybdenum for heating/cooling, and one chromel and one alumel for temperature measurement. An identical mount is located in the high pressure cell so that the sample can be mounted, and heated in high pressures of gas. The sample to be studied is mounted on a 0.5 inch diameter × 0.25 inch thick ceramic disc with four corresponding metal pins vacuum brazed into it. The pins are placed asymmetrically to prevent improper connections. The slit tubes in the Macor block are slightly loose so that absolute alignment is not necessary when plugging the sample holder into the mount on the manipulator. A linear travel rod with round pincers is used to transfer the sample from air through the high pressure cell to the UHV sample manipulator without contaminating the UHV chamber. Samples can be changed in matter of minutes and pressures in the UHV chamber during transfer are 1–5×10⁻⁷Torr. In vacuum the entire sample/mounting block assembly has vertical axis flip via a lever arm and cable drive assembly.

The recent addition of this high pressure cell-sample entry assembly is expected to allow significant contributions to the area of oxide surface chemistry to be made since the more extreme treatments necessary for meaningful chemistry to be studied can be performed in conjunction with surface analysis.
References


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