Development of Polarization-Dependent Infrared Spectroscopy

for Studies of Catalytic Reactions on Pt(111)

BY

Joel D. Krooswyk Bachelor of Science in Chemistry (University of Illinois at Chicago), 2010

THESIS

Submitted for partial fulfillment of the requirements for the Doctor of Philosophy Degree in Chemistry in the Graduate College of the University of Illinois at Chicago, 2016

Defense Committee:

Michael Trenary, Chair and Advisor

Nan Jiang

Timothy Keiderling

Preston Snee

Daniel Killelea, Loyola University Chicago

Copyright

Joel D. Krooswyk

2016

Acknowledgements

Even though the past five years have been stressful and sometimes filled with uncertainty, I am grateful for the experience from working as a teaching and research assistant in the department of chemistry at UIC. Many lessons have been learned and the knowledge gained will definitely influence my decisions in research and other work in the future. I have also been exposed to a wide range of culture, which has reshaped my view of the world. This has come from my time working in Professor Michael Trenary's laboratories. I also have greatly appreciated the opportunity to work on advanced instrumentation and the freedom to think of new ideas for research under the direction of Professor Trenary. My time at UIC has been made easier by a variety of people, whom I would like to thank.

First, I would like to thank Jun Yin for her great mentoring, patience, and time to show me how to perform experiments and maintain a variety of instruments in the laboratory. I am also grateful for the postdoctoral associate, Ira Waluyo, whom I had a privilege of working with for three years. She greatly advanced my speaking and writing skills and was also available anytime I needed help in the laboratory. I also would like to thank the support staff in the machine and electronic shops. Without funding, none of these opportunities would have been available. I appreciate the support from the National Science Foundation. Last, but not least, I would like to thank the committee members for reviewing my thesis.

I would also like to thank my parents for supporting my graduate career. They have encouraged me to persevere even when the research projects were not progressing well. My girlfriend, Amanda, has also been there lending an encouraging voice over the past three years. I cannot say enough how much I have appreciated the support from my family and friends during graduate school.

Contribution of Authors

The three first authored publications that compose the majority of this thesis were not completely individual endeavors. I greatly appreciated the assistance of other authors. In Chapter 1, which provides the background to each project and various techniques, portions of two publications are reprinted with permission from: [Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M., *Chem. Phys. Lett.* **2014**, *593* (0), 204-208. Copyright (2014) Elsevier, and Krooswyk, J. D.; Waluyo, I.; Trenary, M., ACS Catal. **2015**, *5* (8), 4725-4733. Copyright (2015) American Chemical Society]

The experimental work that is described in Chapter 2 was assisted by Jun Yin, Iradwikanari Waluyo, and Chris M. Kruppe. In Chapter 3, the data and results from the publication on low temperature CO oxidation are shown. I performed all of the experimental work, while Jun Yin, Amy L. Asunskis, and Xiaofeng Hu constructed and performed maintenance on the ambient pressure chamber prior to 2011. Professor Michael Trenary edited and assisted in finishing the manuscript. Portions of Chapter 3 are reprinted from: [Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M., *Chem. Phys. Lett.* **2014**, *593* (0), 204-208. Copyright (2014) Elsevier]

Chapter 4 describes the ambient pressure hydrogenation of C_2H_2 to C_2H_6 with data and results published in ACS Catalysis. I performed all of the experimental work and designed the polarization-dependent infrared spectroscopy setup (PD-RAIRS). Iradwikanari Waluyo assisted with chamber maintenance and edited the manuscript. Professor Michael Trenary provided great insight into the data and edited the manuscript. Portions of Chapter 4 are reprinted from: [Krooswyk, J. D.; Waluyo, I.; Trenary, M., *ACS Catal.* **2015**, *5* (8), 4725-4733. Copyright (2015) American Chemical Society]

The ambient pressure hydrogenation of C_2 to C_2H_6 is described in Chapter 5. Chris M. Kruppe assisted with the experiments and maintenance of the chamber while the project was being completed. Professor Trenary edited the manuscript. Portions of Chapter 5 are reprinted from a publication that was recently accepted to a special issue in Surface Science honoring Professor John T. Yates, Jr.

Table of Contents

Chapter

1. Introdu	ction	1
1.1	Outline	1
1.2	Low Temperature Carbon Monoxide Oxidation	2
1.3	Ambient Pressure Acetylene Hydrogenation	5
1.4	In-situ Polarization - Dependent Infrared Spectroscopy	11
1.5	Ambient Pressure C ₂ Hydrogenation	14
1.6	Ex-Situ Techniques in the UHV Chamber	18
1.7	Outline for Thesis	21
2. Experin	ental	23
2.1	Outline	23
2.2	UHV-AP Chamber	24
2.3	PureGas Dry Air Purge Setup	27
2.4	Mirror Change/Installation of Thermocouple in Manipulator	28
2.5	Various Problems with Bruker Vertex 70v FTIR	31
2.6	Sliding Seal Upgrades	33
2.7	Original Experimental Design for Ambient Pressure IR Cell	34
2.8	Experimental Design for Synthesis of High Purity Gases	36
3. Low Te	nperature CO Oxidation from 88 to 150 K on Pt(111)	39
3. <i>Low Ter</i> 3.1	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> Outline	39 39
3. <i>Low Ter</i> 3.1 3.2	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> Outline Reaction Scheme	39 39 40
3. <i>Low Ter</i> 3.1 3.2 3.3	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> Outline Reaction Scheme Experimental	39 39 40 40
3. <i>Low Ter</i> 3.1 3.2 3.3 3.4	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> Outline Reaction Scheme Experimental Polarizer Test	39 40 40 41
3. Low Ten 3.1 3.2 3.3 3.4 3.5	nperature CO Oxidation from 88 to 150 K on Pt(111) Outline Reaction Scheme Experimental Polarizer Test Low Temperature CO Oxidation from 88 to 150 K	39 40 40 41 42
3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6	nperature CO Oxidation from 88 to 150 K on Pt(111) Outline Reaction Scheme Experimental Polarizer Test Low Temperature CO Oxidation from 88 to 150 K CO ₂ adsorbed on Pt(111), O-Pt(111), and O ₂ -Pt(111) from 88 to 150 K	39 40 40 41 42 47
3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7	nperature CO Oxidation from 88 to 150 K on Pt(111) Outline Reaction Scheme Experimental Polarizer Test Low Temperature CO Oxidation from 88 to 150 K CO ₂ adsorbed on Pt(111), O-Pt(111), and O ₂ -Pt(111) from 88 to 150 K Effects of the Superoxo Species on Perturbed CO	39 40 40 41 42 47 49
3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8	nperature CO Oxidation from 88 to 150 K on Pt(111) Outline Reaction Scheme Experimental Polarizer Test Low Temperature CO Oxidation from 88 to 150 K CO ₂ adsorbed on Pt(111), O-Pt(111), and O ₂ -Pt(111) from 88 to 150 K Effects of the Superoxo Species on Perturbed CO Orientation of CO ₂ adsorbed on Pt(111).	39 40 40 41 42 47 49 51
3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9	nperature CO Oxidation from 88 to 150 K on Pt(111) Outline Reaction Scheme Experimental Polarizer Test Low Temperature CO Oxidation from 88 to 150 K CO ₂ adsorbed on Pt(111), O-Pt(111), and O ₂ -Pt(111) from 88 to 150 K Effects of the Superoxo Species on Perturbed CO Orientation of CO ₂ adsorbed on Pt(111). Conclusions.	39 40 40 41 42 47 47 51 52
 Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 Ambien 	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> OutlineReaction SchemeExperimentalPolarizer TestLow Temperature CO Oxidation from 88 to 150 KCO2 adsorbed on Pt(111), O-Pt(111), and O2-Pt(111) from 88 to 150 KEffects of the Superoxo Species on Perturbed COOrientation of CO2 adsorbed on Pt(111)Conclusions	39 40 40 41 42 47 49 51 52 53
 Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 Ambien 4.1 	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> OutlineReaction SchemeExperimentalPolarizer TestLow Temperature CO Oxidation from 88 to 150 KCO2 adsorbed on Pt(111), O-Pt(111), and O2-Pt(111) from 88 to 150 KEffects of the Superoxo Species on Perturbed COOrientation of CO2 adsorbed on Pt(111)Conclusions	39 40 40 41 42 47 52 52 53
 3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4. Ambien 4.1 4.2 	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> OutlineReaction SchemeExperimentalPolarizer TestLow Temperature CO Oxidation from 88 to 150 KCO2 adsorbed on Pt(111), O-Pt(111), and O2-Pt(111) from 88 to 150 KEffects of the Superoxo Species on Perturbed COOrientation of CO2 adsorbed on Pt(111)Conclusions <i>t Pressure C2H2 Hydrogenation from 120 to 370 K on Pt(111)</i> OutlineReaction Scheme	39 40 40 41 42 47 51 52 53 53 54
 3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4. Ambien 4.1 4.2 4.3 	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> OutlineReaction SchemeExperimentalPolarizer TestLow Temperature CO Oxidation from 88 to 150 KCO2 adsorbed on Pt(111), O-Pt(111), and O2-Pt(111) from 88 to 150 KEffects of the Superoxo Species on Perturbed COOrientation of CO2 adsorbed on Pt(111)Conclusionst Pressure C_2H_2 Hydrogenation from 120 to 370 K on Pt(111)OutlineReaction SchemeExperimental	39 40 40 41 42 47 51 52 53 53 54 54
 3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4. Ambien 4.1 4.2 4.3 4.4 	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> OutlineReaction SchemeExperimentalPolarizer TestLow Temperature CO Oxidation from 88 to 150 KCO2 adsorbed on Pt(111), O-Pt(111), and O2-Pt(111) from 88 to 150 K.Effects of the Superoxo Species on Perturbed COOrientation of CO2 adsorbed on Pt(111).Conclusions <i>t Pressure C2H2 Hydrogenation from 120 to 370 K on Pt(111)</i> .OutlineReaction SchemeExperimentalAmbient Pressure Hydrogenation of Monolayer C2H2	39 40 40 41 42 47 52 53 53 54 54 55
 3. Low Ter 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8 3.9 4. Ambien 4.1 4.2 4.3 4.4 4.5 	<i>nperature CO Oxidation from 88 to 150 K on Pt(111)</i> OutlineReaction Scheme.Experimental.Polarizer Test.Low Temperature CO Oxidation from 88 to 150 KCO2 adsorbed on Pt(111), O-Pt(111), and O2-Pt(111) from 88 to 150 K.Effects of the Superoxo Species on Perturbed CO.Orientation of CO2 adsorbed on Pt(111).Conclusions. <i>t</i> Pressure C2H2 Hydrogenation from 120 to 370 K on Pt(111).Outline.Reaction Scheme.Experimental.Ambient Pressure Hydrogenation of Monolayer C2H2.Ambient Pressure Hydrogenation of Multilayer C2H2.	39 40 40 41 42 47 52 53 53 54 54 55 57

4.7 Ambient Pressure C ₂ H ₂ Hydrogenation at 370 K	63
4.8 Ambient Pressure C ₂ H ₄ Hydrogenation at 370 K	65
4.9 Discussion	67
4.10 Conclusions	73
5. Ambient Pressure C ₂ Hydrogenation at 400 K on Pt(111)	74
5.1 Outline	74
5.2 Reaction Scheme	75
5.3 Experimental	75
5.4 Low Coverage C ₂ Hydrogenation at 400 K	76
5.5 High Coverage C ₂ Hydrogenation at 400 K	79
5.6 Ethylidyne (CCH ₃) Hydrogenation at 400 K	81
5.7 Ambient Pressure CO Titration of the C ₂ Hydrogenation Reaction	83
5.8 Ambient Pressure CO Titration of Ethylidyne Decomposition and	
Hydrogenation	85
5.9 Discussion	87
5.10 Conclusions	90
6. Overall Conclusions and Future Work	91
7. Works Cited	93
Appendix A. Auger Analysis of Niobium Oxide	99
A.1 Background/Experimental	99
A.2 Auger Spectra Acquired Before Sputtering Niobium Oxide	102
A.3 Auger Spectra Acquired Before Sputtering Niobium Oxide	107
Appendix B. Permissions	114
Vita	116

List of Tables

Table I.	Peak Assignments for Surface Species Adsorbed on $Pt(111)$ During the Ambient Pressure Hydrogenation of C_2H_2 to C_2H_6
Table II.	Instrumental Parameters for Auger Spectra Acquisition with PHI 600105
Table III.	Instrumental Parameters for Auger Spectra Acquisition with PHI 600106
Table IV.	Summary of the Concentration of Niobium, Carbon, and Oxygen on Different Parts of the Niobium Sample Surface113

List of Figures

Figure 1.1.	Sketch of the Reaction Scheme for the CO Oxidation Reaction on Pt(111)
Figure 1.2.	Sketch of the Surface Species Derived from C ₂ H ₂ on Pt(111)8
Figure 1.3.	Sketch of the Reaction Scheme for the Ambient Pressure Hydrogenation of C_2H_2 to C_2H_6 on Pt(111)11
Figure 1.4.	Sketch Showing the Beam Path for PD-RAIRS Setup on UHV-AP Chamber
Figure 1.5.	Sketch Showing the Orientation of S/P-Polarized Light Exposed to the Pt(111) Surface
Figure 1.6.	Sketch of the Reaction Scheme for the Ambient Pressure Hydrogenation of C_2 to C_2H_6 on Pt(111)
Figure 1.7.	Electron Shell Diagram Depicting Auger Process19
Figure 2.1.	Picture of UHV-AP Chamber with Expanded View of IR Cell24
Figure 2.2.	Diagram of the UHV Chamber with Attached Instrumentation26
Figure 2.3.	Diagram of the IR Cell with Attached Mirror Boxes27
Figure 2.4.	RAIR Spectrum Showing Dry Air Purge Issues
Figure 2.5.	Single Beam Spectra Acquired Before and After Each Mirror Change in the PD-RAIRS Setup
Figure 2.6.	Single Beam Spectra Showing Contamination in Bruker Vertex 70v31
Figure 2.7.	Sketch of the Sliding Seal Setup Between UHV Chamber and AP cell34
Figure 2.8.	RAIR Spectra of CO Oxidation at Ambient Pressure with Ion Gauge35
Figure 2.9.	Picture of the Setup to Synthesize High Purity Gases
Figure 3.1.	Sketch of the Reaction Scheme for the CO Oxidation Reaction on Pt(111)
Figure 3.2.	RAIR Spectra Showing the Difference with the Polarizer in the Terminal Site Peaks for Adsorbed CO species42
Figure 3.3.	RAIR Spectra Monitoring the Low temperature CO oxidation43

Figure 3.4.	RAIR Spectra Confirming Interaction between O ₂ ⁻ and perturbed CO46
Figure 3.5.	RAIR Spectra of CO ₂ adsorbed on Pt(111), O ₂ -Pt(111), and O-Pt(111)48
Figure 3.6.	RAIR Spectra Showing CO ₂ Peaks from Isotope Experiments50
Figure 3.7.	TPD Spectra From CO ₂ Adsorbed on Pt(111) at 88 K52
Figure 4.1.	Sketch of the Reaction Scheme for the Ambient Pressure Hydrogenation of C_2H_2 to C_2H_6 on Pt(111)
Figure 4.2.	RAIR Spectra for the Low Temperature Monolayer Ambient Pressure C ₂ H ₂ Hydrogenation on Pt(111)
Figure 4.3.	RAIR Spectra for the Low Temperature Monolayer Ambient Pressure C ₂ H ₂ Hydrogenation on Pt(111)
Figure 4.4.	RAIR Spectra for the Ambient Pressure C ₂ H ₂ Hydrogenation from 300- 370 K
Figure 4.5.	RAIR Spectra for the Constant Temperature Ambient Pressure C ₂ H ₂ Hydrogenation at 370 K
Figure 4.6.	RAIR Spectra for the Constant Temperature Ambient Pressure C ₂ H ₄ Hydrogenation at 370 K66
Figure 5.1.	Sketch of the Reaction Scheme for the Ambient Pressure Hydrogenation of C_2 to C_2H_6 on Pt(111)
Figure 5.2.	Auger Spectra Showing Clean and Maximum Carbon Coverage on Pt(111)
Figure 5.3.	In-Situ RAIR/ Ex-Situ Auger Spectra for the Low Coverage Ambient Pressure C ₂ Hydrogenation at 400 K79
Figure 5.4.	In-Situ RAIR/ Ex-Situ Auger Spectra for the High Coverage Ambient Pressure C ₂ Hydrogenation on Pt(111) at 400 K80
Figure 5.5.	RAIR Spectra for the Ambient Pressure Ethylidyne Hydrogenation on Pt(111) at 400 K82
Figure 5.6.	RAIR Spectra of Ambient Pressure CO adsorbed on C ₂ -Pt(111) from 300 to 500 K
Figure 5.7.	Ambient Pressure of CO Adsorbed on Pt(111) at 300 K85

Figure 5.8.	RAIR Spectra showing CO Titration of Ethylidyne Decomposition and
	Ambient Pressure Hydrogenation from 300 to 500 K87
Figure A.1.	Picture of the Vacuum Chamber for the PHI 600 System100
Figure A.2.	Picture of the Power Supplies and Various Electronic Equipment for the PHI 600 system
Figure A.3.	Sketch of Niobium Oxide Crystal from Fermilab102
Figure A.4.	Auger Spectrum Acquired from Hole 3103
Figure A.5.	Auger Spectrum Acquired from Near the Groove of Hole 3104
Figure A.6.	Auger Spectrum Acquired from the Groove of Hole 3104
Figure A.7.	Auger Mapping of Hole 3 for Carbon and Oxygen106
Figure A.8.	Auger Spectrum Acquired Near Hole 1107
Figure A.9.	Auger Mapping of Hole 1 for Carbon, Oxygen, and Niobium108
Figure A.10.	Auger Spectrum Acquired of Hole 2109
Figure A.11.	Auger Mapping of Hole 2 for Carbon, Oxygen, and Niobium110
Figure A.12.	Auger Spectrum Acquired from Hole 3111
Figure A.13.	Auger Mapping of Hole 3 for Carbon, Oxygen, and Niobium112

List of Abbreviations

Ambient Pressure
Density Functional Theory
Deuterated Lanthanum α -Alanine Triglycine Sulphate
Energy Dispersive X-Ray Spectroscopy
Infrared Reflection Absorption Spectroscopy
Low Energy Electron Diffraction
Quadrupole Mass Spectrometer
Polarization Dependent
Proportional Integration Derivative
Photoconductive - Mercury Cadmium Telluride
Photovoltaic - Mercury Cadmium Telluride
Reflection Absorption Infrared Spectroscopy
Ultra High Vacuum
Scanning Auger Microscopy
Scanning Electron Microscopy
Scanning Tunneling Microscopy
Temperature Program Desorption

Reflection Absorption Infrared Spectroscopy (RAIRS) has been used to characterize fundamental catalytic reactions on transition metal surfaces in ultra high vacuum (UHV) environments. The technique works well in UHV studies because the only peaks present in the IR spectra are from species adsorbed on the metal surface. To bridge the pressure gap in catalysis, from UHV to atmospheric pressure, ambient pressure catalytic reactions on metal surfaces are performed because the kinetics and thermodynamics can vary from UHV studies. At ambient pressure, a combination of peaks are present in the IR spectra from surface species and the gas environment in the cell. Typically a polarizer is modulated in a setup known as polarization modulation - RAIRS (PM-RAIRS), in which spectra are acquired in a way to cancel out the gas phase peaks present in the spectra. This is a great technique, but provides a lower signal-to-noise ratio than RAIRS. Also, the gas composition in the cell is monitored with GC-MS. In this thesis, I will discuss a new experimental setup for UHV to ambient pressure catalysis studies and show three different experimental studies on Pt(111) to describe the setup in detail. Based on surface selection rules, I use a single rotatable polarizer with a standard RAIRS setup instead of an expensive polarization modulator coupled to a commercial FTIR instrument. This technique is called polarization dependent - RAIRS or PD-RAIRS. It provides the same signal-to-noise ratio as a standard RAIRS setup and allows the gas composition of the cell to be easily monitored in the IR spectra and without a GC-MS.

xi

The three different studies on Pt(111) will then be discussed showcasing the PD-RAIRS technique. First, spectra will be shown that describe a new interaction between molecular oxygen and carbon monoxide at 88 K in a low temperature CO oxidation reaction on Pt(111) in UHV conditions. The installation of the polarizer caused an increase in the S/N ratio of peaks allowing for better determination of species adsorbed on the surface. Next, PD-RAIRS was used to monitor the ambient pressure hydrogenation of acetylene to ethane with a pressure and temperature range from 1.0×10^{-2} to 4.0 Torr and 120 to 370 K. When an ambient pressure of acetylene and hydrogen are present in the cell with the Pt(111) crystal at 300 K and the crystal annealed to higher temperatures, ethylene and ethane are produced at 350 and 370 K, respectively. The spectra show the capabilities of the PD-RAIRS setup in determining both surface and gas phase species present during an ambient pressure catalytic reaction. The last study is on the reactivity of a carbidic layer adsorbed as C_2 species on the Pt(111) surface to ambient pressure of H_2 . For this work, PD-RAIRS was coupled with ex-situ Auger spectroscopy. The PD-RAIR spectra show that the C_2 species are hydrogenated through an ethylidyne (CCH₃) intermediate to ethane at 400 K and 10 Torr of H_2 . After the crystal was exposed to the ambient pressure of H_2 , Auger spectra were acquired and show a decrease in the surface coverage of carbon on Pt(111) confirming the hydrogenation of C_2 to ethane. The data show that the coupling of the two techniques is powerful in characterizing all aspects of catalytic reactions on Pt(111).

xii

Catalytic reactions on transition metal surfaces are very important to a variety of industries. Some examples include oxidation and hydrogenation reactions. Oxidation of carbon monoxide to carbon dioxide is important in PEM fuel cells. Hydrogenation of acetylene is important because the gas is a contaminant in ethylene feedstocks. Studying the different forms of carbon that can be present on the metal surface during hydrogenation reactions is also important because the adsorbed carbon can greatly influence the kinetics and thermodynamics of the reactions. The two forms of carbon that can be present on the surface during a reaction are carbidic and graphitic carbon. Carbidic carbon is reactive and can play a role in catalytic reactions. The formation of a graphitic layer leads to the "coking" of the catalyst, which results in decreased catalytic activity.¹ In this thesis, I will show a variety of ambient pressure catalytic reactions on Pt(111). These reactions bridge the pressure gap from UHV to atmospheric pressure studies and are important because the reaction thermodynamics and kinetics can vary greatly from UHV studies. The presence of the ambient pressure of gas induces a change in desorption temperatures and an increase in coverage of surface species. A new RAIRS technique, Polarization-Dependent Reflection Absorption Infrared Spectroscopy (PD-RAIRS), was developed to study the ambient pressure catalytic reactions.

1.1. Outline

Section 1.2 describes background to the low temperature CO oxidation reaction on Pt(111). Sections 1.3 and 1.4, discuss the background to the ambient pressure hydrogenation of C_2H_2 and the setup and theory for the in-situ PD-RAIRS technique.

Discussion of the background to C₂ hydrogenation and the application of ex-situ techniques follow in sections 1.5 and 1.6. Portions of this chapter have been published in various journals: [Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M., *Chem. Phys. Lett.* **2014**, *593* (0), 204-208., Krooswyk, J. D.; Waluyo, I.; Trenary, M., ACS Catal. **2015**, *5* (8), 4725-4733.]

1.2. Low Temperature CO Oxidation

The oxidation of carbon monoxide is one of the most studied catalytic reactions, especially on platinum surfaces. Platinum is utilized as a catalyst due to a combination of weak adsorption of the CO₂ product, non-dissociative adsorption of CO, and a low dissociation barrier for molecular oxygen, which adsorbs on the Pt(111) surface in two forms: peroxo ($O_2^{2^-}$) and superoxo (O_2^-) in the fcc and bridge sites, respectively.² The peroxo species is only present on the surface at low coverage and the O–O bond is weaker compared to the superoxo species, which forms islands on the surface at high coverage.^{3, 4} Besides experimental studies that show thermal dissociation of molecular oxygen at 115 K, theoretical work concludes that the O₂ dissociation and desorption barriers are 0.32 and 0.36 eV, respectively, on Pt(111).³ Even though it is commonly accepted that the first step of the reaction occurs between an adsorbed oxygen atom and a CO molecule on Pt(111), we observe a new interaction between adsorbed superoxo (O_2^-) and CO molecules at 85 K to produce a perturbed form of CO that is the precursor to CO₂ formation.

Density functional theory (DFT) calculations for the oxidation reaction show that when CO is coadsorbed on the surface with O_2 , a small amount of oxygen needs to desorb for

the remaining O_2 to dissociate.⁵ Also, the calculated energy barrier for oxidation is lower if oxygen initially dissociates on the surface, then reacts with coadsorbed CO.⁶ The energy barriers for the peroxo species for the dissociated and molecular oxygen reaction with adsorbed CO are 1.18 and 1.62 eV, respectively. This is lower than the barriers for the superoxo species, which are 1.41 eV for the dissociated and 1.93 eV for the molecular reaction with adsorbed CO.⁵ These were calculated with O_2 and CO coverages of 0.25 ML each.⁵

Previous temperature-programmed desorption (TPD) studies examined the initial step of CO oxidation on Pt(111).⁷⁻¹¹ Yoshinobu and Kawai coadsorbed O₂ and CO on the surface and found that CO₂ desorbed at 125 K.⁹ The initial coverages at 83 K for coadsorbed O_2 and CO were 0.45 and 0.2 ML⁹, respectively, which differ from the DFT studies. These results indicated that CO₂ is formed from an adsorbed CO molecule and a 'hot' oxygen atom; i.e. an oxygen atom that is not fully equilibrated to the surface following dissociation of molecular oxygen. The coverage of CO₂ produced at 125 K was found from TPD to be 0.06 ML.⁹ Other studies used an external energy source such as low energy photons¹⁰ or laser-induced O₂ dissociation¹² at 85 K, which produced 'hot O atoms' that then reacted with adsorbed CO. In one such study, O₂(ads) was dissociated at 25 K on Pt(111) and adsorbed CO_2 was observed with an asymmetric stretch at 2342 cm^{-1} .¹³ Other metals that produce CO₂ at low temperatures through 'hot' oxygen atoms and adsorbed CO molecules include Ni(111)¹⁴, a Au/Ni alloy¹⁵, and Cu(100)¹⁶. On a Au/Ti $O_2^{17, 18}$ powder catalyst, the initial step was found to involve an interaction between O2 and CO at 120 K, producing adsorbed CO2 and oxygen atoms. Adsorbed

3

 CO_2 from the reaction was observed to have an asymmetric O–C–O stretch vibration at 2341 cm⁻¹ that blue shifted with higher CO_2 coverage.¹⁸

Besides the low coverage of CO₂ produced at 125 K, it is difficult to characterize the intermediates of CO oxidation on Pt(111) since the reaction-limited product (CO₂) is completely desorbed by 150 K.¹⁰ Peaks from adsorbed molecular CO₂ have been observed with high resolution electron energy loss spectroscopy (HREELS) at 93 K. An asymmetric stretch at 2342 cm^{-1} was observed along with a strong bending mode at 664 cm^{-1} , ¹⁰ which suggest that CO₂ physisorbs with the molecular axis neither parallel nor perpendicular to the Pt(111) surface. In contrast, a low energy electron diffraction (LEED) study of molecular CO₂ adsorbed on Pt(111) in a $p(3 \times 1)$ structure indicated that the molecule is oriented parallel to the surface.¹⁹ Chemisorption of CO₂ can occur on Pt(111) when it is coadsorbed with an alkali metal such as potassium.²⁰ This induces charge transfer creating a negatively-charged CO_2^{-} species on the surface with vibrational peaks at 780, 1220, and 1520 cm⁻¹.²⁰ Two peaks were also observed for the physisorbed neutral CO₂ species at 640 and 2350 cm^{-1} , with the latter peak shifting to 2365 cm^{-1} when CO_2 was adsorbed on a surface saturated with molecular oxygen and potassium.²⁰

The temperature region from 85 to 150 K was examined here with RAIRS with different isotopes of CO and O_2 to determine the initial step to CO oxidation on Pt(111). Even though some aspects of this reaction were investigated previously using a similar approach,⁹ the increased sensitivity of the FTIR instrument used here allows new low intensity peaks to be observed. This capability yields new data that suggest an interaction between O_2^- and CO molecules on the Pt(111) surface at 85 K. This gives rise to

4

formation of physisorbed CO_2 at 130 K with molecular oxygen still present on the surface. Annealing to 150 K completely desorbs the CO_2 whereas some molecular oxygen desorbs and the rest dissociates leaving atomic oxygen and unreacted adsorbed terminal site CO on the surface. Evidence that an interaction between CO molecules and adsorbed superoxo species at 85 K produces a perturbed form of CO, which is the precursor to CO_2 formation at 130 K, is shown in Chapter 3. The reaction scheme is shown in Figure 1.1.



Figure 1.1. Sketch of the reaction scheme for the low temperature CO oxidation reaction on Pt(111).

1.3. Ambient Pressure C₂H₂ Hydrogenation

Transition metal catalyzed hydrogenations of unsaturated hydrocarbons are among the most important reactions in heterogeneous catalysis. For this reason, numerous fundamental studies of the simplest hydrocarbons containing multiple carbon-carbon bonds, acetylene and ethylene, have been carried out. The goal has been to identify the elementary steps in which H atoms are added or removed from the various possible C_2H_x

intermediates that form along the reaction pathway. Much of the experimental work has employed ultra high vacuum techniques as these provide well defined conditions for the definitive identification of intermediates and their reactions. However, because it is not always clear if the mechanisms deduced from UHV studies are the same ones followed under actual hydrogenation conditions there is increased interest in operando studies, where realistic reaction conditions are employed.²¹ Here we have used polarizationdependent reflection adsorption infrared spectroscopy (PD-RAIRS) to simultaneously monitor the surface and gas phase species during acetylene hydrogenation over a Pt(111) surface at total gas pressures in the range of 10⁻² to 4 torr.

There have been numerous experimental studies of the C_2H_x species that form on Pt(111) following exposure of the surface to acetylene.²²⁻²⁵ At low temperature, C_2H_2 bonds in a di- σ/π configuration in which each C atom forms σ bonds to two Pt atoms at a bridge site and where the CH bonds are bent away from the surface with the HCCH plane tilted from the surface normal such that the remaining CC π bond can also interact with the surface. At temperatures around 350 K, the ethylidyne species, CCH₃, is observed. A variety of other C₂H_x species have been proposed but their characterization has not been nearly as definitive as for CCH₃. These other species include vinylidene (CCH₂), vinyl (CHCH₂), and ethylidene (CHCH₃). Ethylidyne could be formed by one elementary step from each of these species: hydrogenation of vinylidene, dehydrogenation of ethylidene, or by a 1,2-H shift in vinyl. Vinylidene, in turn, could be formed from a 1,2-H shift in di- σ/π bonded acetylene. A separate but related issue is the mechanism of hydrogenation of acetylene to ethane. A simple step-wise addition of H atoms to C₂H₂ would proceed by way of CHCH₂ (vinyl), ethylene (C₂H₄), ethylidene (CHCH₃), and ethyl (CH₂CH₃)

intermediates. Whether one or more of these intermediates can be detected spectroscopically through in situ measurements during the hydrogenation reaction will depend on two main factors. First, there must be sufficient coverage of the intermediate so that the intensity of at least one vibrational mode is high enough to enable detection within the limited sensitivity of the spectroscopic method. Second, the observed vibrational peaks must be uniquely assignable to a specific species. As shown below, this second requirement poses the bigger challenge.

Shown in Figure 1.2 are the various surface species created from di- σ/π acetylene as it undergoes various surface reactions as described in this section (Section 1.3).



Figure 1.2. Surface species that result from acetylene hydrogenation, disproprotionation, and dehydrogenation reactions on Pt(111). These species are present on the surface in both UHV and ambient pressure acetylene hydrogenation experiments.

In addition to the growing interest in using in-situ spectroscopic methods to investigate surface reactions such as ethylene and acetylene hydrogenation, recent theoretical work using Density Functional Theory (DFT) has provided new opportunities for interpreting experimental work. For example, Zhao et al.²⁶ investigated the mechanism of ethylidyne

formation from ethylene on Pt(111) and reported the adsorption geometries, binding energies, and vibrational frequencies of the various possible C_2H_x species as well as the activation energies for each step of their interconversions. An important conclusion was that simple isomerization reactions involving intramolecular 1,2-H transfers, such as the formation of vinylidene from acetylene, ethylidene from ethylene, or ethylidyne from vinyl, have high barriers and are therefore unlikely to occur. A similar conclusion was reached in a DFT study²⁷ of ethylidyne formation from acetylene on Pt(111), although in the latter case no calculated vibrational frequencies were reported. The stabilities and geometric structures of the intermediates are similar to those reported in much earlier work.^{28, 29} These computational studies have been extended to incorporate kinetic Monte Carlo (kMC) methods by Alexandrov et al.,³⁰ who concluded that the rate determining step in ethylidyne formation from ethylene on Pt(111) is the hydrogenation of vinylidene. Podkolzin et al.³¹ used DFT methods to determine how reactant coverages affect the mechanism of acetylene hydrogenation over Pt(111). They concluded that both ethylidyne and vinylidene would be present as spectator species and specifically considered the stabilities of other intermediates in the presence of high coverages of these spectator species. Recently, Zhao and Greeley have used DFT to calculate both the intensities and frequencies of the vibrational modes of various C₂H_x intermediates on Pt(111) and to thereby simulate RAIR spectra for direct comparison with the corresponding experimental spectra.³² They concluded that experimental spectra that had previously been assigned to ethylidene could be better assigned to vinylidene. Peak assignments for surface species and comparison to DFT calculations will be shown in Chapter 4.

The results reported in Chapter 4 clearly show that the surface is covered by ethylidyne as gas phase acetylene is first converted to gas phase ethylene and then the gas phase ethylene is hydrogenated to ethane. The hydrogenation reactions proceed with no significant change in the ethylidyne coverage. The IR spectra of a gas phase mixture that initially consists of $H_2(g)$ and $C_2H_2(g)$ first show a rise in $C_2H_4(g)$ as $C_2H_2(g)$ is consumed followed by a decrease in $C_2H_4(g)$ as $C_2H_6(g)$ forms. In separate experiments these results starting from $C_2H_2(g)$ are compared with results obtained when starting with $C_2H_4(g)/H_2(g)$ mixtures. The latter experiments are similar to recent work by Tilekaratne et al.³³ in which RAIRS was used to probe a Pt(111) surface during ethylene hydrogenation, but in their work mass spectrometry instead of IR spectroscopy was used to monitor the gas phase species. In both their study and in ours, ethylidyne was the only surface species detected during ethylene hydrogenation. However, for acetylene hydrogenation we find additional weak spectral features with RAIRS indicating the presence of one or more other surface species.

A reaction scheme that combines all of the ambient pressure studies is shown in Figure 1.3. The PD-RAIRS data are shown and the mechanism for the hydrogenation of acetylene to ethane is further discussed in Chapter 4.



Figure 1.3. Sketch of the reaction scheme for the hydrogenation of acetylene to ethane at ambient pressure on Pt(111).

1.4. PD-RAIRS for In-Situ Monitoring of Catalytic Reactions

The technique used in my research to study ambient pressure reactions with surface and gas phase species is PD-RAIRS. The RAIRS technique is widely used for characterizing fundamental reactions and is a powerful method to monitor species adsorbed on transition metal surfaces during a catalytic reaction under UHV conditions. A commercial FTIR instrument is coupled to a UHV chamber. The beam is collimated onto the metal crystal through a set of mirrors, and then focused into a MCT detector as illustrated in Figure 1.4.



Figure 1.4. Sketch of the PD-RAIRS beam path for the UHV-AP Chamber.

The MCT detector has a faster scanning speed (40 kHz) versus the internal DL-aTGS (10 kHz) detector, so a greater number of scans can be acquired in a shorter period of time. Peaks appear in the IR spectra from surface species with a dipole moment in the \hat{z} -direction (perpendicular to the surface, as shown in Figure 1.5), and under UHV conditions no peaks for gas phase species are observed in the spectra. In ambient to atmospheric pressure catalytic reactions, peaks in the spectra that can be assigned to gas phase species overlap with peaks assigned to surface species.



Figure 1.5. The electric field component of the IR light is composed of two polarizations, E_p and E_s . E_p represents the component perpendicular to the surface (P-Polarized), which is surface sensitive. E_s represents the electric field parallel to the surface (S-Polarized) which is not surface sensitive.

To monitor ambient to atmospheric pressure catalytic reactions, an expensive photoelastic modulator is usually used in a setup known as polarization modulation - IRRAS/RAIRS (PM-IRRAS/RAIRS), with the spectra denoted as $(R_p - R_s)/(R_p + R_s)$ because the gas phase species contribute equally to the p- and s-polarized spectra. The denominator serves to normalize the spectra against the variation of light intensity versus wavenumber due to variations of the source intensity, optical throughput, and detector response. Spectra due to surface species can be obtained without a reference spectrum of a clean sample. Using a similar setup, Schennach et al. created a PM-IRRAS setup with two polarizers.³⁴ One polarizer is in front of the sample to equalize the p- and s- polarized intensities. The polarizer after the sample is rotated between 0 and 90 degrees to acquire 512 to 1024 scans of p- and s-polarized light.³⁴ This is similar to my design and was the basis for the design of the PD-RAIRS system.

The PD-RAIRS system shown in Figure 1.4 has high stability, so the spectra are easily reproduced. Conventional RAIR spectra are obtained with p-polarized light represented

by $\Delta R_p/R_p$, where ΔR_p is equal to p-polarized reflectance of the surface after gas is admitted to the cell minus the reflectance (R_p) of the clean surface before gas is admitted to the cell. The experiment is repeated with s-polarized light to obtain a $\Delta R_s/R_s$ spectrum. The spectra are then corrected for minor baseline drifts. If exactly the same pressures of gas-phase species are achieved, then the intensities of the gas phase species in the $\Delta R_p/R_p$ and $\Delta R_s/R_s$ spectra should be exactly equal, such that the difference defined in Figures 4.3 (c), 4.4 (c), and 4.5 (c) defined as $\Delta R/R = \Delta R_p/R_p - \Delta R_s/R_s$ should be devoid of any gas phase peaks yielding spectra with only features assigned to surface species.

Using a single polarizer is more simple and leads to a higher signal-to-noise ratio. It also has the advantage of imparting the ability to simultaneously monitor the surface and the gas phase species without the need of a mass spectrometer. All of the PM-RAIRS setups have a mass spectrometer connected to the IR cell to monitor gas phase species. Acetylene hydrogenation was studied with this method and is discussed in great detail in Chapter 4.

1.5. Ambient Pressure C₂ Hydrogenation

The reactivity of carbonaceous layers adsorbed on transition metal catalysts during catalytic reactions is important because it can alter the reaction kinetics and products. If the coverage of the carbon is high enough, the reaction will not proceed. This is called "coking" of the catalyst.¹ Since the carbon present on the surface can be either carbidic or graphitic depending on the reaction temperature, the reactivity of these species needs to be studied in detail. This study focuses on the reactivity towards ambient pressure H₂ of a carbidic layer mainly consisting of C₂ molecules created by the decomposition of C₂H₂

on Pt(111) at 750 K. Unlike a graphitic or graphene layer formed from ethylene or acetylene decomposition on the surface at temperatures greater than 800 K,³⁵ C₂ can be hydrogenated and ultimately removed from the surface through formation of ethane.

The stability and hydrogenation of C_2 on Pt(111) has been studied previously by Deng et al. under ultra high vacuum (UHV) conditions using reflection absorption infrared spectroscopy (RAIRS), temperature programmed reaction spectroscopy (TPRS), and Auger electron spectroscopy.³⁶ They showed that the exposure of acetylene and ethylene to Pt(111) held at 750 K produced adsorbed C_2 molecules and C atoms, respectively. While the surface carbon was completely dehydrogenated at 750 K, this temperature was still low enough to prevent formation of a graphitic layer, which STM studies have shown begins at 800 K.³⁵ An exposure of C_2H_2 to Pt(111) at 750 K produced a carbon coverage of 0.34 ML as determined from the Auger spectra.³⁶ The crystal was then cooled to 88 K and H₂ was coadsorbed. After the crystal was annealed to 400 K, three species, methylidyne (CH), ethynyl (C₂H), and ethylidyne (CCH₃) were detected on the surface at coverages of 0.04, 0.05, and 0.11 ML, respectively. This showed that most of the surface carbon had been hydrogenated to C₂Hx species.³⁶

In contrast to the experimental results implying that C_2 is stable on Pt(111), Density Functional Theory (DFT) calculations have found that C atoms are more stable than C_2 molecules³⁷ and are the product of the decomposition of ethynyl on the Pt(111) surface.³⁸, ³⁹ However, an earlier proposed method for estimating surface reaction energies concluded that dissociation of C_2 to C on Pt(111) should be endothermic.⁴⁰ Fischer-Tropsch catalysis involves production of hydrocarbons from carbon-carbon coupling reactions starting with CH_x (x = 0, 1, 2 or 3) formed from the decomposition of methane

15

or CO on metal surfaces.⁴¹ Coupling of C₁ species has been seen experimentally on metals such as $Ru(0001)^{42}$ and Pt(111).⁴³ Smirnov, et al. showed that atomic carbon deposited on Pt(111) formed C₂, which was then hydrogenated to ethylidyne.⁴⁴ Also, Deng et al., exposed Pt(111) to a mixture of ${}^{12}C_2H_2$ and ${}^{13}C_2H_2$ and showed with RAIRS that the C₂ molecules were not formed by a surface coupling reaction.³⁶ The stability and reactivity of these species were also confirmed in a recent scanning tunneling microscopy (STM) study.⁴⁵

While the hydrogenation of C_2 on Pt(111) at ambient pressure has not been previously studied, the reaction of carbon atoms created through the decomposition of ethylene at 600 K with H₂ at atmospheric pressure was monitored in a ¹⁴C radiotracer study.⁴⁶ While the initial reaction was fast, the process slowed down quickly and most of the carbon atoms were not hydrogenated to methane. Ethylidyne reacting under one atmosphere of H₂ was also monitored from 300 to 470 K and was found to be hydrogenated quickly at temperatures greater than 345 K.⁴⁶ The hydrogenation of ethylidyne is of great interest because it is a spectator species during ethylene and acetylene hydrogenated at 300 K in 100 Torr of H₂ because the needed surface sites are not available due to the high coverage of H atoms.⁴⁷

Carbon monoxide has been used as a probe of the properties of ethylidyne on Pt(111) in UHV and ambient pressure environments.^{48, 49} Ethylidyne acts as an electron donor, causing a large red shift in the terminal site CO peak and creating a disordering effect in the adsorbed bridge site CO molecules.⁴⁸ In a recent study, the coadsorption of CO on Pt(111) was found to increase the ethylene hydrogenation temperature from 300 to 400

16

K, which is the temperature where CO desorbs making surface sites available for the reaction.⁴⁹

Since the previous experimental work showed that C_2H_2 decomposition on Pt(111) at 750 K produces mainly C_2 molecules, the focus here is on the hydrogenation of C_2 to ethane under ambient pressure H_2 . The rate limiting step is ethylidyne formation, which was confirmed by adsorbing ethylidyne on the surface and performing several experiments in which the pressure in the cell was varied from 1.0×10^{-2} to 10 Torr of H_2 at 400 K. When the H_2 pressure is greater than 1.0 Torr, the hydrogenation reaction proceeds quickly and ethylidyne is fully hydrogenated. Ambient pressure CO was also used to probe C_2 hydrogenation. The data show that C_2 does not block CO from adsorbing on the surface to any significant extent, but the CO blocks surface sites needed for the hydrogenated after exposure of C_2H_2 to Pt(111) at 750 K, a conclusion that cannot otherwise be reached with RAIRS alone. In ethylidyne hydrogenation experiments, coadsorbed CO was found to block hydrogen adsorption sites, which increases the hydrogenation temperature of ethylidyne from 400 to 450 K.

This is a great example of in-/ex-situ experiments and the capabilities of the UHVambient pressure vacuum chamber for monitoring catalytic reactions. The experiments are further discussed in Chapter 5. A reaction scheme for the hydrogenation of C_2 to ethane is shown in Figure 1.6.



Figure 1.6. Sketch of the reaction scheme for the hydrogenation of C_2 species adsorbed on Pt(111) to ethane through an ethylidyne intermediate at 400 K and 10 Torr of H_2 .

1.6. Ex-Situ Experimental Techniques in UHV Chamber

Since some species, such as C_2 adsorbed on Pt(111), cannot be seen in the RAIR spectra, ex-situ techniques in the UHV chamber are needed to complement the in-situ PD-RAIRS studies. Data supporting the coupling of two techniques (PD-RAIRS and Auger) are shown in Chapter 5. The UHV chamber coupled to the ambient pressure cell has an Auger, LEED, and QMS to analyze the catalyst surface before and after ambient pressure experiments. There is also an ion gun used to clean the crystal in between experiments. The crystal is sputtered with Argon at 5.0×10^{-5} Torr while the ion gun filament is held at 10 mA and the incident energy is 1.0 kV. This produces approximately 5.0 μ A of ions on the surface.

The Auger spectra and LEED images are acquired with a LK Technologies RVL2000 Auger-LEED instrument. A single electron gun with an energy range between 0 and 2.5 keV is utilized for both. It is located in the center of a phosphor screen for LEED studies. For acquisition of the Auger spectra, the incident electron energy is 2.5 keV and collected with a mini-CMA detector with a bias of 1.6 kV. The derivative signal is collected due to the high background of electrons and is plotted uncorrected for any deviations. For the LEED, the incident electron energy varies between 0-200 eV depending on the distance of the electron gun and phosphor screen to the sample and adsorbates on the surface of the catalyst. It has a reverse facing screen and a camera is utilized with a long exposure time to capture the image projected on the screen.

Pierre Auger theorized that a surface bombarded with electrons can undergo a process in which a hole is created in a low energy shell, an electron from a higher energy orbital then falls into the shell, and the energy released by that electron expels an electron in a higher orbital out of the surface. This is a three electron process; therefore, hydrogen and helium cannot be detected with Auger. The peaks are defined by three letters, for example KLL as shown in Figure 1.7.



Figure 1.7. Illustration of the Auger process with three electrons from the KLL orbitals with 2.5 keV electron incident energy.

A K shell electron is ejected, the L electron fills the hole, and then the last L electron is expelled from the surface from the energy from the first L electron. Since the energy of the incident beam is 2.5 keV, this is a very surface sensitive process because the electrons cannot travel far into the bulk of the catalyst.

LEED is used to check the order of the clean surface and the orientation of different molecules/atoms adsorbed on the surface. The diffraction image can also be used to calculate coverage of adsorbates. In the case of clean Pt(111), the diffraction pattern shows a 1×1 hexagonal pattern because the crystal has a close-packed 111 surface. After adsorbing oxygen on the surface at 300 K, the diffraction pattern shows a 2×2 pattern, which demonstrates that the oxygen atoms reside in the three-fold hollow sites. This is not established from the LEED directly, but from LEED IV analysis and other methods.

The inverse of the determinate of the matrix supporting the 2×2 pattern is calculated to estimate the coverage on the surface, which would be 0.25 ML for the 2×2 pattern.

$$1/D = 1/\begin{pmatrix} 2 & 0\\ 0 & 2 \end{pmatrix} = 0.25$$

Since the chamber base pressure is approximately 2.0×10^{-10} Torr, a quadrople mass spectrometer can be used without any additional vacuum pumps. The gas exposed to the chamber needs to be very pure to conduct fundamental studies of catalytic reactions so the majority of gas cylinders purchased will have a gas purity higher than 99.99%. Since the gas cylinders are at high pressure, small gas bottles are usually filled with less than an atmosphere of gas. After the filling, the gases are analyzed with the mass spectrometer to ensure purity. To complement the IR studies, TPD experiments are utilized to determine the molecules that desorb off the catalyst surface at a given temperature. The crystal is cooled to 88 K and heated at approximately 2 K/s controlled by a PID controller connected to a power supply to a certain temperature, such as 1200 K for Pt(111). Eight m/z values can be monitored in each experiment so the parent peak and fragments can be monitored. For example, to determine if CO or N₂ is desorbing from the surface, m/z values 12, 14, 16, and 28 are monitored. 12, 16, and 28 are for CO, and 14, 28 for N₂.

1.7. Outline for Thesis

Chapter 2 discusses the UHV-AP chamber and the modifications over the past five years. The results, discussions, and conclusions from my three first author publications are shown in Chapters 3,4, and 5. Chapter 3 discusses the low temperature CO oxidation reaction on Pt(111) between molecular oxygen and weakly bound CO molecules. In Chapter 4, the ambient pressure hydrogenation of acetylene to ethane is discussed along with the new PD-RAIRS setup. Chapter 5 shows the data from C₂ hydrogenation at ambient pressure and the further utilization of the PD-RAIRS setup. The in- and ex-situ capabilities are also shown and confirm that the combination UHV-ambient pressure chamber is very powerful for monitoring all aspects of catalytic reactions on transition metal surfaces. Conclusions from Chapters 3,4, 5 and future work for the AP cell are presented in Chapter 6. All of the works cited are presented in Chapter 7. In the appendix, data is presented from a niobium oxide sample analyzed with a Physical Electronics, Inc. (PHI) 600 Scanning Auger Microscopy (SAM) System. The study is followed by copyright permissions and my Vita.

2.1. Outline

Chapter 2 describes the UHV-AP chamber that I have used to perform the majority of my graduate research. The installation of the Bruker Vertex 70v is discussed in section 2.2. Numerous upgrades were made to the PD-RAIRS setup. The dry air purge system was restored in the laboratory as described in section 2.3. Next the mirrors for the RAIRS setup were changed, as outlined in section 2.4. The Bruker Vertex 70v instrument had internal problems, which are described in section 2.5. In section 2.6, the original experiments that were to be performed with the chamber are discussed. For several projects, high purity gases were synthesized. The synthetic setup is described in section 2.7.
2.2. UHV - Ambient Pressure Vacuum Chamber coupled to Bruker Vertex 70v



Figure 2.1. The picture on the left shows the UHV-Ambient pressure chamber coupled to the Bruker 70v. On the right, an expanded view of the IR cell, mirror boxes, and detector is shown.

The chamber shown in Figure 2.1 was mostly completed when I started my graduate research in January 2011 and is based on a chamber designed by Szanyi and Goodman.⁵⁰ As described in Chapter 1 and shown in Figure 2.2, the UHV chamber has a Pfeiffer Prisma QMS200 for TPD and RGA, a LK Technologies RVL2000 LEED-Auger, and an ion gun to sputter the sample. The chamber is evacuated to base pressure of approximately 3.0×10^{-10} Torr by a turbomolecular pump, variable voltage (3-7 kV) ion pump, and titanium sublimation pump. During an ambient pressure experiment, the main chamber is evacuated with the ion pump and the pressure remains between 10^{-10} and 10^{-9} Torr even with the IR cell pressure at 10 Torr. There are three seals with differential

pumping as described in Section 2.5 that seal around the manipulator so that high to ultra high vacuum conditions are maintained in the main chamber. The pressure in the IR cell can be varied from 10^{-10} to 760 Torr and there are two gauges to monitor the pressure. A nude ion gauge is for the pressure range from 10^{-10} to 10^{-5} Torr and a convectron gauge for pressures greater than 10^{-4} Torr. The convectron gauge is non-linear with respect to gases such as H₂ past 1.0 Torr. The non-linearity is shown in the data for the hydrogenation of C₂ to ethane in Chapter 5. With assistance from Jun Yin, I installed and performed calibration tests on the Bruker 70v FTIR instrument connected to the AP cell starting in April 2011. The instrumental setup consists of the FTIR instrument, mirror boxes, and an MCT detector as shown in Figure 2.3.



Figure 2.2. The sketch shows a top view of the main chamber with the layout of the various instruments and pumping apparatus. The main chamber is evacuated with the turbomolecular, ion, and tsp pumps when experiments are performed in the main chamber. During ambient pressure experiments, it is only evacuated with the ion pump.



Figure 2.3. Sketch of the top view of the IR cell with attached mirror boxes and beam path for the PD-RAIRS setup. The IR source is from the Bruker 70v not shown in the sketch. Gas is leaked into the cell through the leak valve and is evacuated with the main chamber turbomolecular pump through the MDC angle valve.

2.3. PureGas Dry Air Purge Setup

While the instrument is under vacuum to prevent any miscancellations from water and carbon dioxide in the spectra, the mirror boxes are purged with a PureGas purge unit. The purge unit utilizes high pressure (~90 psi) house air. After the air passes through four dessicant towers, two for water and two for carbon dioxide, it is considered dry air. All

four solenoids and towers were replaced, but peaks representing gas phase CO_2 and H_2O were still present in the spectra as shown in Figure 2.4. One of the sealing ports in the valve body was cracked off, resulting in air released constantly from one of the towers. This was fixed by the machine shop. Also, larger ports were installed in the H_2O dessicant towers to remove a greater amount of H_2O from the air.



Figure 2.4. Transmittance spectrum acquired of a clean Pt(111) surface with the purge unit not working properly.

2.4. Mirror Change/Thermocouple Installation to Remove Spectral Miscancellations

During the calibration tests, it was noted that there were dips in the low mid-IR wavenumber region as shown in Figure 2.4 with a negative peak at approximately ~1250 cm⁻¹ and also peaks present around ~2900 cm⁻¹ (not shown). These were due to spectral miscancellation issues and fixed accordingly: new mirrors in the mirror box and a

thermocouple was installed in the manipulator for low temperature experiments. The original mirrors had a SiO₂ coating to protect the gold surface. SiO₂ has IR active modes with intense peaks around 1000-1200 cm⁻¹ as shown in the single beam spectra in Figure 2.5. New un-coated gold parabolic mirrors were ordered from Edmund Optics, while the plane mirror was replaced using two microscope slides (SiO₂) coated with 1000 Å of gold. The microscope slides were ordered from Deposition Research Laboratory, Inc. Replacing the mirrors fixed most of the spectral miscancellations and the signal also increased as shown in Figure 2.5 because the bare gold mirrors are more reflective than the coated ones.



Figure 2.5. Single beam spectra acquired before and after each mirror change. The spectrum in blue was the original setup in April 2011. All four mirrors were coated with SiO_2 for protection of the gold layer. The red spectrum was acquired after changing the two parabolic mirror closest to the crystal to unprotected gold. The green spectrum shows the final single beam spectrum after the plane mirror and the two parabolic mirrors were changed to unprotected gold.

The final spectral miscancellations were removed with the thermocouple installation. In low temperature experiments after the liquid nitrogen is added, the manipulator contracts, resulting in movement of the crystal. This affects the signal and background in the IR spectra. Maintaining a constant level of liquid nitrogen throughout the experiment results in a flat baseline without any spectra miscancellations.

2.5. Various Issues with Bruker Vertex 70v



Figure 2.6. Single beam spectra acquired with the SiC glowbar source and internal DL-ATGS detector before and after the source mirror was replaced on July 3, 2014.

Besides the mirrors and the movement of the crystal causing spectra miscancellations, there were some miscancellations from internal problems in the Bruker Vertex 70v. To determine if the miscancellations were from the external RAIRS setup or internal, spectra were acquired with the internal DL-ATGS detector. The lower spectrum in Figure 2.6 shows the single beam spectrum when there was contamination in the instrument. After discussing the problem with Bruker, it was determined that the problem was polyvinyl alcohol (PVA) present in the instrument, which could have been from the sample compartment paint outgassing and coating the optics of the instrument. On April 4, 2012, the first service call was performed on the instrument. There is a gold mirror that collimates the beam behind the SiC source in the Vertex 70v that had red rings burned into the surface. After the technician replaced the mirror, the problem disappeared.

The single beam spectrum remained relatively clean for approximately two years, but the PVA issue returned in 2014. A second service call was performed by Bruker on July 3, 2014, in which, the source mirror was again replaced. The same red rings were observed on the source mirror. After some discussion with multiple sources at Bruker, it was determined that the filters on the vent outlets might have been contaminated with PVA. I removed the filters and installed lines to the dry air purge system in the laboratory. Also, the technician from Bruker noted that the source should be "preconditioned". This is a process of installing the new SiC source in a purged instrument, such as the Bruker Tensor 27 in the physical chemistry laboratory for up to one week, or ordering one from Bruker.

The last issue with the instrument was the HeNe laser. The laser is used to maintain alignment of the mirrors in the interferometer. Almost every day at the end of 2014 into 2015, the instrument would freeze and stop scanning. The messages in the BIOS were logged and an error for the temperature sensor in the interferometer kept appearing. After months of data logging and assistance from a service manager at Bruker, who also noted besides the error that the intensity of the laser was also too low for stable operation. A new laser was ordered and installed and the problem with the temperature sensor also

32

disappeared. The only commonality relating the two issues is that the same wiring circuit is used for the laser and temperature sensor.

2.5. Sliding Seal Upgrades

The ambient pressure cell was upgraded because the sliding seals were leaking during cold temperature experiments and the seals would be replaced every four to six months. During an experiment when the manipulator is cooled with liquid nitrogen, it is in contact with the seals causing a degradation in the plastic over time. The original setup utilized three seals with a teflon jacket and 17-7 PH SS spring, teflon top ring, and stainless steel bottom ring. In between the seals were teflon rings connected to stainless steel lines to the turbomolecular pump for differential pumping. After conducting some research into the materials with help from an engineer from Saint Gobain, custom seals were ordered from Saint Gobain. The teflon outer ring was upgraded to an A02 Fluoroloy plastic and the inner spring upgraded to Elgiloy UNS R30003 (Co-Cr-Ni Alloy) for more resistance to deformation. Also, the teflon top ring was replaced with a torlon plastic ring because the teflon would become deformed over time. This setup has been utilized for over two and half years without any need for replacements.



Figure 2.7. Sketch of the manipulator in the IR cell with a view of the sealing apparatus between the UHV and ambient pressure cell. The gray lines outline the main chamber, mirror boxes, and IR cell to show the location of the sliding seals.

2.6. Original Experimental Design for the UHV-AP Chamber

The original idea for the chamber was to study the pressure gap from UHV to ambient pressure reactions from 10^{-10} to 1.0 Torr. To test this hypothesis, oxygen was flowed into the chamber starting at 10^{-9} Torr with the Pt(111) crystal at 88 K. After each spectrum was acquired, the oxygen pressure was increased by an order of magnitude and a new spectrum acquired. After the pressure was increased to 10^{-6} Torr, the peak representing

molecular oxygen at 877 cm⁻¹ started to disappear (not shown) and a peak that could be assigned to CO_2 appeared.



Figure 2.8. 0.4 L of CO was adsorbed on Pt(111) at 88 K. The pressure in the cell was then raised to 1.0×10^{-5} Torr of O₂ while the Pt(111) was held at 88 K. Spectra were then acquired consecutively (4 min/spectra) while constant temperature and pressure are maintained.

At 1.0×10^{-5} Torr, the molecular oxygen peak completely disappeared, which indicated that the pressure induced the dissociation of oxygen (not shown). As shown in Figure 2.8,

CO was first adsorbed on the surface and after exposure to 1.0×10^{-5} Torr of O₂, a large coverage of CO₂ was produced. To verify that this was a surface mediated reaction, ¹³CO was purchased from Sigma Aldrich and adsorbed on the Pt(111) surface. A peak assigned to ¹³CO₂ was not observed, while the peak for ¹²CO₂ appeared.

This reaction was monitored with a hot cathode ion gauge, which operates between 1700 and 2300 °C. After turning off the ion gauge, no peaks were visible in the spectra representing CO_2 . This showed that the CO_2 was produced from the oxidation of CO on the ion gauge by "cracking" the oxygen flowing over the gauge. The "cracking" temperature of oxygen is around 1500 °C and since the crystal was held at 88 K during the reactions, the CO_2 would readily adsorb on the surface. This study was not pursued further and was part of the reasoning to change the focus of my research to reactions at ambient pressure with the PD-RAIRS setup.

2.7. Synthesis of High Purity Gases

Besides the three first author publications shown in this thesis, I have also performed various work for other projects such as: ethylamine on Pt(111) and methylamine on Ru(001). My first 2nd authored paper focused on the decomposition of ethylamine to acetonitrile through a new surface intermediate, aminovinylidene. The first author, Iradwikanari Waluyo performed DFT calculations to verify that the IR peaks can be assigned to the species. Experimentally, isotopes of ethylamine needed to be purchased or synthesized to monitor the shift in the peaks in the IR spectra. ¹⁵N-ethylamine was extremely expensive to purchase, so I devised a way to synthesize and collect the gas

with the assistance of Dr. Matthew O'Connor from Professor Daesung Lee's research group.

A procedure was followed according to previous literature to synthesize ¹⁵N-ethylamine-HCl⁵¹, which is a solid white salt. I then designed an experimental setup as shown in Figure 2.9 to collect the gas. It consists of a three neck flask that has one port to vacuum, one to a glass line running to a stainless steel lecture bottle, and the other capped off with a septa. Before the setup was constructed, all glassware was baked in an oven to remove water. The lecture bottle was evacuated on a gas manifold connected to a turbo-molecular pump and baked overnight.

At the start of the experiment, the glass line is filled with potassium hydroxide (KOH) and each end has a cotton plug so the rest of the system is not contaminated. The three neck flask is also filled with KOH so the bottom is completely covered. The apparatus is then assembled and evacuated with a mechanical pump to approximately 0.03 Torr. After it has been evacuated for approximately two hours, the lecture bottle is submerged in liquid nitrogen to collect the gas. The ethylamine salt is then dissolved in a minimal amount of water using a ultrasonic water bath. The dissolved salt is then injected into the flask through the septa and the gas is collected in the lecture bottle. The gas in the lecture bottle is then purified through several freeze pump thaw cycles on a gas manifold and checked with mass spectrometry for purity. This method was also used to synthesize all of the gases for the study of methylamine on Ru(001) by Yuan Ren.

37



Figure 2.9. Setup to collected high purity gases in a stainless steel lecture bottle.

3.1. Outline

The first data published from the UHV-AP chamber is presented in Chapter 3. After the polarizer was installed, CO oxidation was examined under UHV conditions and a temperature range of 88 to 150 K. The results show a perturbed form of CO that interacts with molecular O_2 , which produces a physisorbed CO_2 species at 130 K. The reaction scheme is shown in Section 3.2. Section 3.3 outlines the experimental details, which includes how to minimize CO adsorption on Pt(111) at low temperatures. Section 3.4 details the benefits of using a polarizer in UHV type experiments. Section 3.5 shows the RAIRS data acquired after O_2 and CO are coadsorbed on Pt(111) at 88 K and annealed to temperatures up to 150 K. Section 3.6 shows RAIRS data from CO_2 adsorbed on clean Pt(111) and O_2 and O-covered Pt(111). The effect of the superoxo species on the perturbed CO is discussed in Section 3.7. TPD data from CO_2 was also acquired and shown in Section 3.8 and confirms that CO_2 is physisorbed on Pt(111). Conclusions for this project are described in Section 3.9.

Data in this chapter were published in an Editor's Choice article in Chemical Physics Letters. [Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M., *Chem. Phys. Lett.* **2014**, *593* (0), 204-208. Copyright (2014) Elsevier]

3.2. Reaction Scheme



Figure 3.1. Sketch of the reaction scheme for the low temperature CO oxidation reaction on Pt(111). Adsorbed superoxo (O_2^-) reacts with a perturbed CO molecule at 110 K, which forms CO₂ at 130 K. CO₂ then desorbs at 150 K, which shows the molecule is physisorbed on the Pt(111) surface.

3.3. Experimental

The base pressure of the chamber is 2.0×10^{-10} Torr for the UHV chamber and 5.0×10^{-10} Torr for the IR cell. During the experiments, the UHV chamber is isolated from the IR cell. The Pt(111) crystal was first cleaned by exposing the surface to 2.0×10^{-7} Torr for 60 minutes at 850 K. It is then annealed to 1200 K for two minutes to desorb any O₂ and ensure that the surface is well ordered. Auger spectra and LEED images were then acquired after the crystal cooled to 300 K to check that the surface is clean and well ordered. All of the gas exposures are in Langmuir (1 L = 1 × 10⁻⁶ Torr s).

RAIR Spectra were acquired at a resolution of 4 cm⁻¹ with 1024 scans per spectrum. The details of the experiment setup were described in Chapter 2. Since this is a UHV experiment, spectra were only acquired with p-polarized light. The data for all $^{16}O_2$ experiments were acquired with a PV-MCT with a low wavenumber cutoff of 850 cm⁻¹. For experiments with $^{18}O_2$, a PC-MCT was used with a low wavenumber cutoff of 800 cm⁻¹. All spectra were acquired at 85 K. The crystal was annealed to each target

temperature for 30 s and then cooled to 85 K before acquiring the spectra. The heating rate used for TPD was 2 K/s. Two different isotopes of O_2 and CO, ${}^{16}O_2$ and ${}^{18}O_2$ and ${}^{12}CO$ and ${}^{13}CO$, were used. ${}^{16}O_2$ and ${}^{12}CO$ were research grade (99.998%) gases purchased from Matheson Tri-Gas. ${}^{18}O_2$ was purchased from Cambridge Isotopes, while the ${}^{13}CO$ from Sigma-Aldrich. Dry ice was used as the source for CO_2 and was purified multiple times using the freeze-pump-thaw method before use. Gas purity was checked with a mass spectrometer.

3.4. Polarizer Test

As shown in Figure 3.2, the installation of the ZnSe polarizer caused a large increase in the intensity of the peaks. The red and blue spectra show the spectra acquired after the crystal was exposed to 3 L of O_2 and 3 L of CO at 85 K without and with the polarizer, respectively. There is an approximately two and a half multiplication in the signal after the polarizer was installed. After checking the IR intensity for the p- and s-polarized light, it was determined that approximately 40% of the light is p-polarized, while 60% is s-polarized. The polarizer removes 60% of the light that is not surface sensitive. Even though the peaks for terminal site CO at 2112 cm⁻¹ and perturbed form of CO at 2181 cm⁻¹ as shown in Figure 3.1 are easily seen without the polarizer, the CO₂ peak in Figure 3.3 would not be seen without it.



Figure 3.2. Spectra acquired after $3 L O_2$ and 3 L CO are exposed to Pt(111) at 88 K. The red and blue spectra were acquired with and without the polarizer, respectively.

3.5. Low Temperature CO Oxidation from 88 to 150 K

Figure 3.3 reveals the evolution of the superoxo species, the perturbed CO species, the terminal site CO, and the adsorbed CO₂ product after first adsorbing O₂ followed by CO at 85 K and then annealing to a set of temperatures up to 150 K. This O₂ exposure produces a saturation coverage of molecular oxygen, which adsorbs as a superoxo species with a peak at 873 cm⁻¹ as seen in Figure 3.3(a) corresponding to a coverage of 0.44 ML.² After CO is adsorbed, the superoxo peak shows a blue shift to 881 cm⁻¹ and a decrease in intensity and a peak due to the perturbed CO is observed at 2181 cm⁻¹(Fig. 3.3(b)). Also, the terminal site CO stretch as shown in Figure 3.3(c) at 2112 cm⁻¹ is blue-shifted from its value of 2089 cm⁻¹ on a clean Pt(111) surface. The broadening and blue shifts of both the superoxo and terminal site CO species have been observed previously

on $Pt(111)^{13}$ and $Cu(100)^{52}$ and are due to an inhomogeneous surface and overlayer compression created by the coadsorption of both species on the Pt(111) surface.



Figure 3.3. Legend from 3.3(a) applies to all spectra. (a) The transformation of the superoxo species from 85 to 150 K. The peak at 873 cm⁻¹ appears after a 3 L O_2 exposure, and shifts to 881 cm⁻¹ after a 3 L CO exposure at 85 K (red line). Evolution of the strongly (b) and weakly (c) perturbed terminal site CO species from 85 to 150 K. The FWHM of the terminal site CO in (b) at 130 K is 18 cm⁻¹ and at 150 K it is 9.4 cm⁻¹. (d) Evidence of a CO₂ intermediate at 130 K after annealing from 85 K.

After annealing to 110 K, many features change in the spectra. The superoxo species starts to desorb/dissociate, which is indicated by the decrease in intensity and slight red shift of v(OO) to 872 cm⁻¹. The terminal site CO peak increases in intensity, and also undergoes a small red shift, while the secondary CO peak decreases in intensity and shifts to a higher frequency. At 130 K, no peak is observed for the superoxo species, which indicates that it has mostly desorbed or dissociated. Since the cutoff for the MCT detectors is 850/800 cm⁻¹, any peroxo species that might be present cannot be detected. The terminal site CO peak is further red shifted at 130 K, while the perturbed CO peak is not observed. A peak at 2361 cm^{-1} is observed (Figure 3.3(d)) and is due to the asymmetric stretch of CO₂. At 150 K, the same trend as at 110 and 130 K is seen for terminal site CO, but there is no peak due to CO_2 , which indicates that it has desorbed. A weakly adsorbed CO species that closely resembles the one observed at 2181 cm^{-1} in Figure 3.3(b) has been observed on two other surfaces in ambient pressure oxidation reactions. The peak appears at 2192 cm^{-1} at 300 K on a TiO₂ catalyst⁵³ and at 2179 cm⁻¹ on a Au/TiO₂ catalyst¹⁸ at 120 K. Both disappear with the formation of CO₂ and were assigned as the precursor to CO_2 bound to a Ti⁴⁺ cation. This agrees with our data in Figure 3.3, which show that with the disappearance of the superoxo and perturbed CO species after annealing, an adsorbed CO_2 species appears. Therefore, the formation of CO₂ from CO oxidation on Pt(111) at 130 K must involve the perturbed CO species, which strongly interacts with superoxo O_2^- . An O–O--C=O complex has been previously described based on DFT calculations on a Au/TiO₂ catalyst.¹⁸ Even though a superoxo peak is not observed at 130 K here, the overlayer compression effect indicated by a large FWHM of 18 cm⁻¹ and a blue shift of the CO terminal site peak indicates that there is

still some molecular oxygen on the surface when CO_2 is formed. If the oxygen is fully dissociated/desorbed at 130 K, the FWHM of the terminal site CO species should be approximately 9 cm⁻¹, which was established previously when CO was adsorbed on a Pt(111) surface covered with atomic oxygen in a disordered structure.⁹ Even though there is a very low intensity peak at 1850 cm⁻¹ in the spectra (not shown) after annealing to 110 K, which could be assigned to the CO stretch mode of an O–O--C=O complex, it could also be due to background CO adsorbed on bridge sites. Furthermore, it does not shift when ¹⁸O₂ is substituted for ¹⁶O₂. After CO₂ has desorbed at 150 K, v(CO) of the terminal site CO peak remains blue shifted at 2102 cm⁻¹ with a FWHM of 9.4 cm⁻¹, which indicates that there is atomic oxygen left on the surface.

In a separate experiment to determine if the order in which CO and O_2 are adsorbed affects the results, 0.6 L of CO was first exposed to the surface at 85 K followed by 3 L of O_2 . The surface was then annealed to 130 K. As shown in Figure 3.4, a peak is observed for CO at 2089 cm⁻¹, which correlates to a coverage of approximately 0.33 ML. This is based on a previous study that determined that bridge site occupancy begins on Pt(111) for coverages greater than 0.33 ML.⁵⁴ The peak at 2050 cm⁻¹ is background contamination from ¹³CO used in a prior experiment. After the addition of 3 L of O_2 , a peak is observed at 866 cm⁻¹ for the superoxo species. Also, there is a shift in the CO peak to 2102 cm⁻¹ and a decrease in the peak intensity coupled with an increase in the FWHM. This is due to overlayer compression effects caused by the coadsorption of the O_2^- species.^{13, 52} After annealing to 130 K, the terminal site CO peak shifts to 2100 cm⁻¹ and a peak for the superoxo species is not observed. Also, peaks are not observed for the perturbed CO or for CO₂.



Figure 3.4. Legend from Figure 3.4(a) applies to both (a) and (b). (a) Evolution of the terminal site CO species after 0.6 L of CO and then 3 L of O_2 were adsorbed at 85 K followed by annealing to 130 K. (b) The v(OO) stretch region of superoxo O_2^- .

The peak area of the superoxo species following O_2 exposure to the CO–Pt(111) surface is only 17% of its value for the Pt(111) surface saturated with O_2 (Figure 3.3(a)). The presence of CO on the surface blocks oxygen adsorption, thus inhibiting the low temperature reaction from occurring. This experiment also confirms that the peak at 2181 cm⁻¹ is the precursor to the low temperature product since no adsorbed CO₂ is observed in the spectra of Figure 3.4. A previous electron stimulated desorption ion angular distribution (ESDIAD) experiment⁵⁵ and DFT studies on Pt(111)⁵⁶ indicated that the intermediate in the reaction between an adsorbed CO molecule and an O atom is a CO species tilted with respect to the surface normal; although the CO molecule corresponding to the 2181 cm⁻¹ peak may be tilted, there is nothing in the RAIRS data to prove or refute this.

3.6. CO₂ adsorbed on Pt(111), O-Pt(111), and O₂-Pt(111) from 88 to 150 K

To establish the spectral signature of CO_2 coadsorbed with molecular oxygen, as opposed to atomic oxygen, CO_2 was directly adsorbed on clean Pt(111), on an O₂-saturated surface, and on a Pt(111) surface saturated with atomic oxygen in a disordered structure. This information is needed to confirm that molecular oxygen remains on the surface after CO_2 is formed at 130 K. The results are shown in Figure 3.5.



Figure 3.5. (a) RAIR spectra of CO₂ adsorbed on Pt(111) at 85 K and annealed to 110, 130 and 150 K. The peak intensity at 85 and 110 K is the same, so the two spectra coincide. The CO₂ peak following the 150 K anneal is due to CO₂ adsorption from the background. (b) CO₂ adsorbed on an O–Pt (111) surface and annealed to 110, 120, 130 and 150 K. RAIR spectra of the superoxo v(OO) (c) and $v_{as}(CO_2)$ (d) following CO₂ exposure to an O₂ saturated surface at 85 K and after annealing to the indicated temperatures. The color legend from Figure 3.5(c) also applies to Figure 3.5(d).

The spectra in Figure 3.5(a) show the result of exposing the clean Pt(111) surface to 0.4 L of CO_2 followed by annealing to the indicated temperatures. It shows the asymmetric

stretch of CO_2 at 2347 cm⁻¹, which does not shift after annealing to higher temperatures. To create the O-Pt(111) surface, the surface was saturated with O₂ at 85 K, annealed to 150 K and cooled to 85 K. This surface was then exposed to 0.4 L of CO₂. The result is shown in Figure 3.5(b). At 85 K the $v_{as}(CO_2)$ peak is observed at 2353 cm⁻¹ and no shift is observed upon annealing. The peak is broader than on the clean surface, an effect due to the inhomogeneous environment associated with the disordered oxygen layer. The oxygen also inhibits the adsorption of CO_2 as indicated by the lower intensity compared to CO_2 on clean Pt(111). Figure 3.5(c) and (d) shows RAIR spectra for 3 L of O_2 and 0.4 L of CO₂ coadsorbed on Pt(111) at 85 K. Even though there is a more intense CO_2 peak at 2355 cm⁻¹ than in Figure 3.5(b), as was the case for adsorbed atomic oxygen, $O_2^{-}(ads)$ also results in less CO_2 adsorption compared to the clean surface. The peak shape indicates that most of the adsorbed CO_2 is affected by the superoxo species, with a small amount unaffected as shown by the shoulder at 2347 cm^{-1} . After annealing to 120 K, the peak shifts to 2359 cm^{-1} , with a superoxo peak seen at 868 cm^{-1} indicating O_2 is still adsorbed on the surface. At 130 K, the CO_2 peak red shifts to 2353 cm⁻¹, which also corresponds to a decrease in the intensity of the superoxo peak indicating that O_2^{-} (ads) has partially desorbed and/or dissociated. The CO₂ asymmetric stretch at 2359 cm⁻¹ on the O_2 saturated surface at 120 K is close to the value of 2361 cm⁻¹ for the CO_2 product in Figure 3.5(d), suggesting that the superoxo species is still adsorbed on the surface during the CO oxidation reaction at 130 K.

3.7. Effects of the Superoxo Species on Perturbed CO

To probe the effect of the superoxo species on the perturbed CO species, ${}^{18}O_2$ was coadsorbed with ${}^{13}C^{16}O$ and then separately with ${}^{12}C^{16}O$. The same was done for ${}^{16}O_2$

with ${}^{13}C^{16}O$. For ${}^{13}C^{16}O$, v(CO) for the perturbed CO species appears at 2131 cm⁻¹ when coadsorbed with either oxygen isotope (not shown). Furthermore, v(CO) is not shifted when ${}^{18}O_2$ is substituted for ${}^{16}O_2$, which indicates that there is no vibrational coupling between the two molecules. Rather, the interaction is entirely a chemical effect. Peaks for the CO₂ product corresponding to ${}^{18}O^{13}C^{16}O$, ${}^{13}C^{16}O_2$, ${}^{18}O^{12}C^{16}O$ appear at 2276, 2294, and 2341 cm⁻¹, respectively, as shown in Figure 3.6. These are comparable to the peak positions of 2263, 2280, 2329, and 2346 cm⁻¹ of the isotopes ${}^{18}O^{13}C^{16}O$, ${}^{13}C^{16}O_2$, ${}^{18}O^{12}C^{16}O_2$, respectively, for solid CO₂ at 10 K.⁵⁷



Figure 3.6. Four different peaks belonging to isotopes of CO₂ formed at 130 K from separate isotopic CO oxidation experiments. Peaks at 2276, 2294, 2341, and 2361 cm⁻¹ correlate to ${}^{18}O^{13}C^{16}O$, ${}^{16}O^{13}C^{16}O$, ${}^{18}O^{12}C^{16}O$, and ${}^{12}C^{16}O_2$.

3.8. Orientation of CO₂ adsorbed on Pt(111)

If CO₂ adsorbs with its molecular axis strictly parallel to the surface, the asymmetric stretch should not be observable with RAIRS according to the surface dipole selection rule. Its observation is therefore consistent with DFT calculations⁵⁶ indicating that CO₂ adopts a bent structure on Pt(111) with one oxygen and the carbon atom bound to the surface. A bent structure implies a strong interaction with the surface whereas the fact that the asymmetric stretch occurs at essentially the same position on Pt(111) as in solid CO_2 suggests a weak interaction typical of physisorbed molecules. To confirm that the low temperature product is physisorbed rather than chemisorbed on the Pt(111) surface,⁷ TPD experiments were performed. Our TPD results shown in Figure 3.7 agree with previous studies^{10, 19} that molecular CO₂ starts desorbing from Pt(111) at 95 and 110 K for multilayer and monolayer, respectively, and is completely desorbed by 150 K, implying that it is a weakly bound physisorbed species. In comparison to Ag(110) and Cu(110), O_2 and/or oxygen atoms do not increase the desorption temperature of CO_2 on Pt(111).^{58, 59} In a Cs⁺ reactive ion scattering study, carbon dioxide was found to be physisorbed on the O–Pt(111) surface, as it is on the clean Pt(111) surface, and to desorb completely by 140 K.⁶⁰ These results along with the absence of IR peaks for a negatively charged CO_2^{-} species indicate that the low temperature product from the CO oxidation reaction is also physisorbed on the surface.



Figure 3.7. TPD of 0.1, 0.3, and 0.5 L CO₂ exposures from 88 to 200 K. Multilayer and monolayer desorption occur at 95 and 110 K, respectively.

3.9. Conclusions

RAIRS has been used to identify a new interaction on Pt(111) at 85 K between adsorbed superoxo O_2^- and CO molecules, which produces a perturbed CO species. After annealing to 130 K, the superoxo and perturbed CO species disappear and physisorbed CO₂ appears, thus providing evidence of an O–O--C=O complex as a precursor to CO₂ formation. Both the perturbed CO and CO₂ species only appear with a high coverage of O_2^- , which cannot occur if CO is adsorbed first on the Pt(111) surface.

Chapter 4 - Ambient Pressure C₂H₂ Hydrogenation from 120 to 370 K on Pt(111)

4.1. Outline

The spectra from the hydrogenation of acetylene are the first ambient pressure data published on the UHV-AP chamber and show the capabilities of the chamber at ambient pressure and of the single rotatable polarizer to monitor both gas and surface species in the spectra. The reaction scheme is shown in Section 4.2. Section 4.3 outlines the experimental details for the different trials performed. First, in sections 4.4 and 4.5, mono- and multilayer acetylene hydrogenation from 120 to 300 K were studied at a pressure of 1.0×10^{-2} Torr of H₂. Next, ambient pressure studies at 300 to 370 K of a mixture of 1:100 C₂H₂ to H₂ were carried out. Section 4.6 shows an annealing experiment from 300 to 370 K. The data show that ethylene and ethane are produced at 350 and 370 K. To show the capabilities and test the polarizer during a constant temperature study similar to a real catalytic reaction, 4.0×10^{-2} Torr and 4.0 Torr of C₂H₂ and H₂ were added to the cell at 370 K. Ethane was produced after 24 minutes as shown in section 4.7. A separate experiment was then done, as described in section 4.8. Ethylene and hydrogen were added to the cell at a ratio of 1:10. After adding the hydrogen, ethylene was immediately hydrogenated to ethane. The discussion of the peaks and experimental results are shown in Section 4.9. Conclusions from the results are presented in Section 4.10.

Data in this chapter were published in an article in ACS Catalysis. (Reprint from [Krooswyk, J. D.; Waluyo, I.; Trenary, M., *ACS Catal.* **2015**, *5* (8), 4725-4733. Copyright (2015) American Chemical Society])

53

4.2. Reaction Scheme



Figure 4.1. Sketch of the reaction scheme for the ambient pressure hydrogenation of acetylene to ethane on Pt(111). Acetylene adsorbs on Pt(111) as di- σ -acetylene at 300 K. After ambient pressure of H₂ is added to the cell, acetylene is either hydrogenated to vinyl (CHCH₂) as shown in the top pathway in the figure, or hydrogenated to three spectator species, ethylidyne (CCH₃), di- σ -ethylene (C₂H₄), and ethylidyne (CHCH₃) as shown in the lower part of the figure. After annealing the crystal to 350 K, acetylene is completely hydrogenated to ethylene. Further annealing to 370 K results in the hydrogenation of ethylene to ethane, with π -ethylene (C₂H₄) as an intermediate species.

4.3. Experimental

The cleaning process of the crystal was discussed in Chapter 3.3. Oxidation treatment was performed after each experiment (in-between the acquisition of p- and s- polarized spectra) and the crystal was annealed to 1200 K for two minutes before the start of each experiment. For the low temperature data, either monolayer or multilayer acetylene coverage was created by exposing the crystal to 2 or 5 L (1 L = 1×10^{-6} Torr s), respectively, of C₂H₂. A static pressure of H₂ was then added to the cell. For temperatures from 300 to 370 K, a static pressure of C₂H₂ and H₂ or C₂H₄ and H₂ was added to the cell. In the experiments where the crystal was annealed to a set of temperatures, the crystal was annealed to each temperature for 30 s and then cooled to the initial temperature for spectral acquisition. The PD-RAIRS technique has been described in Chapters 1 and 2. For the low temperature studies shown in Figures 4.2 and 4.3, 1024 scans were acquired with p-polarized light. P- and s-polarized light spectra were collected for Figures 4.4, 4.5. and 4.6. $\Delta R_p/R_p$ and $\Delta R_s/R_s$ denote the two polarizations, and the spectra in which s- is subtracted from p-polarized spectra are denoted as $\Delta R/R$.

Atomic absorption grade acetylene (99.6%) was purchased from Airgas and purified with several freeze-pump-thaw cycles. Since the gas is stabilized with acetone, the gas was checked with mass spectrometry for acetone (m/z 52) impurities. Research grade ethylene (99.99%) and ultra high purity hydrogen (99.999%) were purchased from Matheson Tri-Gas and Airgas, respectively, and used without any further purification. All gases were checked for impurities with mass spectrometry and none were detected.

4.4. Ambient Pressure Hydrogenation of Monolayer C₂H₂

Figure 4.2 shows RAIR spectra in the C–H stretch region following exposure to acetylene at 120 K followed by annealing to the indicated temperatures in a background of 1.0×10^{-2} Torr of H₂(g). As shown previously,²³ the peak at 2994 cm⁻¹ is attributed to acetylene bound to the surface in a di- σ/π structure. This is the only peak of this species that has sufficient intensity to be observed and for this reason only spectra in the C–H stretch region were recorded in this experiment. When hydrogen is added and the surface annealed to 220 K, a separate peak is resolved at 2980 cm⁻¹, which is assigned to the v_s(CH₂) mode of vinyl (CHCH₂). An unresolved shoulder on the low wavenumber side of the 2994 cm⁻¹ peak of acetylene seen in the top spectrum persists and is most likely due to a form of acetylene with a slightly different bonding environment as the intensity of this shoulder relative to the main acetylene peak at 2994 cm⁻¹ remains roughly the same

55

for all spectra in Figure 4.2. A new peak appears at 2918 cm⁻¹ after annealing to a slightly higher temperature of 230 K and its intensity increases by a factor of 2.5 after a 240 K anneal, which also causes a small shift to 2916 cm⁻¹. As further discussed below, this peak can be assigned to either the v(CH) mode of vinyl or to di- σ bonded ethylene. As previous studies have shown, the most intense RAIRS peaks for both vinyl²⁵ and di- σ bonded ethylene⁶¹⁻⁶³ occur in the C–H stretch region. By 250 K the 2994 and 2980 cm⁻¹ peaks have disappeared and the one at 2916 cm⁻¹ is greatly diminished. As previous work has shown that di- σ bonded ethylene can be hydrogenated to ethane, which would desorb at 252 K,⁶⁴ it is assumed that the disappearance of the peaks in Figure 4.2 is due to the hydrogenation of acetylene to ethane via vinyl and ethylene intermediates.



Figure 4.2. 2 L of C_2H_2 adsorbed on Pt(111) at 120 K. 1.0×10^{-2} Torr of H_2 was then added and the crystal annealed to 220, 230, 240 and 250 K.

4.5. Ambient Pressure Hydrogenation of Multilayer C₂H₂

Somewhat different results are obtained when starting with a higher acetylene coverage, as shown by the spectra in Figure 4.3, which were obtained following a 5 L acetylene exposure at 120 K followed by adding 1.0×10^{-2} Torr of H₂(g) to the cell and annealing the surface to the indicated temperatures. As before, a prominent peak at 2994 cm⁻¹ due to di- σ/π acetylene is observed but it is now accompanied by additional peaks, with the most prominent at 3195 cm⁻¹. Following our previous study,²⁵ this peak as well as the one at 1364 cm⁻¹ are assigned to a weakly adsorbed form of acetylene whereas the just barely observable peak at 3338 cm⁻¹ is assigned to multilayer acetylene. No changes are

observed upon addition of $H_2(g)$ at 120 K, and only a small decrease in the weakly adsorbed acetylene is observed with the 260 K anneal. In contrast, the form of acetylene with peaks at 3195 and 1364 cm⁻¹ desorbs after annealing to 210 K under UHV conditions indicating that this form of acetylene is stabilized by the presence of $H_2(g)$. After annealing to 300 K only ethylidyne with peaks at 1129, 1338, 2796, and 2882 cm⁻¹, assigned to v(CC), $\delta_s(CH_3)$, $2 \times \delta_{as}(CH_3)_s$, and $v_s(CH_3)$, are visible in the spectrum.



Figure 4.3. 5 L of C_2H_2 adsorbed on Pt(111) at 120 K. 1.0×10^{-2} Torr of H_2 was then added and the crystal annealed to 260 and 300 K.

4.6. Ambient Pressure C₂H₂ Hydrogenation from 300 to 370 K

Figure 4.4 shows three sets of results for the hydrogenation of acetylene. With the crystal at 300 K, 1.0×10^{-2} Torr of C₂H₂(g) was admitted to the cell and the topmost spectra obtained. This was then followed by adding 1.0 Torr of H₂ with the surface still at 300 K. With both gases remaining in the cell, the surface was then annealed to the indicated temperatures. The spectra in Figure 4.4(a) were obtained with p-polarized light such that both surface and gas phase peaks are observed, whereas the spectra in Figure 4.4(b) were obtained with s-polarized light so that only gas phase peaks appear. The spectra in Figure 4.4(c) are the difference between the spectra of Figures 4.4(a) and 4.4(b), showing that all gas phase peaks are subtracted revealing only peaks due to species on the surface.

Peaks due to three different gas-phase species are evident in Figure 4.4(b). After adding acetylene to the cell, peaks due to $C_2H_2(g)$ appear at 1305 and 1343 cm⁻¹ due to the P and R rotational branches of a combination band of the symmetric and asymmetric bending modes, whereas the peaks at 3269 and 3309 cm⁻¹ are the P and R branches of the asymmetric C–H stretch fundamental.⁶⁵ The $C_2H_2(g)$ peaks are unaffected by the addition of $H_2(g)$ to the cell at 300 K and are visible up to an annealing temperature of 330 K. However, they disappear after annealing to 350 K, indicating that all the acetylene has been hydrogenated by this temperature. At 320 K, a gas phase peak at 949 cm⁻¹ first appears and reaches its maximum intensity for a 350 K anneal, but then is completely absent after annealing to 370 K. This peak is assigned to the $\rho_w(CH_2)$ mode of ethylene, which has B_{1u} symmetry for the D_{2h} point group.⁶⁶ The B_{3u} CH stretch of $C_2H_4(g)$ appears at 2988 cm⁻¹. For the 370 K spectrum no peaks due to $C_2H_2(g)$ or $C_2H_4(g)$ are present and a series of partially resolved peaks in the C–H stretch region between 2881 and 2987 cm⁻¹

59
are due to gas phase ethane.⁶⁶ By detecting only gas phase species, the s-polarized spectra of Figure 4.4(b) clearly reveal that acetylene is first hydrogenated to ethylene, and then the ethylene is hydrogenated to ethane. The temperature onset for the appearance of the gas phase hydrogenation products revealed by the spectra of Figure 4.4(b) can be correlated with the spectra of the surface species in Figure 4.4(c).

Only weak peaks at 902, 2976, and 3025 are observed after 1.0×10^{-2} Torr of acetylene is added to the IR cell with the surface at 300 K. The presence of some di- σ/π acetylene is evident by the unresolved intensity at 2994 cm⁻¹. When $H_2(g)$ is added to the cell, the intensity at 2994 cm^{-1} disappears and ethylidyne peaks at 1340 and 2879 cm^{-1} first become visible and then as the temperature increases the weaker ethylidyne peaks at 1118 and 2793 cm⁻¹ are also observable. The intensities of the ethylidyne peaks reach their maximum for the 350 K anneal and then decrease somewhat after annealing to 370 K. In addition to the prominent peaks due to ethylidyne, there are a number of very weak peaks that can be due to several possible C_2H_x species including vinylidene (CCH₂), vinyl (CHCH₂), ethyldidene (CHCH₃), ethylene (both di- σ and π -bonded), ethyl (CH₂CH₃) and ethynyl (CCH). The simplest pathway from adsorbed acetylene to gas phase ethane would involve the sequential addition of hydrogen to from vinyl, ethylene, ethylidene, and ethyl intermediates: $C_2H_2 \rightarrow CHCH_2 \rightarrow C_2H_4 \rightarrow CHCH_3 \rightarrow CH_2CH_3$. The spectroscopic and other evidence for and against one of more of these species are discussed below.

The most notable feature of the results in Figure 4.4 is the strong contrast between the abrupt changes in the gas phase species as the temperature is raised as seen in Figure 4.4(b) and the very modest changes in the surface species as revealed in Figure 4.4(c).

For example, when the surface is heated from 330 to 350 K, all of the $C_2H_2(g)$ disappears and is accompanied by an increase in the amount of $C_2H_4(g)$, and similarly when the temperature is increased from 350 to 370 K all of the $C_2H_4(g)$ is hydrogenated to $C_2H_6(g)$. During these hydrogenation reactions, the ethylidyne coverage remains high, reinforcing earlier findings that it is a spectator species in acetylene and ethylene hydrogenation. While the ethylidyne coverage remains high during the hydrogenation reactions, the weak peaks due to other species remain low for all annealing temperatures. An assumption in annealing experiments is that intermediates present at elevated temperatures where a particular reaction occurs will remain on the surface after the temperature is lowered. An alternative is to obtain spectra as a function of time while holding the temperature constant where a reaction occurs.



Figure 4.4. P polarized (a), S polarized (gas phase species) (b), and the S subtracted from P polarized spectra (c) for 1.0×10^{-2} Torr of C₂H₂ leaked into the cell at 300 K. 1.0 Torr of H₂ was then added and the crystal was annealed to 320, 330, 350, and 370 K.

4.7. Ambient Pressure C₂H₂ Hydrogenation at 370 K

The spectra in Figure 4.5 were obtained after first adding 4.0×10^{-2} torr of C₂H₂(g) to the cell, recording the topmost spectrum, adding 4.0 torr of $H_2(g)$, and then taking spectra versus time all with the sample temperature held constant at 370 K. The results from Figure 4.4 imply that complete hydrogenation of acetylene to ethane can occur at this temperature. As for Figure 4.4, Figure 4.5 shows results for p- and s-polarized (a and b) light and their difference (c). The spectra of the gas phase species in Figure 4.5(b) clearly reveal the stepwise hydrogenation of acetylene to ethylene to ethane. From 8 to 24 minutes, the spectra indicate that the ethylidyne coverage is roughly constant. At this temperature, peaks due to species other than ethylidyne are larger relative to the ethylidyne peaks, especially in the C-H stretch region where peaks centered at 2928 and 2966 cm⁻¹ are seen. Because the results in Figure 4.5 were obtained at 370 K, the peaks are all broader than for the annealing experiments of Figure 4.3 where the spectra were all obtained at 300 K. In the lower wavenumber range, a distinct peak at 1377 cm⁻¹ is observable but only broad unresolved structure is seen from about 1400 to 1470 cm⁻¹. The peak at 949 cm⁻¹ marked with an asterisk is attributed to gas phase ethylene that was not fully cancelled in the subtraction of the s-polarized spectra from the p-polarized spectra.



Figure 4.5. P polarized (a), S polarized (gas phase species) (b), and the S subtracted from P polarized spectra (c) for 4.0×10^{-2} Torr of C₂H₂ leaked into the cell at 370 K. 4.0 Torr of H₂ was then added and consecutive scans were acquired (1024 scans/spectra, approximately ~ 4 minutes per spectra).

4.8. Ambient Pressure C₂H₄ Hydrogenation at 370 K

As gas phase ethylene is observed in the course of hydrogenation of acetylene, it is useful to compare the acetylene results with those obtained starting with ethylene. Figure 4.6 shows the analogous results to those of Figure 4.5 and were obtained by adding 4.0×10^{-2} Torr of C₂H₄(g) to the cell, recording the topmost spectrum, and then adding 0.40 Torr of $H_2(g)$ and recording spectra at 4 min intervals with the Pt crystal at 370 K. The gas phase ethylene peaks are labeled at 949, 1445, 2989, 3077, and 3124 cm⁻¹. The first three vibrational modes have symmetries such that the oscillating dipole moment is parallel to the C=C axis yielding a prominent Q branch in the rotational fine structure, whereas the last two peaks are P and R branches of a vibrational mode with oscillating dipole moment perpendicular to the C=C axis. Upon addition of $H_2(g)$, the gas phase ethylene peaks are replaced by the those of ethane and there is essentially no change with time of the gas phase species. The spectra of the surface species are again dominated by ethylidyne. The ethylidyne coverage before and 4 minutes after adding $H_2(g)$ is unchanged even as all the gas phase ethylene is hydrogenated to ethane. Between 4 and 16 min the ethylidyne coverage decreases by 30% indicating a slow hydrogenation pathway. Slight shifts in the ethylidyne peak positions accompany this change in coverage. Separate control experiments verified that there is no decrease in the ethylidyne coverage at 370 K in the absence of $H_2(g)$. The hydrogenation of surface ethylidyne is not accompanied by any detectable change in the amount of $C_2H_6(g)$, as indicated by the spectra in Figure 4.6(b). Once again, this demonstrates that ethylidyne is mainly a spectator species rather than an intermediate in the hydrogenation reaction.



Figure 4.6. P polarized (a), S-polarized (b), and the S subtracted from P polarized spectra (c) for 4.0×10^{-2} Torr of C₂H₄ leaked into the cell at 370 K. 4.0×10^{-1} of H₂ was then added and consecutive scans were acquired (1024 scans/spectra, approximately ~ 4 minutes per spectra).

4.9. Discussion

A principal goal of in situ spectroscopic studies of surface catalyzed reactions is to identify the molecular species present on the surface during the reaction. The presumption is that the detected surface species are reaction intermediates and that their spectroscopic identification will thus establish the reaction mechanism. However, the results presented here are in accord with previous studies with in-situ spectroscopy that reveal that the spectra are often dominated by spectator species. This is most clear in our results for ethylene hydrogenation at 370 K where the conversion of $C_2H_4(g)$ to $C_2H_6(g)$ occurs over an ethylidyne covered surface with no other surfaces species detected. This was established earlier by Cremer et al.⁶⁷ using sum frequency generation (SFG) and by Ohtani et al.⁶³ using polarization-dependent RAIRS. These spectroscopic studies confirmed even earlier work showing that ethylidyne was not an intermediate in ethylene hydrogenation over Pt(111).⁶⁸ In contrast to our work in which ethylidyne is the only surface species detected under hydrogenation conditions, di- σ - and π -bonded ethylene were also detected by SFG but at a lower surface temperature of 295 K.⁶⁷ Ohtani et al.⁶³ detected π -bonded ethylene at a surface temperature of 150 K at an ethylene pressure of 0.98 Torr, but only in the absence of $H_2(g)$, and they observed di- σ ethylene at temperatures up to 320 K in the presence of 0.98 Torr of $C_2H_4(g)$ and 4.9 Torr of $H_2(g)$. Earlier RAIRS results by Kubota et al. had shown that π -bonded ethylene was present on the Pt(111) surface at a temperature of 112 K in an ambient pressure of $C_2H_4(g)$.⁶⁹⁻⁷¹ Cremer et al.⁶⁷ concluded that π -bonded, rather than di- σ -bonded, ethylene leads to ethane formation by way of an ethyl intermediate. Frei and coworkers also detected an ethyl intermediate in ethylene hydrogenation over a Pt/Al₂O₃ catalyst.^{72, 73} Our results

show that ethylene hydrogenation can take place under conditions where the coverages of these intermediates are too low to be detected even with relatively high sensitivity. As the higher temperature we used is more representative of the conditions used in practical hydrogenation catalysis, our results reveal some of the subtleties of operando studies with surface vibrational spectroscopy.

In contrast to our spectra of ethylene hydrogenation, for acetylene hydrogenation we observe other surface species in addition to ethylidyne. The challenge then is to identify these species and to decide if they are merely spectators or intermediates in the formation of ethylidyne or in the hydrogenation of acetylene. As shown in Figure 4.4, admitting 1.0×10^{-2} Torr of C₂H₂(g) to the cell at 300 K leads to distinct peaks at 3025 and 2975 cm⁻¹ with some intensity at 2994 cm⁻¹. A possible peak a 902 cm⁻¹ is also seen. Previous experiments performed by annealing a Pt(111) surface covered with acetylene adsorbed at low temperature to 300 K left some adsorbed acetylene on the surface while also generating a new set of peaks, some of which were attributed to vinyl.²⁵ This could occur by a simple disproportionation reaction, $2HCCH \rightarrow CHCH_2 + CCH$, suggesting that vinyl formation should be accompanied by ethynyl. At the same time, isomerization of HCCH to the more stable vinylidene species, CCH₂, could also occur as has been found on the Pd(111) surface.^{74, 75} The formation of multiple C_2Hx species upon annealing an acetylene covered surface to 300 K is revealed by the multiple peaks observed with surface vibrational spectroscopy and by scanning tunneling microscopy⁷⁶ where individual molecules are resolved and are clearly of several different types. Based on this prior work, we assign the peak at 2976 to vinyl, the peak at 3025 to ethynyl, and the peak at 2994 cm⁻¹ to di- σ/π bonded acetylene. The 902 cm⁻¹ peak could be due to the

CH₂ rocking mode of vinyl or vinylidene, although the calculated values are quite a bit higher but also sensitive to coverage.

When hydrogen is added with the crystal at 300 K there are no changes to the gas phase spectrum indicating that no hydrogenation of $C_2H_2(g)$ to $C_2H_4(g)$ occurs, but ethylidyne appears on the surface as indicated by the peaks at 2881 and 1340 cm⁻¹. Peaks due to one or more other species are observed as well at 2963 and 2929 cm⁻¹. The former is most likely due to ethylidene, but the latter is a poor match to $di-\sigma$ -bonded ethylene, which has been observed at values from 2904 to 2924 cm⁻¹ in previous studies.^{61, 63, 69-71} Gas phase ethylene first appears at 320 K and is most abundant at 350 K, but by 370 K is completely hydrogenated to $C_2H_6(g)$. The only change in the surface species that correlates with the appearance and disappearance of $C_2H_4(g)$ is the weak peak at 970 cm⁻ ¹. For π -bonded ethylene, the only peak of sufficient intensity is the CH₂ wagging mode, which has been observed with RAIRS on Pt(111) at 954 cm⁻¹ in the presence of 0.98 Torr of ethylene⁶³ and at 975 cm⁻¹ in UHV in the presence of coadsorbed nitrogen atoms.⁷⁷ For π -bonded ethylene on Pd(111), the corresponding peak is observed at 1100 cm⁻¹ on the clean surface and at 933 cm⁻¹ for the hydrogen covered surface.⁷⁸ Although the annealing temperature results of Figure 4.4 therefore suggest that π -bonded ethylene is the intermediate in the conversion of ethylene to ethane, the coverage of π -bonded ethylene is too low to observe in the time dependent spectra of Figure 4.5 obtained at 370 K. The most remarkable finding from Figure 4.5 is the complete transformation of the gas phase composition from $C_2H_2(g)$ to $C_2H_4(g)$ to $C_2H_6(g)$ with almost no change in the surface composition, which is dominated by ethylidyne, with smaller amounts of two species that we tentatively identify as ethylidene and di- σ ethylene.

The peak that we observe at 2928 cm⁻¹ is only slightly higher in frequency than peaks assigned to di- σ ethylene observed in the range of 2904 to 2924 cm⁻¹ in previous studies.^{61, 63, 69-71} In a recent DFT study, the v_s(CH₂) mode of di- σ ethylene was calculated to be at 2913 cm⁻¹ and to be by far the most intense in the RAIR spectrum of this species. It is therefore reasonable to assign the 2928 cm⁻¹ peak observed here to di- σ ethylene, although more definitive identification of a polyatomic adsorbate is possible when multiple peaks are observed, as in the case of ethylidyne or even for higher coverages of di- σ ethylene.⁶¹

There are compelling arguments both for and against assigning the peaks observed here at 1379, 1462, and 2963 cm⁻¹ to ethylidene. In the organometallic coordination compound, μ_2 -CHCH₃)Os₂(CO)₈, ten peaks were observed and assigned to modes of ethylidene, including ones at 1369, 1447, and 2950 cm⁻¹ assigned to δ_s (CH₃), $\delta_{as}(CH_3)$ and $v_{as}(CH_3)$, respectively.⁷⁹ Only peaks at 2950 and 1030 cm⁻¹ for the complex are listed as having strong intensity.⁷⁹ A similar set of three peaks that we observe here and tentatively assign to ethylidene have also been observed on Pt(111) at 1387, 1444, and 2960 cm⁻¹ in the course of ethylene conversion to ethylidyne⁸⁰, at 1391, 1444, and 2964 cm^{-1} in the conversion of acetylene to ethylidyne²⁵, and most recently at 1393, 1443, and 2958 cm⁻¹ in the conversion of vinyl iodide to ethylidyne.⁸¹ The similarity in frequencies and relative intensities of these three peaks indicates that they are due to a common intermediate, and based on the similarity to the organometallic complex, that this species is ethylidene. Newell et al. presented RAIR spectra for ethyl deposited onto Pt(111) through exposure to supersonic molecular beams of ethane, and its subsequent conversion to ethylidyne by way of an intermediate species that yielded clear and distinct peaks at 2980, 2917, 1255, and 1010 cm⁻¹, which they assigned to modes of ethylidene.⁸² Of particular note is that the strongest peak shown in their spectra is the one at 1255 cm^{-1} , while there are no features in this region in our spectra. Other evidence that does not favor our identification of ethylidene comes from the recent work of Zhao and Greeley, who presented simulated spectra for various C_2H_x species based on frequencies and intensities from DFT calculations.³² For ethylidene, their theoretical RAIRS spectrum is qualitatively different from both our spectra and the spectra of Newell et al. The simulated ethylidene spectrum shows the C-H stretch region dominated by an intense peak at 2864 cm⁻¹ due to $v_s(CH_3)$, with a much weaker peak at 3046 cm⁻¹ due to $v_{as}(CH_3)$ ³². Furthermore, they predict three peaks of comparable intensity at 1403, 1245 and 1048 cm⁻¹, with two weaker peaks at 1326 and 935 cm⁻¹. Based on this complete mismatch between theory and experiment, they argue that the experimental spectra are better assigned to vinylidene, which has a much simpler simulated spectrum dominated by an intense $\delta(CH_2)$ peak at 1415 cm⁻¹, and weaker peaks at 2960 and 900 cm⁻¹. In contrast to the experimental spectra, the simulated vinylidene spectrum features only a single peak in the region from 1300 to 1450 cm⁻¹, and therefore fails to account for our experimental observation of two peaks in this region, assuming the peaks in the experimental spectra are due to a single species. The ability of the calculations to simulate RAIRS spectra accurately is suggested by their results for ethylidyne, where the frequencies and relative intensities agree quite well with experimental spectra. A separate argument against ethylidene is that the activation energy for its dehydrogenation to ethylidyne is so low that it is not predicted to be stable enough to be detected spectroscopically.²⁶ Although a good match between experimental and simulated RAIR spectra would constitute fairly

definitive evidence for a particular surface species, this has yet to be achieved for either ethylidene or vinylidene on Pt(111). Therefore, although there is some evidence that favors assigning the peaks that we observe here at 1379, 1462, and 2963 cm⁻¹ to ethylidene, this assignment is not supported by DFT calculations³² or by the experimental results of Newell et al.,⁸² possibly indicating that the experimental spectra are due to a mixture of at least two species, one of which may be vinylidene.

Vibrational		
modes	Species	Peak (cm ⁻¹)
ν(CH)	Acetylene	2994
ω(CH ₂)	$\mu_3-\eta_2-vinylidene$	902,910
$v_{as}(CH_2)$	$\mu_3 - \eta_2 - vinylidene$	2976
v(CH)	$\mu_3-\eta_2-ethynyl$	3025
v(CC)	Ethylidyne	1118
$\delta_{s}(CH_{3})$	Ethylidyne	1340
$\delta_{as}(CH_3)$	Ethylidyne	1439
2×δ _s (CH ₃)	Ethylidyne	2798
$v_{s}(CH_{3})$	Ethylidyne	2879
$\delta_{s}(CH_{2})$	di- σ -ethylene	1420
$v_{s}(CH_{2})$	di- σ -ethylene	2929
$\delta_{s}(CH_{3})$	Ethylidene	1378
$\delta_{as}(CH_3)$	Ethylidene	1462
$v_{as}(CH_3)$	Ethylidene	2963
ω(CH ₂)	π -ethylene	970

Table I. Peak assignments for surface species adsorbed on Pt(111) during the ambient pressure hydrogenation of C_2H_2 to C_2H_6 .

4.10. Conclusions

The results presented here in which surface species are detected during the catalyzed conversion of gas phase acetylene to ethane by way of a gas phase ethylene intermediate indicate that the surface spectra are dominated by spectator species to the hydrogenation reaction. While previous work had clearly revealed that hydrogenation of ethylene readily proceeds over an ethylidyne-covered surface, the results presented here indicate that di- σ -bonded ethylene and ethylidene are also spectator species for acetylene and ethylene hydrogenation. This implies that while operando spectroscopy of surfaces can readily detect surfaces species during reaction, these species are less likely to be intermediates, which may not build up to detectable coverages during reaction conditions. The determination of intermediates will likely to continue to be inferred from indirect observations rather than via direct spectroscopic detection.

5.1. Outline

In this chapter, a reactive C_2 layer formed from the decomposition of C_2H_2 at 750 K is studied with both in-situ IR and ex-situ Auger spectroscopy. The RAIRS data show the ethylidyne intermediate in the reaction, while the Auger spectra confirm that the carbon is hydrogenated through a decrease in the carbon signal after exposing the crystal to ambient pressure H_2 . The reaction scheme is shown in Section 5.2. Section 5.3 outlines the experimental details for the different trials performed. Sections 5.4 and 5.5 describe low and high coverage carbon hydrogenation experiments. The Pt(111) crystal was held at 400 K and 10 Torr of H₂ was added to the cell. To confirm the hydrogenation of the ethylidyne intermediate, the crystal was covered with ethylidyne and exposed to H2 with a pressure range of 1.0×10^{-2} to 10 Torr of H₂ at 400 K. This data is shown in Section 5.6. Section 5.7 shows CO adsorbed on C_2 -Pt(111) and clean Pt(111) surfaces, respectively. Separate experiments on the hydrogenation and decomposition of ethylidyne titrated with CO are described in Section 5.8. The discussion of the peaks and experimental results are given in Section 5.9. Conclusions from the results are presented in Section 5.10.

Portions from this chapter are reprinted from a manuscript recently accepted to a special issue in Surface Science honoring Professor John T. Yates, Jr. The authors are Joel D. Krooswyk, Christopher M. Kruppe, and Michael Trenary.

5.2. Reaction Scheme



Figure 5.1. Sketch of the reaction scheme for the hydrogenation of C_2 species adsorbed on Pt(111) to ethane through an ethylidyne intermediate at 400 K and 10 Torr of H₂. C₂ species are adsorbed on Pt(111) by exposing C_2H_2 while the crystal is held at 750 K in UHV. After the crystal is allowed to cool to 400 K, 10 Torr of H₂ is added to the cell. C₂ is hydrogenated to ethane through an ethylidyne (CCH₃) intermediate indicating a sequential reaction occurs at 400 K.

5.3. Experimental

The experiments were performed in the UHV chamber coupled to an ambient pressure cell described in Chapter 2. At the start of every experiment, the Pt(111) crystal was annealed to 1200 K for two minutes to desorb any CO and ensure that the surface was well ordered. As shown in each figure, a certain coverage of C₂ or CCH₃ was formed by exposing the Pt(111) surface to C₂H₂ or C₂H₄, respectively, before adding an ambient pressure of H₂ and/or CO to the cell. The units are in Langmuir (1×10⁻⁶ Torr s = 1 L). In Figures 5.2 and 5.3, 512 scans were acquired for the time shown while the crystal was held at 400 K. Each spectrum was acquired in approximately two minutes. For all other spectra in Figures 5.4, 5.5 and 5.6, 1024 scans were acquired. In Figures 5.4, a constant temperature was held at 400 K while acquiring the spectra, while in Figures 5.5 and 5.6, spectra were acquired at 300 K after the crystal was annealed to the target temperature for

30 seconds. In Figures 5.5 and 5.6, when an ambient pressure of CO was added to the cell, gas phase CO peaks were also present in the spectra. These peaks were removed from the spectra by rotating the polarizer, acquiring the spectra with s-polarized light, and performing spectral subtraction ($\Delta R_p/R_p - \Delta R_s/R_s$) to reveal the actual intensity of the peaks representing CO adsorbed on the surface. This method of RAIRS, denoted as PD-RAIRS, and the chamber design were described previously.^{83, 84}

After the crystal was raised into the main chamber (UHV) following the exposure to H_2 , it was annealed to 1100 K to desorb any CO from the surface. The crystal was allowed to cool to room temperature and Auger spectra were then acquired. The Auger spectra were acquired with the LK Technologies RVL2000 Auger-LEED. For data acquisition, the derivative signal was directly collected from the instrument and plotted without any modification. After the Auger spectra were acquired, the crystal was cleaned by oxidation treatment.

Atomic adsorption grade (99.6%) C_2H_2 was purchased from Airgas. It was purified by the freeze pump thaw method and checked for acetone with mass spectrometry, parent peak m/z = 52. This gas was also used in previous work.⁸³ Ethylene (99.99%) and carbon monoxide (99.99%) were purchased from Matheson Tri-Gas, while the ultra high purity hydrogen (99.999%) was purchased from Praxair. All were checked for purity with mass spectrometry. No impurities were detected.

5.4. Low Coverage C₂ Hydrogenation

Figure 5.3(a) shows RAIR spectra following the exposure of H_2 to a C_2 covered Pt(111) surface. Before the spectra were acquired, C_2 was formed on the surface by exposure of

0.6 L of C₂H₂ to the crystal held at 750 K. The carbon coverage was approximately 0.30 ML as determined from the Auger spectra shown in Figure 5.3(b). This coverage was calculated to an estimated accuracy of \pm 15% from the ratio of the 273 to 237 eV peaks multiplied by 0.62 as described in previous work.⁸⁵ In order to verify the accuracy of this estimate, 10 L of C₂H₄ was exposed to a clean Pt(111) surface at 300 K, which formed 0.25 ML of ethylidyne (CCH₃).⁸⁵ The crystal was then annealed to 1100 K. This should have produced a carbon coverage of 0.50 ML. As shown in Figure 5.2, a coverage of 0.57 ML was calculated from the Auger spectra. The 14% higher than expected carbon coverage could be due to CO or other carbon-containing species present on the surface.



Figure 5.2. Auger spectra for calibrating carbon coverage on Pt(111). First, an Auger spectrum was acquired of the clean Pt(111) crystal at 300 K. 10 L C₂H₄ was then adsorbed at 300 K and annealed to 1100 K. After the crystal cooled to 300 K, another spectrum was acquired. As shown, approximately 0.57 ML carbon was adsorbed on the surface after the 1100 K anneal.

Figure 5.3(a) shows a spectrum acquired at 300 K followed by a spectrum after adding 1.0×10^{-2} Torr of H₂. The next spectrum was recorded after annealing to 400 K, a temperature where ethylidyne is stable and where hydrogen should mostly be desorbed making empty sites available. With the crystal at 400 K, 10 Torr of H₂ was then added and spectra were acquired versus time over a period of one hour. The first spectrum shows ethylidyne peaks at 1115 and 1344 cm⁻¹, due to the v(CC) and δ_s (CH₃) modes, respectively. After the first three spectra at 400 K, no peaks are visible. The results in Figure 5.3 show that C₂ was hydrogenated to ethylidyne, which was then removed from the surface, presumably by hydrogenation to ethane. After the crystal was raised into the UHV chamber, it was annealed to 1100 K and cooled to 300 K. An Auger spectrum was then acquired to determine carbon coverage. As shown in Figure 5.3(b), after H₂ exposures of 20 and 60 minutes, the carbon coverages decreased to 0.17 and 0.09 ML, respectively. The Auger spectra confirmed that carbon was removed from the surface by hydrogenation.



Figure 5.3. Figure 5.3(a) shows spectra acquired after the Pt(111) crystal held at 750 K was exposed to 0.6 L C_2H_2 and allowed to cool to 300 K. 1.0×10^{-2} Torr of H_2 was then added at 300 K. After the crystal was annealed to 400 K, another 100% line was acquired. After 10.0 Torr of H_2 was added, consecutive spectra were acquired (512 scans/spectrum). Figure 5.3(b) shows an Auger spectrum acquired of a clean Pt(111) surface at 300 K. The crystal was then exposed to 0.6 L C_2H_2 at 750 K and another spectrum acquired at 300 K. The next two spectra were acquired at 300 K after the crystal was exposed to 10.0 Torr H_2 for 20 and 60 minutes respectively, raised into the UHV chamber, and annealed to 1100 K.

5.5. High Coverage C₂ Hydrogenation

The experiment shown in Figure 5.4 is identical to that of Figure 5.3, but with a higher C_2 coverage. As shown in Figure 5.4(b), after a 1.0 L exposure of C_2H_2 at 750 K, the carbon coverage was approximately 0.52 ML. The first spectrum in Figure 5.4(a) shows that no ethylidyne was formed after adding 1.0×10^{-2} Torr of H₂ at 300 K. After annealing to 400 K and acquiring the top spectrum, the H₂ pressure was increased to 10 Torr and subsequent spectra were acquired at two minute intervals. Immediately after the increase

in H_2 pressure, the ethylidyne peaks at 1118 and 1343 cm⁻¹ appeared. Comparison of Figures 5.3 and 5.4 shows that a 70% higher carbon coverage leads to a 60% higher ethylidyne coverage and the ethylidyne remained on the surface for 18 minutes, which differs from the spectra in Figure 5.3, where the peaks were only present for six minutes. After the crystal was exposed to H_2 for 60 minutes, it was raised into the main chamber and an Auger spectrum was acquired, which indicated that approximately 0.28 ML of carbon remained on the surface.



Figure 5.4. Figure 5.4(a) shows spectra acquired after the Pt(111) crystal held at 750 K was exposed to 1.0 L C₂H₂ and allowed to cool to 300 K. 1.0×10^{-2} Torr of H₂ was then added at 300 K. After the crystal was annealed to 400 K, another 100% line was acquired. After 10.0 Torr of H₂ was added, consecutive spectra were acquired (512 scans/spectrum). Figure 5.4(b) shows an Auger spectrum acquired of a clean Pt(111) surface at 300 K. The crystal was then exposed to 1.0 L C₂H₂ at 750 K and another spectrum acquired at 300 K. The next spectrum was acquired at 300 K after the crystal was exposed to 10.0 Torr H₂ for 60 minutes respectively, raised into the UHV chamber, and annealed to 1100 K.

5.6. Ethylidyne Hydrogenation at 400 K

To more clearly establish the nature of hydrogenation of the ethylidyne formed from hydrogenation of C₂, the hydrogenation of ethylidyne formed directly from ethylene was also studied. Figures 5.5(a), (b), and (c) show the v(CC) and $\delta_s(CH_3)$, and $v_s(CH_3)$ modes at 1117, 1339, and 2882 cm⁻¹, respectively, of 0.22 ML of ethylidyne formed by a 10 L exposure of C₂H₄ to the surface at 400 K. The cell was then pressurized with 1.0 Torr of H_2 and consecutive spectra were acquired. The peaks related to ethylidyne completely disappeared after 28 minutes. Figure 5.5(d) shows a plot of the peak area of the δ_s (CH₃) bending mode versus time using H₂ pressures from 1.0×10^{-2} to 10 Torr. The top set of data points shows that approximately 10% of the ethylidyne decomposed at 400 K after 28 minutes under UHV conditions (no H₂ added). Four separate experiments were then performed, varying the hydrogen pressure from 1.0×10^{-2} to 10 Torr of H₂. There is a large change in the hydrogenation rate and in the final ethylidyne coverage. An exponential function was fitted to each of the data sets, and the best fits were obtained for 1.0 and 10 Torr of H_2 . This indicates that the reaction is first order in ethylidyne coverage. An accurate determination of the order with respect to hydrogen pressure could not be obtained because of non-linearity of the pressure gauge readings in this range. As the kinetics of ethylidyne hydrogenation has already been thoroughly described in previous publications, we have not performed a complete analysis of the limited data acquired here.



Figure 5.5. Figures 5.5(a), (b), and (c) show the v(CC), δ_s (CH₃), and v_s (CH₃) modes after the crystal was exposed to 10 L of C₂H₄ at 400 K. 1.0 Torr of H₂ was then added and consecutive spectra were acquired (1024 scans/spectrum, approximately four minutes per spectrum). Figure 5.5(d) shows the δ_s (CH₃) peak area after forming CCH₃ and adding the indicated pressures of H₂. The curves are exponential fits to the data. Time t = 0 corresponds to when the scanning of the ethylidyne spectrum was finished but prior to the addition of H₂ to the cell.

5.7. Ambient Pressure CO Titration of the C₂ Hydrogenation Reaction The nature of the interaction of adsorbates with metal surfaces can often be determined through RAIRS experiments of coadsorbed CO. In particular, if C₂ were to block CO adsorption, then the C_2 coverage could be titrated during hydrogenation by monitoring the CO coverage with RAIRS. A Pt(111) surface with a carbon coverage of 0.52 ML was prepared as for Figure 5.4(b). Figure 5.6(a) and (b) show peaks at 1852 and 1873 cm⁻¹ for CO on bridge sites and at 2097 cm⁻¹ for CO on terminal sites in an ambient of 1.0×10^{-2} Torr of CO above the clean surface at 300 K (blue spectrum), which should correspond to 0.6 ML of CO based on previous STM work.⁸⁶ This can be compared with the green spectrum for 1.0×10^{-2} Torr of CO above the carbon-covered surface, which yields approximately 0.5 ML of adsorbed CO, based on the reduction in integrated RAIRS peak areas and the assumption that the areas are proportional to coverage. However, this assumption is often not valid at high CO coverages, where screening effects lead to a reduction in intensity.⁵⁴ Therefore the reduction in intensity on the carbon covered surface may be lower than 0.5 ML. The red spectrum was obtained after adding 1.0 Torr of H₂ and annealing the crystal to 500 K, which in the absence of CO would have removed C₂. The absence of any significant difference between the red and green spectra indicates that the presence of coadsorbed CO poisons the C₂ hydrogenation reaction. As an aside, we note that for the clean surface, the two bridge-site CO peaks are slightly lower in intensity in the presence of 1.0×10^{-2} Torr of CO than for CO adsorbed on Pt(111) in UHV. This is attributed to an overlayer compression effect associated with the higher coverage achieved under an ambient pressure of CO.



Figure 5.6. Figures 5.6(a) and (b) show the v(CO) peaks assigned to the bridge and terminal site CO, respectively. The green spectrum shows the CO peaks after 1.0×10^{-2} Torr of CO was added to the cell at 300 K with the Pt(111) surface covered with 0.52 ML of carbon. The red spectrum was obtained after adding 1.0 Torr of H₂ and annealing to 500 K. For comparison, the blue spectrum shows results for the clean Pt(111) surface that was exposed to 1.0×10^{-2} Torr CO.

This is confirmed with the acquisition of spectra after the cell was evacuated to 10⁻⁷, 10⁻⁸, and 10⁻⁹ Torr as shown in Figure 5.7 and shown in a previous study with RAIRS.⁸⁷ The peak at 1873 cm⁻¹ disappeared as shown in the spectra, with the two peaks remaining in the spectra at 1851 and 2097 cm⁻¹ after the cell was evacuated. Similar results were seen in a previous RAIRS study.⁸⁷



Figure 5.7. Bridge (Figure a) and Terminal Site (Figure b) Peaks of CO adsorbed on Pt(111) at 300 K and 1×10^{-2} Torr of CO (blue line). Cell was then evacuated to 10^{-7} , 10^{-8} , and 10^{-9} Torr.

5.8. Ambient Pressure CO Titration of Ethylidyne Decomposition and Hydrogenation

Although CO is not useful for titrating the C₂ reaction, it can be used effectively to titrate the hydrogenation of ethylidyne and to study the influence of other species adsorbed on Pt(111) during the reaction. This is shown in Figures 5.8(a) and (b). In both figures, 5 L of C₂H₄ was exposed to the surface at 300 K, which created a saturated ethylidyne layer as indicated by the peaks at 1120, 1339, and 2882 cm⁻¹. For Figure 5.8(a), the surface was then exposed to 5 L of CO and peaks appeared at 1800 and 2024 cm⁻¹, due to bridge and terminal site CO. The CO pressure was raised to 1.0×10^{-2} Torr, which increased the CO coverage and caused a splitting of the bridge site CO peak at 1800 cm⁻¹ into peaks at 1742 and 1807 cm⁻¹ and a blue shift of the terminal site CO to 2037 cm⁻¹. The increase in CO pressure also caused blue shifts in the three ethylidyne peaks: 1120 to 1126 cm⁻¹, 1342 to 1352 cm⁻¹, and 2882 to 2894 cm⁻¹. After heating to 500 K, the ethylidyne peaks

largely disappeared yet the CO peaks were not restored to their values on the clean surface. Evacuation of the cell had little effect. After heating an ethylidyne covered surface to 500 K, previous work has shown that hydrogen-containing species such as CH and CCH remain on the surface and the results of Figure 5.8(a) imply that such species have a large effect of the amount and frequencies of coadsorbed CO.

Figure 5.8(b) shows the analogous results to those of Figure 5.8(a) but in the presence of 1.0 Torr of H₂. Note that the intensity scales are different in Figures 5.6(a) and 5(b) and that the ethylidyne and CO peaks have similar intensities and frequencies in the two sets of spectra before annealing to 400 K. However, after annealing to 450 K, a large increase in CO peak intensities and frequencies is seen in Figure 5.8(b), which continues upon annealing to 500 K, with only a modest change in the bridge site CO peaks upon evacuation of the cell. The fact that the final CO spectrum in Figure 5.8(b) is essentially the same as for clean Pt(111), demonstrates that the ethylidyne has largely been removed by hydrogenation leaving the surface free of the C_xH_y species that were present on the surface after ethylidyne decomposition in the case of Figure 5.8(a). Note that a just barely detectable ethylidyne peak is still present at 1352 cm⁻¹ in both Figures 5.8(a) and (b) even after the 500 K anneal, indicating that coadsorbed CO prevents complete hydrogenation or complete decomposition at 500 K.



Figure 5.8. In Figure 5.8(a), 5 L of C_2H_4 was exposed to a clean Pt(111) surface at 300 K. In Figure 5.8(a), 5 L of CO was then exposed to the ethylidyne covered surface. 1.0×10^{-2} Torr of CO was then added. The crystal was then annealed to 500 K. In Figure 5.7 (b), after the 5 L C_2H_4 , 1×10^{-2} Torr CO, and 1.0 Torr of H₂ were added, the crystal annealed to 400, 450 and 500 K. In both Figures, the cell was then evacuated to a pressure of approximately 10^{-9} Torr.

5.9. Discussion

As shown in Figures 5.3 and 5.4, C_2 is hydrogenated to ethane through an ethylidyne intermediate when the Pt(111) crystal is exposed to ambient pressure H₂. Since the quantity of gas phase ethane is too low to detect with RAIRS, unlike in our previous study of acetylene hydrogenation, Auger spectroscopy was used to show that hydrogenation removes carbon from the surface. The higher C_2 coverage in Figure 5.4 compared to Figure 5.3 leads to a higher ethylidyne coverage upon hydrogenation. The higher ethylidyne coverage may also be partly due to a lower rate of ethylidyne removal

by hydrogenation to ethane because fewer sites are available for the hydrogenation reaction. Because the rate at which C_2 is hydrogenated to ethylidyne at 400 K is comparable to the rate at which ethylidyne is hydrogenated to ethane under an ambient pressure of H_2 , the ethylidyne coverage remains lower than obtained by Deng et al.,³⁶ by coadsorbing hydrogen and C₂ at low temperature and annealing in UHV to higher temperatures. Under the latter conditions there is only enough hydrogen to hydrogenate C_2 , but not enough to hydrogenate ethylidyne. In the UHV study of Deng et al.,³⁶ 79% of the adsorbed carbon was found to be in the form of C_2 , with the remaining in the form of C atoms. It is therefore likely that the carbon left on the surface even after the 60 minute exposure to H₂ was in the form of carbon atoms. A previous study showed that atomic carbon on Pt(111) could not be hydrogenated even at atmospheric pressure and 600 K.⁸⁵ If we assume that only the C_2 species are hydrogenated, leaving the majority of the remaining carbon in the form of C atoms, the carbon coverage in the form of C₂ species remaining on the surface from the experiment shown in Figure 5.3 will be 0.11 and 0.03 ML after 20 and 60 minutes, respectively. These results show that the C_2 species are almost completely hydrogenated after the one hour exposure. In contrast, for the higher initial carbon coverage used in Figure 5.4, the carbon coverage assigned to C₂ species would be 0.17 ML after one hour of exposure to an ambient of 10 Torr of H₂.

As shown in Figure 5.5, ethylidyne is readily hydrogenated at 400 K because the needed surface sites are available. A previous study indicated that on top sites are occupied by H atoms at 300 K and under 10^{-1} Torr of H₂.⁸⁸ As ethylidyne occupies the fcc three-fold hollow sites, it does not block H atom adsorption sites and the reaction is unimpeded. As noted earlier, we could not determine the actual reaction order with respect to hydrogen

pressure. However, the reaction rate clearly rises rapidly with hydrogen pressure. To produce C_2H_6 from CCH₃, three hydrogen atoms must be added and this presumably occurs in a stepwise fashion to produce ethylidene (CHCH₃) and ethyl (CH₂CH₃) intermediates on the surface. These two species will not be seen in the spectra as they are readily hydrogenated at much lower temperatures than 400 K,^{72, 89} implying that they would react as soon as they formed.

Carbon monoxide cannot be used to titrate the C₂ coverage during the hydrogenation reaction because CO blocks H₂ adsorption and dissociation. An ambient pressure of CO produces an overlayer compression effect on the C_2 -covered surface similar what is seen at high CO coverage on the clean Pt(111) surface. As evident from comparison of the CO spectra in Figures 5.6 and 5.8, much less CO can adsorb on the ethylidyne-covered surface, making hydrogen sites available. This is a plausible explanation of why ethylidyne but not C_2 can be hydrogenated in the presence of coadsorbed CO. The fact that the CO spectrum in Figure 5.8(a) in the presence of the ethylidyne-decomposition products, which still contain hydrogen but do not give rise to observable RAIRS peaks under these conditions, is so different from the spectrum of CO on the surface prepared through C_2H_2 exposure at 750 K, implies that the latter surface is covered with carbon only. For ethylidyne hydrogenation, CO can be used to titrate the ethylidyne coverage as it is removed from the surface. A comparison of Figures 5.6 and 5.8 shows that in the presence of coadsorbed ethylidyne, the terminal site CO peak shifts from 2097 to 2037 cm⁻¹ and the disordered bridge site peaks shift from 1852 and 1873 to 1741 and 1807 cm⁻¹ ¹, respectively. This agrees with previous work on the coadsorption of CO with ethylidyne.⁴⁸ Finally, the temperature of ethylidyne hydrogenation is increased by 50 K to 450 K, corresponding to the onset of CO desorption, which frees sites needed for the hydrogenation reaction to proceed. This agrees with the work by Chen, et al. which studied the inhibition of ethylene hydrogenation by CO.⁴⁹

5.10. Conclusions

The decomposition of acetylene at 750 K produces C_2 molecules on Pt(111) that are hydrogenated to ethane at 400 K in the presence of 1.0×10^{-2} to 10 Torr of H₂ through an ethylidyne intermediate. Rapid hydrogenation of a saturation coverage of ethylidyne in 10 Torr of H₂ indicates that the formation of ethylidyne is the rate limiting step in the hydrogenation of C₂ to ethane. On the C₂-covered surface, CO saturates to a coverage similar to that of the clean surface and is high enough to block hydrogen from adsorbing and reacting with C₂. Therefore CO cannot be used to titrate the C₂ coverage during hydrogenation. However, in the case of an ethylidyne-covered surface, the saturation CO coverage is low enough to permit ethylidyne hydrogenation to proceed. When CO was coadsorbed with the products of ethylidyne decomposition, the CO spectra revealed the presence of hydrogen-containing species, even though those species could not be directly detected with RAIRS. The CO spectra thus implied that the carbon layer produced from the decomposition of C₂H₂ at 750 K produces a surface that is free of all hydrogencontaining carbon species.

Chapter 6 - Overall Conclusions and Future Work

In conclusion, the development of the PD-RAIRS technique has led to a variety of new discoveries from UHV to AP catalytic reactions. First, the use of a polarizer led to the discovery of the mechanism for low temperature CO oxidation on Pt(111) shown in Chapter 3. An interaction between the superoxo and perturbed CO species produced a physisorbed CO_2 molecule at 130 K. The interaction between the two is a chemical effect, which was determined using multiple isotopes of O_2 and CO.

Chapter 4 shows the first work using the polarizer to monitor both surface and gas phase species in the hydrogenation of acetylene to ethane on Pt(111). The polarizer enhances the signal for the low temperature studies from 120 to 300 K. These studies are similar to UHV studies and are also used to show the difference between UHV and AP experiments. When ambient pressure C_2H_2 and H_2 are added to the cell at 300 K and the crystal is annealed to higher temperatures, ethylene and ethane are produced at 350 and 370 K, respectively. Due to the overlap of spectators and time of spectral acquisition, reaction intermediates are difficult to see in the spectra in these experiments. This has also been seen in other PM-RAIRS experiments, so the reaction mechanism is inferred. The low and high temperature reactions provide a complete picture of the hydrogenation of C_2H_2 to C_2H_6 .

Since carbonaceous species form on the Pt(111) surface during hydrogenation reactions, such as ethylidyne, and greatly affect the catalytic reaction by blocking surface sites, they should be studied in detail. In Chapter 5, the hydrogenation of C_2 species from the decomposition of C_2H_2 was studied. Ethylidyne appeared in the spectra, which indicated

that it is an intermediate in the reaction. Auger spectra were acquired after the Pt(111) crystal was exposed to H_2 , which confirmed that the C_2 species were hydrogenated to ethane. This project shows the powerful in-situ and ex-situ techniques available to characterize the surfaces of transition metal catalysts.

Besides studying the reaction mechanisms in these catalytic reactions on Pt(111), all of these studies are useful to apply to future work on platinum alloys and other catalysts, such as Pd-Cu(111) single atom alloys. The Pd-Cu(111) system is designed to replace expensive palladium and platinum catalysts by using a low percentage of the expensive metal on an inexpensive support, such as copper. PD-RAIRS studies are currently underway on the Pd-Cu(111) surface and should show that acetylene is hydrogenated to ethylene through a vinyl intermediate. This catalyst should also be selective, so the hydrogenation of acetylene stops at ethylene and does not proceed to ethane.

- 1. Bartholomew, C. H., Mechanisms of Catalyst Deactivation. *Appl. Catal.*, A. **2001**, *212* (1–2), 17-60.
- 2. Steininger, H.; Lehwald, S.; Ibach, H., Adsorption of Oxygen on Pt(111). *Surf. Sci.* **1982**, *123* (1), 1-17.
- Miller, D. J.; Öberg, H.; Näslund, L.-Å.; Anniyev, T.; Ogasawara, H.; Pettersson, L. G. M.; Nilsson, A., Low O₂ Dissociation Barrier on Pt(111) Due to Adsorbate-Adsorbate Interactions. J. Chem. Phys. 2010, 133 (22), 224701.
- 4. Stipe, B. C.; Rezaei, M. A.; Ho, W., Atomistic Studies of O₂ Dissociation on Pt(111) Induced by Photons, Electrons, and by Heating. *J. Chem. Phys.* **1997**, *107* (16), 6443-6447.
- 5. Eichler, A.; Hafner, J., Reaction Channels for the Catalytic Oxidation of CO on Pt(111). *Phys. Rev. B* **1999**, *59* (8), 5960-5967.
- 6. Andreas, E., CO Oxidation on Transition Metal Surfaces: Reaction Rates from First Principles. *Surf. Sci.* **2002**, *498* (3), 314-320.
- 7. Matsushima, T., Angular Distribution of the Desorption of CO₂ Produced on Pt(111) Surface at Low Temperatures. *Surf. Sci.* **1982**, *123* (1), L663-L666.
- Allers, K. H.; Pfnur, H.; Feulner, P.; Menzel, D., Fast Reaction-Products from the Oxidation of CO on Pt(111) - Angular and Velocity Distributions of the CO₂ Product Molecules. J. Chem. Phys. **1994**, 100 (5), 3985-3998.
- 9. Yoshinobu, J.; Kawai, M., Thermal Excitation of Oxygen Species as a Trigger for the CO Oxidation on Pt(111). *J. Chem. Phys.* **1995**, *103* (8), 3220-3229.
- 10. Mieher, W. D.; Ho, W., Bimolecular Surface Photochemistry: Mechanisms of CO oxidation on Pt(111) at 85 K. J. Chem. Phys. **1993**, 99 (11), 9279.
- 11. Matsushima, T., The Mechanism of the CO₂ Formation on Pt(111) and Polycrystalline Surfaces at Low Temperatures. *Surf. Sci.* **1983**, *127* (3), 403-423.
- Deliwala, S.; Finlay, R. J.; Goldman, J. R.; Her, T. H.; Mieher, W. D.; Mazur, E., Surface Femtochemistry of O₂ and CO on Pt(111). *Chem. Phys. Lett.* **1995**, *242* (6), 617-622.
- 13. Yoshinobu, J.; Kawai, M., Surface Matrix Isolation Method for Photoinduced Oxidation of Carbon Monoxide on Pt(111). *J. Mol. Catal. A: Chem.* **1999**, *141* (1–3), 57-61.
- Knudsen, J.; Merte, L. R.; Peng, G.; Vang, R. T.; Resta, A.; Lægsgaard, E.; Andersen, J. N.; Mavrikakis, M.; Besenbacher, F., Low-Temperature CO Oxidation on Ni(111) and on a Au/Ni(111) Surface Alloy. ACS Nano 2010, 4 (8), 4380-4387.
- 15. Lahr, D. L.; Ceyer, S. T., Catalyzed CO Oxidation at 70 K on an Extended Au/Ni Surface Alloy. *J. Am. Chem. Soc.* **2006**, *128* (6), 1800-1801.
- 16. Sueyoshi, T.; Sasaki, T.; Iwasawa, Y., Oxygen Atoms on Cu(100) Formed at 100 K, Active for CO Oxidation and Water–Hydrogen Abstraction, Characterized by HREELS and TPD. J. Phys. Chem. B 1997, 101 (23), 4648-4655.
- 17. Stiehl, J. D.; Kim, T. S.; McClure, S. M.; Mullins, C. B., Reaction of CO with Molecularly Chemisorbed Oxygen on TiO₂-Supported Gold Nanoclusters. *J. Am. Chem. Soc.* **2004**, *126* (42), 13574-13575.

- Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T., Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO₂ Catalyst. *Science* 2011, *333* (6043), 736-739.
- 19. Kao, C.-L.; Carlsson, A.; Madix, R. J., The Adsorption Dynamics of Molecular Carbon Dioxide on Pt(111) and Pd(111). *Surf. Sci.* **2002**, *497* (1–3), 356-372.
- 20. Liu, Z. M.; Zhou, Y.; Solymosi, F.; White, J. M., Spectroscopic Study of K-Induced Activation of CO₂ on Pt(111). *Surf. Sci.* **1991**, *245* (3), 289-304.
- 21. Jones, C. W.; Tao, F.; Garland, M. V., Introduction to Special Issue on Operando and In Situ Studies of Catalysis. *ACS Catal.* **2012**, *2* (11), 2444-2445.
- Ibach, H.; Lehwald, S., Identification of surface radicals by vibration spectroscopy: Reactions of C₂H₂, C₂H₄, and H₂ on Pt (111). *J. Vac. Sci. Technol.* **1978**, *15* (2), 407-415.
- 23. Avery, N. R., Thermal evolution of acetylene adsorbed on platinum(111). *Langmuir* **1988**, *4* (2), 445-448.
- Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A., Temperature-Dependent Rearrangements and Reactions of Acetylene Adsorbed on Pt(111) Monitored in the Range 125-381 K by Sum Frequency Generation. J. Phys. Chem. B 1997, 101 (33), 6474-6478.
- 25. Deng, R. P.; Jones, J.; Trenary, M., Spectroscopic characterization of vinyl formed from acetylene on Pt(111). *J. Phys. Chem. C* **2007**, *111* (3), 1459-1466.
- 26. Zhao, Z.-J.; Moskaleva, L. V.; Aleksandrov, H. A.; Basaran, D.; Rösch, N., Ethylidyne Formation from Ethylene over Pt(111): A Mechanistic Study from First-Principle Calculations. *J. Phys. Chem. C* **2010**, *114* (28), 12190-12201.
- 27. Lu, X.; Liu, L.; Li, Y.; Guo, W.; Zhao, L.; Shan, H., Theoretical Analysis of the Conversion Mechanism of Acetylene to Ethylidyne on Pt(111). *Phys. Chem. Chem. Phys.* **2012**, *14* (16), 5642-5650.
- Kua, J.; Goddard, W. A., Chemisorption of Organics on Platinum. 2. Chemisorption of C₂H_x and CH_x on Pt(111). *J. Phys. Chem. B* 1998, *102* (47), 9492-9500.
- 29. Jacob, T.; Goddard, W. A., Chemisorption of (CH_x and C₂H_y) Hydrocarbons on Pt(111) Clusters and Surfaces from DFT Studies. *J. Phys. Chem. B* **2005**, *109* (1), 297-311.
- 30. Aleksandrov, H. A.; Moskaleva, L. V.; Zhao, Z.-J.; Basaran, D.; Chen, Z.-X.; Mei, D.; Rösch, N., Ethylene conversion to ethylidyne on Pd(111) and Pt(111): A first-principles-based kinetic Monte Carlo study. *J. Catal.* **2012**, *285* (1), 187-195.
- 31. Podkolzin, S. G.; Alcalá, R.; Dumesic, J. A., Density functional theory studies of acetylene hydrogenation on clean, vinylidene- and ethylidyne-covered Pt(111) surfaces. *J. Mol. Catal. A: Chem* **2004**, *218* (2), 217-227.
- 32. Zhao, Z.-J.; Greeley, J. P., Identification of surface intermediates during ethylidyne formation on Pt(111) by calculation of infrared intensities and deuterium isotope shifts. *Surf. Sci.* **2015**, (0).
- Tilekaratne, A.; Simonovis, J. P.; López Fagúndez, M. F.; Ebrahimi, M.; Zaera, F., Operando Studies of the Catalytic Hydrogenation of Ethylene on Pt(111) Single Crystal Surfaces. ACS Catal. 2012, 2 (11), 2259-2268.

- 34. Schennach, R.; Hirschmugl, C.; Gilli, E.; Tysoe, W. T., A New Method for Performing Polarization Modulation Infrared Reflection-Adsorption Spectroscopy of Surfaces. *Appl. Spectrosc.* **2009**, *63* (3), 369-372.
- 35. Land, T. A.; Michely, T.; Behm, R. J.; Hemminger, J. C.; Comsa, G., STM Investigation of Single Layer Graphite Structures Produced on Pt(111) by Hydrocarbon Decomposition. *Surf. Sci.* **1992**, *264* (3), 261-270.
- 36. Deng, R.; Herceg, E.; Trenary, M., Identification and Hydrogenation of C_2 on Pt(111). J. Am. Chem. Soc. **2005**, 127 (50), 17628-17633.
- Jacob, T.; Goddard, W. A., Chemisorption of (CH_x and C₂H_y) Hydrocarbons on Pt(111) Clusters and Surfaces from DFT Studies. *J. Phys. Chem. B* 2004, *109* (1), 297-311.
- 38. Chen, Y.; Vlachos, D. G., Hydrogenation of Ethylene and Dehydrogenation and Hydrogenolysis of Ethane on Pt(111) and Pt(211): A Density Functional Theory Study. *J. Phys. Chem. C* **2010**, *114* (11), 4973-4982.
- 39. Watwe, R. M.; Cortright, R. D.; Nørskov, J. K.; Dumesic, J. A., Theoretical Studies of Stability and Reactivity of C₂ Hydrocarbon Species on Pt Clusters, Pt(111), and Pt(211). *J. Phys. Chem. B* **2000**, *104* (10), 2299-2310.
- 40. Carter, E. A.; Koel, B. E., A Method for Estimating Surface Reaction Energetics: Application to the Mechanism of Ethylene Decomposition on Pt(111). *Surf. Sci.* **1990**, 226 (3), 339-357.
- 41. Brady, R. C.; Pettit, R., Mechanism of the Fischer-Tropsch Reaction. The Chain Propagation Step. J. Am. Chem. Soc. **1981**, *103* (5), 1287-1289.
- 42. Zhou, Y.; Henderson, M. A.; Feng, W. M.; White, J. M., Decomposition of Methyl Iodide on Ru(001). *Surf. Sci.* **1989**, 224 (1–3), 386-406.
- 43. Fairbrother, D. H.; Peng, X. D.; Viswanathan, R.; Stair, P. C.; Trenary, M.; Fan, J., Carbon-Carbon Coupling of Methyl Groups on Pt(111). *Surf. Sci.* **1993**, *285* (1–2), L455-L460.
- 44. Smirnov, M. Y.; Gorodetskii, V. V.; Cholach, A. R.; Zemlyanov, D. Y., Hydrogenation of Isolated Atoms and Small Clusters of Carbon on Pt(111) Surface: HREELS/TDS Studies. *Surf. Sci.* **1994**, *311* (3), 308-321.
- 45. Okada, T.; Kim, Y.; Trenary, M.; Kawai, M., Identification at the Single Molecule Level of C₂H_x Moieties Derived from Acetylene on the Pt(111) Surface. *J. Phys. Chem. C* 2012, *116* (34), 18372-18381.
- 46. Davis, S. M.; Zaera, F.; Gordon, B. E.; Somorjai, G. A., Radiotracer and Thermal Desorption Studies of Dehydrogenation and Atmospheric Hydrogenation of Organic Fragments Obtained from [¹⁴C]Ethylene Chemisorbed Over Pt(111) Surfaces. *J. Catal.* **1985**, *92* (2), 240-246.
- Tilekaratne, A.; Simonovis, J. P.; López Fagúndez, M. F.; Ebrahimi, M.; Zaera, F., Operando Studies of the Catalytic Hydrogenation of Ethylene on Pt(111) Single Crystal Surfaces. ACS Catal. 2012, 2 (11), 2259-2268.
- Ainsworth, M. K.; McCoustra, M. R. S.; Chesters, M. A.; Sheppard, N.; De La Cruz, C., An Infrared Study of Ethene and CO Coadsorption on Pt(111) and a Pt/SiO₂ Catalyst: Ambiguities in the Interpretation of Difference Spectra. *Surf. Sci.* 1999, 437 (1–2), 9-17.
- 49. Chen, P.; Kung, K. Y.; Shen, Y. R.; Somorjai, G. A., Sum Frequency Generation Spectroscopic Study of CO/Ethylene Coadsorption on the Pt(111) Surface and CO Poisoning of Catalytic Ethylene Hydrogenation. *Surf. Sci.* **2001**, *494* (3), 289-297.
- 50. Szanyi, J.; Goodman, D. W., Combined Elevated Pressure Reactor and Ultrahigh Vacuum Surface Analysis System. *Rev. Sci. Instrum.* **1993**, *64* (8), 2350-2352.
- 51. Szammer, J.; Simon-Trompler, E.; Mlinko, S., Synthesis of Bisaramil Labelled with Carbon-14 and Deuterium. *J. Labelled Comp. Radiopharm.* **1994**, *34* (4), 313-321.
- 52. Kim, C. M.; Yi, C. W.; Goodman, D. W., CO–NO and CO–O₂ Interactions on Cu(100) between 25 and 200 K Studied with Infrared Reflection Absorption Spectroscopy. *J. Phys. Chem. B* **2005**, *109* (5), 1891-1895.
- 53. Liao, L. F.; Lien, C. F.; Shieh, D. L.; Chen, M. T.; Lin, J. L., FTIR Study of Adsorption and Photoassisted Oxygen Isotopic Exchange of Carbon Monoxide, Carbon Dioxide, Carbonate, and Formate on TiO₂. J. Phys. Chem. B. 2002, 106 (43), 11240-11245.
- 54. Hayden, B. E.; Bradshaw, A. M., The adsorption of CO on Pt(111) studied by infrared reflection—Absortion spectroscopy. *Surf. Sci.* **1983**, *125* (3), 787-802.
- 55. Szabo, A.; Kiskinova, M.; Yates, J. J. T., Carbon Monoxide--Oxygen Interaction on the Pt(111) Surface: An Electron Stimulated Desorption Ion Angular Distribution (ESDIAD) Study. *J. Chem. Phys.* **1989**, *90* (8), 4604-4612.
- Alavi, A.; Hu, P.; Deutsch, T.; Silvestrelli, P. L.; Hutter, J., CO Oxidation on Pt(111): An Ab Initio Density Functional Theory Study. *Phys. Rev. Lett.* 1998, 80 (16), 3650-3653.
- 57. Bennett, C. J.; Jamieson, C. S.; Kaiser, R. I., Mechanistical Studies on the Formation of Carbon Dioxide in Extraterrestrial Carbon Monoxide Ice Analog Samples. *Phys. Chem. Chem. Phys.* **2009**, *11* (21), 4210-4218.
- 58. Force, E. L.; Bell, A. T., Infrared Spectra of Adsorbed Species Present During the Oxidation of Ethylene Over Silver. *J. Catal.* **1975**, *38* (1–3), 440-460.
- 59. Stuve, E. M.; Madix, R. J.; Sexton, B. A., An EELS Study of CO₂ and CO₃ Adsorbed on Oxygen Covered Ag(110). *Chem. Phys. Lett.* **1982**, *89* (1), 48-53.
- 60. Han, S. J.; Lee, C. W.; Yoon, H.; Kang, H., Discovery of CO₂ Precursor in the Reaction of CO and O on Pt(111). *J. Chem. Phys.* **2002**, *116* (7), 2684-2687.
- 61. Fan, J.; Trenary, M., Symmetry and the Surface Infrared Selection Rule for the Determination of the Structure of Molecules on Metal Surfaces. *Langmuir* **1994**, *10*, 3649-3657.
- 62. Ohtani, T.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K., Suppression of formation of ethylidyne on Pt(111) by reversibly adsorbed di-sigma-bonded ethylene studied by in situ IRAS. *Surf. Sci.* **1998**, *415* (1-2), L983-L987.
- 63. Ohtani, T.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K., In-Situ Observation of Hydrogenation of Ethylene on a Pt(111) Surface under Atmospheric Pressure by Infrared Reflection Absorption Spectroscopy. *J. Phys. Chem. B* **1999**, *103* (22), 4562-4565.
- 64. Godbey, D.; Zaera, F.; Yeates, R.; Somorjai, G. A., Hydrogenation of Chemisorbed Ethylene on Clean, Hydrogen, and Ethylidyne Covered Platinum (111) Crystal Surfaces. *Surf. Sci.* **1986**, *167* (1), 150-166.

- 65. Wiggins, T. A.; Plyler, E. K.; Tidwell, E. D., Infrared Spectrum of Acetylene. *J. Opt. Soc. Am.* **1961**, *51* (11), 1219-1225.
- 66. Herzberg, G., *Infrared and Raman Spectra*. Van Nostrand Reinhold Company: New York, 1945.
- 67. Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A., Ethylene Hydrogenation on Pt(111) Monitored in Situ at High Pressures Using Sum Frequency Generation. *J. Am. Chem. Soc.* **1996**, *118* (12), 2942-2949.
- 68. Zaera, F.; Somorjai, G. A., Hydrogenation of ethylene over platinum (111) singlecrystal surfaces. *J. Am. Chem. Soc.* **1984**, *106* (8), 2288-2293.
- 69. Kubota, J.; Ichihara, S.; Kondo, J. N.; Domen, K.; Hirose, C., π -bonded ethene on Pt(111) surface studied by IRAS. *Surf. Sci.* **1996**, *357-358*, 634-638.
- 70. Kubota, J.; Ichihara, S.; Kondo, J. N.; Domen, K.; Hirose, C., Reversibly Adsorbed π -Bonded Ethene on Pt(111) Surfaces by Infrared Reflection Absorption Spectroscopy. *Langmuir* **1996**, *12* (7), 1926-1927.
- 71. Kubota, J.; Ohtani, T.; Kondo, J. N.; Hirose, C.; Domen, K., IRAS study of π bonded ethylene on a Pt(111) surface in the presence of gaseous ethylene and hydrogen. *Appl. Surf. Sci.* **1997**, *121–122* (0), 548-551.
- 72. Ko, M. K.; Frei, H., Millisecond FT-IR Spectroscopy of Surface Intermediates of C₂H₄ Hydrogenation over Pt/Al₂O₃ Catalyst under Reaction Conditions. *J. Phys. Chem. B* **2004**, *108* (6), 1805-1808.
- Wasylenko, W.; Frei, H., Direct Observation of Surface Ethyl to Ethane Interconversion upon C₂H₄ Hydrogenation over Pt/Al₂O₃ Catalyst by Time-Resolved FT-IR Spectroscopy. *Journal of Physical Chemistry B* 2005, *109* (35), 16873-16878.
- Ormerod, R. M.; Lambert, R. M.; Hoffmann, H.; Zaera, F.; Wang, L. P.; Bennett, D. W.; Tysoe, W. T., Room-Temperature Chemistry of Acetylene on Pd(111): Formation of Vinylidene. *J. Phys. Chem.* 1994, 98 (8), 2134-2138.
- 75. Azad, S.; Kaltchev, M.; Stacchiola, D.; Wu, G.; Tysoe, W. T., On the Reaction Pathway for the Hydrogenation of Acetylene and Vinylidene on Pd(111). *J. Phys. Chem. B* **2000**, *104* (14), 3107-3115.
- Okada, T.; Kim, Y.; Trenary, M.; Kawai, M., Identification at the Single Molecule Level of C₂H_x Moleties Derived from Acetylene on the Pt(111) Surface. *J. Phys. Chem. C* 2012, *116* (34), 18372-18381.
- 77. Yin, J.; Trenary, M.; Meyer, R., Site Switching from Di-sigma Ethylene to pi-Bonded Ethylene in the Presence of Coadsorbed Nitrogen on Pt(111). *J. Phys. Chem. C* **2010**, *114* (28), 12230-12233.
- 78. Stacchiola, D.; Azad, S.; Burkholder, L.; Tysoe, W. T., An Investigation of the Reaction Pathway for Ethylene Hydrogenation on Pd(111). *J. Phys. Chem. B* **2001**, *105* (45), 11233-11239.
- 79. Anson, C. E.; Sheppard, N.; Powell, D. B.; Norton, J. R.; Fischer, W.; Keiter, R. L.; Johnson, B. F. G.; Lewis, J.; Bhattacharrya, A. K., Assignments of the Infrared and Raman Spectra of the Os₂(μ₂-CHCH₃) Group of [(μ₂-CHCH₃)Os₂(CO)₈] and of its d1 and d4 Isotopologs as Models for the Spectra of Such Ethylidene Groups on Metal Surfaces. *J. Am. Chem. Soc.* **1994**, *116* (7), 3058-3062.
- 80. Deng, R. P.; Herceg, E.; Trenary, M., Formation and hydrogenation of ethylidene on the Pt(111) surface. *Surf. Sci.* **2004**, *560* (1-3), L195-L201.

- 81. NIST Chemistry WebBook. http://webbook.nist.gov/chemistry/.
- 82. Newell, H. E.; McCoustra, M. R. S.; Chesters, M. A.; De La Cruz, C., The Thermal Chemistry of Adsorbed Ethyl on the Pt(111) Surface: Infrared Evidence for an Ethylidene Intermediate in the Ethyl to Ethylidyne Conversion. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (24), 3695-3698.
- Krooswyk, J. D.; Waluyo, I.; Trenary, M., Simultaneous Monitoring of Surface and Gas Phase Species during Hydrogenation of Acetylene over Pt(111) by Polarization-Dependent Infrared Spectroscopy. ACS Catal. 2015, 5 (8), 4725-4733.
- 84. Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M., Spectroscopic evidence for a CO–O₂ complex as a precursor to the low temperature oxidation of CO on the Pt(111) surface. *Chem. Phys. Lett.* **2014**, *593* (0), 204-208.
- 85. Davis, S. M.; Gordon, B. E.; Press, M.; Somorjai, G. A., A radiotracer technique for adsorption and catalysis studies: Application to ¹⁴C-benzene chemisorption and rehydrogenation on Pt(111). *J. Vac. Sci. Technol.* **1981**, *19* (2), 231-235.
- Longwitz, S. R.; Schnadt, J.; Vestergaard, E. K.; Vang, R. T.; Lægsgaard, E.; Stensgaard, I.; Brune, H.; Besenbacher, F., High-Coverage Structures of Carbon Monoxide Adsorbed on Pt(111) Studied by High-Pressure Scanning Tunneling Microscopy[†]. J. Phys. Chem. B 2004, 108 (38), 14497-14502.
- 87. Andersen, M.; Johansson, M.; Chorkendorff, I., Isotopic Exchange of CO Adsorbed on Pt(111). J. Phys. Chem. B 2005, 109 (20), 10285-10290.
- 88. McDougall, G.; Yates, H., Thermal Evolution and Hydrogenation of Ethylidyne on Pt(111) Studied by RAIRS. In *Catalysis and Surface Characterization* Royal Society of Chemistry: London, 1992; Vol. Spec. Publ. 114, pp 109-117.
- 89. Deng, R.; Herceg, E.; Trenary, M., Formation and Hydrogenation of Ethylidene on the Pt(111) Surface. *Surf. Sci.* **2004**, *560* (1–3), L195-L201.

Appendix A - Auger Analysis of Niobium Oxide AA.1. Background/Experimental

A niobium oxide sample was provided by Fermilab to be analyzed with the PHI Scanning Auger Microscopy (SAM) 600 System. Niobium is a great material for semiconductors, but is very suspetable to contamination from carbon and oxygen on the surface and bulk of the material. The goal of the project was to determine if the sample was covered in a thick oxide layer and if there were any other contamination, such as carbon adsorbed on the surface. This was achieved by acquiring Auger spectra before and after sputtering the crystal, which showed the oxide layer was easily removed by sputtering. Even after sputtering the sample, the concentration of carbon and oxygen adsorbed on the surface varied greatly.

Base pressure of the system is approximately 5.0×10^{-10} Torr after bakeout. The vacuum pressure is maintained by a large ion pump. Figures A.1 and A.2 show pictures of the chamber and electronics, respectively.



Figure A.1. Picture of the vacuum chamber for the PHI 600 system.



Figure A.2. Picture of the power supplies and various electronic equipment for the PHI 600 system.

The PHI SAM 600 system was upgraded previously with RBD electronics so the data can be acquired with a personal computer. Three different scanning functions can be performed with the system. First, the derivative signal can be acquired for a standard Auger spectrum. After acquiring the Auger spectra and identifying the elements present on the surface, 2D images based on each Auger peak signal called "maps" can also be acquired. The system can also be used for depth profiling, which is the process where the crystal is sputtered with Ar ions while up to three peaks are monitored. The pressure in the chamber remains approximately 10⁻⁸ Torr while sputtering due to the differentially pumped ion gun. Usually a vacuum chamber is backfilled with 10⁻⁵ Torr of argon gas to sputter, which is too high of pressure to acquire Auger spectra. The 10⁻⁸ Torr pressure allows the acquisition of signal composed of Auger electrons.

The niobium sample was provided by Fermilab. Four holes were drilled into the crystal at Fermilab so different parts of the bulk could be analyzed with Auger spectroscopy. Out of the four holes drilled into the Niobium sample; hole 3 was used for the initial surface analysis of the niobium crystal.



Figure A.3. Sketch of niobium sample to depict the location of the Auger scans acquired.

AA.2. Auger Spectra Acquisition Before Sputtering

The three spectra obtained from hole 3 were the following: one scan in the middle of the hole (Figure A.4), one in the groove (Figure A.5), and one to the right of the groove,

(Figure A.6). As shown in the figures, the peak identification and atomic concentration of each element present on the surface is listed.



Figure A.4. Auger spectrum acquired from hole 3.

Near Groove 3 Scan



Figure A.5. Auger spectrum acquired near the groove of hole 3.



Groove 3 Scan

Figure A.6. Auger spectrum acquired of the groove of hole 3.

Each parameter was unchanged between acquisitions except for the position of the crystal. The settings are located in Table II.

	$2.5*10^{-9}$
Pressure of chamber	torr
Beam Voltage	5000 V
Filament Current	1.60 A

Table II. Chamber and instrumental parameters while acquiring Auger spectra.

The atomic concentration corresponding to each spectrum was calculated by applying the formula:

$$C_{X} = \frac{I_{X}}{S_{X} d_{X}} / \sum_{a} \frac{I_{a}}{S_{a} d_{a}}$$

In the equation, I_x , S_x , and d_x represent the peak-to-peak amplitude, relative sensitivity factor, and the correction factor. The maximum and minimum for each peak was acquired for the peak-to-peak intensity. Relative sensitivity factors for carbon and oxygen peaks were obtained from *Handbook of Auger Electron Spectroscopy*. For carbon and oxygen, it was 0.15 and 0.4, respectively. D_x for carbon and oxygen are equivalent, so it cancels out during calculations. Since the niobium peak was not discernable on the spectra collected, it was not included in the analysis. As noted on the spectra, the atomic concentrations of carbon and oxygen differ on the surface of niobium. This is due to contamination on the surface and some parts of the sample are niobium oxide.





Auger Mapping

Figure A.7. Auger maps of carbon and oxygen. The size and magnification were 254 μm and 393x, respectively.

Pressure of chamber	2.2*10 ⁻⁹ torr
Beam Voltage	5000 V
Filament Current	1.60 A

Table III. Chamber and instrumental parameters while mapping the surface.

The Auger maps in Figure A.7 show that sample surface of hole 3 is covered in carbon and oxygen. As shown in the map of oxygen, located around the groove is a different shaded area, which could be niobium oxide.

AA.3. Auger Spectral Acquisition After Sputtering

The niobium sample was sputtered and Auger spectra were acquired for holes 1, 2 and 3. Shown in Figures A.8 to A.13 are the spectra from scans near hole 1, hole 2, and the groove of hole 3 and maps of holes 1, 2 and 3.



Hole 1 Results

Figure A.8. Auger spectrum acquired near hole 1 after sputtering.



Oxygen



Figure A.9. Auger maps of carbon, oxygen and niobium of hole 1 after sputtering. The size and magnification were $254 \mu m$ and 393x, respectively.

On the surface of the niobium sample near hole 1, the carbon and niobium concentrations decreased and increased, respectively as indicated by Figure A.8. As indicated by the

scanning and mapping, there is a high concentration of carbon adsorbed on the surface even after sputtering for 31 cycles (approx. two hours).



Hole 2 Results

Figure A.10. Auger spectrum acquired of hole 2.



Niobium





Oxygen



Figure A.11. Auger maps of carbon, oxygen and niobium of hole 2 after sputtering. The size and magnification were $254 \mu m$ and 393x, respectively.

Hole 3 Results



Figure A.12. Auger spectrum acquired the groove near hole 3.

Carbon

Niobium





Oxygen



Figure A.13. Auger maps of carbon, oxygen and niobium of hole 3 after sputtering. The size and magnification were $254 \mu m$ and 393x, respectively.

In conclusion, as shown by the spectra and maps of each element for holes 1, 2 and 3, the concentration of the niobium on the surface increased as the sample was sputtered. The concentration of each element various significantly across the sample surface as shown in Table IV. Besides oxygen present on the surface, there is a high level of carbon contamination, which could affect binding sites, etc., if experimental studies are performed with the sample. More Auger spectra could be collected and analyzed to provide a more complete picture of the sample surface. The results could also be coupled with results from Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). SEM produces 3D images, while EDS spectra show the concentration of elements in the bulk of the crystal. This project was not pursued further due to budget cuts at Fermilab.

Spectral Scan	% Niobium	% Carbon	% Oxygen
Near hole 1	40.42	50.76	8.822
Hole 2	63.34	25.85	10.81
Groove near hole 3	37.33	32.91	29.75

Table IV. Summary of the concentration of niobium, carbon, and oxygen on different parts of the Niobium crystal surface.

Appendix B - Copyright Permissions





Title:	Spectroscopic evidence for a CO- O2 complex as a precursor to the low temperature oxidation of CO on the Pt(111) surface
Author:	Joel D. Krooswyk,Jun Yin,Amy L. Asunskis,Xiaofeng Hu,Michael Trenary
Publication	Chemical Physics Letters
Publisher:	Elsevier
Date:	11 February 2014
Copyright © 20	14 Elsevier B.V. All rights reserved.

RightsLink



LOCOUT	
LOGOUI	

Logged in as:

Joel Krooswyk

Order Completed

Thank you very much for your order.

This is a License Agreement between Joel Krooswyk ("You") and Elsevier ("Elsevier"). The license consists of your order details, the terms and conditions provided by Elsevier, and the <u>payment terms and</u> <u>conditions</u>.

Get the printable license.

License Number	3745411127587
License date	Nov 10, 2015
Licensed content publisher	Elsevier
Licensed content publication	Chemical Physics Letters
Licensed content title	Spectroscopic evidence for a CO-O2 complex as a precursor to the low temperature oxidation of CO on the Pt(111) surface
Licensed content author	Joel D. Krooswyk, Jun Yin, Amy L. Asunskis, Xiaofeng Hu, Michael Trenary
Licensed content date	11 February 2014
Licensed content volume number	593
Licensed content issue number	n/a
Number of pages	5
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Development of Polarization-Dependent Infrared Spectroscopy for Studies of Catalytic Reactions on Pt(111)
Expected completion date	Dec 2015
Estimated size (number of pages)	110
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD





ACS Publications Title: Simultaneous Monitoring of Surface and Gas Phase Species during hydrogenation of Acetylene over Pt(111) by Polarization-Dependent Infrared Spectroscopy Author: Joel D. Krooswyk, Iradwikanari Wakryo, Michael Trenary Publication: ACS Catalysis Publisher: American Chemical Society Date: Aug 1, 2015 Copyright © 2015, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
 Please print this page for your records and send a copy of it to your publisher/graduate
- school.

 Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

Education	Doctor of Philosophy (PhD) in Physical Chemistry University of Illinois at Chicago, 2015
	Bachelor of Science in Chemistry (BsC) University of Illinois at Chicago, 2010
Publications	 Ren, Y.; Waluyo, I.; Krooswyk, J. D.; Trenary, M. J. Phys. Chem. C 2016, In Preparation. Krooswyk, J. D.; Kruppe, C.; Trenary, M. Surf. Sci. 2016, Accepted. Krooswyk, J. D.; Waluyo, I.; Trenary, M. ACS CATALYSIS. 2015, 5, 4725. Krooswyk, J. D.; Yin, J.; Asunskis, A. L.; Hu, X.; Trenary, M. Chem. Phys. Lett. 2014, 593, 204. Waluyo, I.; Krooswyk, J. D.; Yin, J.; Ren, Y.; Trenary, M. J. Phys. Chem. C 2013, 117, 4666. Yin, J.; Krooswyk, J. D.; Hu, X.; Meyer, R. J.; Trenary, M. J. Phys. Chem. C 2012, 116, 19300. Waluyo, I.; Krooswyk, J. D.; Yin, J.; Ren, Y.; Trenary, M. ChemCatChem 2012, 4, 1075. Krooswyk, J. D.; Tyrakowski, C. M.; Snee, P. T. J. Phys. Chem. C 2010, 114, 21348.
Presentations	Joel Krooswyk, Michael Trenary. "Acetylene Hydrogenation on Pt(111) using PM-RAIRS." Chicago Catalysis Club 2013 Symposium. BP Research Center, Naperville, IL. 7 May 2013. Poster Presentation. Joel Krooswyk, Michael Trenary. "Acetylene Hydrogenation on Pt(111) using PM-RAIRS." American Chemical Society. Indianapolis Convention Center, Indianapolis, IN. 14 September 2013. Poster Presentation. Joel Krooswyk, Michael Trenary. "C ₂ Hydrogenation at Ambient Pressure on Pt(111)." American Vacuum Society Prairie Chapter. Loyola University Chicago, Chicago, IL. 5 September 2014. Poster Presentation.

Joel Krooswyk, Michael Trenary. " C_2 Hydrogenation at Ambient Pressure on Pt(111)." American Vacuum Society. Baltimore Convention Center, Baltimore, MD. 10 November 2014. Oral Presentation.

Professional Memberships

American Chemical Society (ACS) American Vacuum Society (AVS) Chicago Catalysis Club (CCC)