Selective Hydrogenation Reactions on Single Crystal and Bimetallic Surfaces

BY

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THESIS

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This thesis is dedicated to

My mother (Mrs. Mary I. Esan) for all her struggles, prayers, and constant support that has kept me going, even in very dark moments;

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Contribution of Authors

Chapters 1 and 2 in this thesis consist of an introduction to my dissertation, including its significance, and a brief summary of the experimental methods used in my research.

Chapter 3 presents my first project working with a UHV system with Dr. Joel Krooswyk, who introduced me to some of the techniques and tools used in a surface science laboratory. I performed all the experimental work and data analyses presented in this chapter with guidance provided by my advisor Prof. Michael Trenary.

All the experimental work described in Chapter 4 was performed by me with assistance from Dr. Yuan Ren. The deconvolution procedure was developed with assistance from Dr. Xu Feng. Portions of the work are reprinted from a work published in The Journal of Physical Chemistry C (Esan, D. A.; Ren, Y.; Feng, X.; Trenary, M. *J. Phys. Chem. C*, **2017**, 121 (8), pp 4384 – 4392. Copyright © 2017, American Chemical Society). Dr. Xu Feng and Prof. Michael Trenary contributed to writing and editing of the manuscript.

Chapter 5 includes portions of a work published in Physical Chemistry Chemical Physics (Esan, D. A.; Trenary, M.; *Phys. Chem. Chem. Phys.*, **2017**, 19, pp 10870 – 10877) and reproduced with permission from the PCCP Owner Societies. I performed all the experimental work and data analyses and wrote the manuscript with editing assistance from Prof. Michael Trenary.

Chapters 6 and 7 describe work performed on Pt/Ru(001) surfaces. I carried out all the research and data analyses with some valuable discussions with Dr. Xu Feng. Portions of the work have been accepted for publication in Topics in Catalysis A, special issue in honor of Prof. Cynthia Friend. I wrote the manuscript with editing assistance from Prof. Michael Trenary.

Chapter 8 presents the work done on single layer graphene grown on Ru(001), which is presently being prepared for publication. I did all the experimental work with assistance from Mark Muir. Work on the manuscript is ongoing with assistance from Prof. Michael Trenary.

Table of Contents

Cha	pter	Page
1.	Introduction	1
2.	Experimental Methods	5
	2.1 Introduction to Infrared Spectroscopy	5
	2.1.1 Fourier-Transform Infrared (FTIR) Spectroscopy	6
	2.1.2 Reflection Absorption Infrared Spectroscopy (RAIRS)	8
	2.2 Temperature-Programmed Reaction Spectroscopy (TPRS)	12
	2.3 Auger Electron Spectroscopy (AES)	13
	2.4 Low Energy Electron Diffraction (LEED)	16
	2.5 Setup of Ultra High Vacuum (UHV) System	18
3.	Preparation and Ambient-Pressure Hydrogenation of p(2×2)-N on Pt(111)	21
	3.1 Preface	21
	3.2 Introduction	21
	3.3 Experimental	22
	3.4 Results and Discussion	23
	3.4.1 Preparation of $p(2 \times 2)$ -N layer	23
	3.4.2 Hydrogenation of $p(2 \times 2)$ -N layer – RAIRS Results	26
	3.4.3 Hydrogenation of $p(2\times 2)$ -N layer – TPRS Results	29
	3.5 Conclusion	32
4.	Adsorption and Hydrogenation of Acrolein on Ru(001)	33
	4.1 Introduction	33
	4.2 Experimental	36
	4.3 TPRS Results	38
	4.3.1 Acrolein on Ru(001)	38
	4.3.2 Coadsorption of H ₂	40
	4.4 RAIRS Results	43
	4.4.1 Adsorption of Acrolein on Bare and H ₂ -covered Ru(001)	43
	4.4.2 Acrolein Hydrogenation at 160 K	45

	4.4.3	Acrolein Hydrogenation at 250 K	47
	4.5 Discussio	n	50
	4.5.1	Evidence for Propanal	49
	4.5.2	Evidence for 1-Propanol	52
	4.5.3	Implications for Selective Acrolein Hydrogenation	54
	4.6 Conclusio	on	55
5.	Surface Che	mistry of Propanal, 2-Propenol, and 1-Propanol on Ru(001)	56
	5.1 Introducti	on	56
	5.2 TPRS Res	sults	59
	5.2.1	Desorption of 2-Propenol, Propanal, and 1-Propanol	59
	5.2.2	Desorption of Other Species	61
	5.2.3	TPRS Yields	62
	5.3 RAIRS R	esults	63
	5.3.1	2-Propenol	63
	5.3.2	Propanal	65
	5.3.3	1-Propanol	69
	5.4 Discussio	n	71
	5.4.1	2-Propenol TPRS and RAIRS Data	71
	5.4.2	Propanal TPRS and RAIRS Data	73
	5.4.3	1-Propanol TPRS and RAIRS Data	74
	5.5 Conclusio	on	76
6.	Preparation	and Characterization of Pt/Ru(001) Bimetallic Surfaces	78
	6.1 Introducti	on	78
	6.2 Old Evap	orator Design and its Limitations	80
	6.3 Evaporato	or Redesign and Optimization	84
	6.4 Optimizat	tion of Deposition Process – Growth and Characterization of	86
	Varying Plati	num Coverages Using AES, LEED, CO-RAIRS, & CO-TPD	
	6.5 Conclusio	on	91
7. Bime	Selective Hydetallic Surface	drogenation of Acrolein to Propanal on a Pseudomorphic Pt/	Ru(001) 92

7.1 Introduction	92
7.2 Results – Choice of Platinum Coverages	93

7.3 TPRS Results	94
7.3.1 Acrolein and its Hydrogenation Products	95
7.3.2 Other Desorption Products	98
7.4 RAIRS Results	100
7.5 Discussion	103
7.5.1 Comparison of TPRS Results on Pt/Ru(001) with Pt(111) and	
Ru(001) Surface	103
7.5.2 TPRS and RAIRS Results on ~1 ML Pseudomorphic	
Pt/Ru(001) NSA – Deviation From Pt(111) and Ru(001) Surfaces	107
7.5.3 Comparison With Other Bimetallic NSAs	109
7.6 Conclusion	111

8. Surface-Enhanced Infrared Response of Isolated Platinum Nanostructures on Single Layer Graphene (SLG) on Ru(001) 112

8.1 Introduction	112
8.2 Growth of Single Layer Graphene (SLG) on Ru(001)	113
8.3 Fabrication of Isolated Platinum Nanoclusters on SLG/Ru(001) and	
Characterization using AES, CO-RAIRS, and CO-TPD	116
8.4 Pt/SLG/Ru(001) Surface after Temperature-Programmed	
Desorption Experiment	125
8.5 Conclusion	127

9. Conclusion

128

Append	lix	131
A	A1 Deconvolution of TPD/TPRS Data	131
A	A2 Quantification of TPRS Yields	134
A	A3 Cleaning Platinum Layers on Ru(001) Substrate	136
A	A4 Solution to Mass Drift and Mass Bleed Issues in Pfeiffer-Va	acuum QMS 200
C	on Ambient-Pressure Chamber	138
A	A5 Copyright Permissions	141

Cited Literature	142
Vita	148

List of Tables

Table		Page
Table 4.1	Calculated TPRS yields, relative to CO, for varying acrolein and H_2 /acrolein exposures on Ru(001)	42
Table 5.1	Yields in units of $\times 10^{-3}$ ML of the products observed with TPRS following exposure to 2-propenol, propanal, and 1-propanol	62
Table 5.2	Comparison of vibrational assignments for 2-propenol (CH ₂ =CHCH ₂ OH)	65
Table 5.3	Comparison of vibrational assignments for propanal (CH ₃ CH ₂ CHO)	67
Table 5.4	Comparison of vibrational assignments for 1-propanol (CH ₃ CH ₂ CH ₂ OH)	71
Table 7.1	Yields in units of $\times 10^{-3}$ ML of acrolein, CO, and propanal desorbing from the indicated surfaces during TPRS experiments after exposure to 1.0 L of acrolein at 90 K. The yields were calculated as described in Appendix A2	107
Table 8.1	Integrated TPD Area of saturation coverage of CO on different Pt/Ru(001) and Pt/SLG/Ru(001) surfaces and the ML equivalent	121
Table 8.2	RAIR Enhancement Factors (REF) calculated for different Pt/SLG/Ru(001 surfaces relative to Pt/Ru(001) NSAs of similar coverages (as indicated in brackets) and to bare Ru(001)	1) 122
Table A1	Cracking ratios for propanal, 2-propenol, and 1-propanol	132
Table A2	Calculated mass spectrometer correction factors (C)	135

List of Figures

Figure		Page
Figure 2.1	A simple schematic of the Michelson interferometer. The solid line shows the median ray while the dashed lines show the extremes of the collimated beam.	7
Figure 2.2	Constructive (top) and destructive (bottom) interference resulting from electromagnetic waves from fixed (solid line) and moving (dashed) mirrors at different retardation (δ) values.	8
Figure 2.3	Schematic of the components of the electric vector when infrared radiation strikes a metal surface at high incidence (or grazing) angle (θ_I).	ı 9
Figure 2.4	Schematic of the image dipole effect on metal surfaces.	10
Figure 2.5	Sample RAIR spectrum of CO on a Ru(001) surface with (a) a double sided, forward-backward interferogram of a SiC MIR source, (b) single-beam spectrum of background (blue) and sample (black), and (c) double-beam spectrum in transmittance mode obtained from the ratio of sample to background simple-beam spectra using a liquid-nitrogen cooled MCT detector.	11
Figure 2.6	Schematic representation of the KLL Auger process in a solid. In the ground state, the atom is excited by photon or electron impact leading to a hole in the K shell. This hole is filled by an L electron during transition and the excess energy is transferred to another L electron that is then ejected from the atom. The final state is a doubly ionized atom.	14
Figure 2.7	(a) Chamber where most of the work in this thesis was performed, (b) ambient-pressure chamber, with (c) enlarged view of the IR cell, mirror boxes, and IR detector.	18
Figure 2.8	Schematic of the front and back view of the UHV chamber shown in Figure 2.7a. The chamber is equipped with a FTIR spectrometer, AES, QMS, LEED, ion sputtering gun, and a homemade evaporator.	19
Figure 3.1	RAIR spectra of the thermal evolution of $Pt(111)$ exposed to 3.0 L O ₂ and 1.0 L NH ₃ at 85 K. All spectra were collected at 85 K after annealing to the indicated temperatures.	24
Figure 3.2	LEED image of $p(2 \times 2)$ -N atoms on Pt(111) surface at room temperature.	25

Figure 3.3	RAIR spectra of the p(2×2)-N layer exposed to 1.0×10^{-2} Torr H ₂ at 120 K and subsequent annealing to the indicated temperatures for 1 minute.	26
Figure 3.4	RAIR spectra showing the time evolution of the p(2x2)-N layer on Pt(111) exposed to 1.0×10^{-2} Torr H ₂ at 120 K (left) and 1.0×10^{-1} Torr H ₂ at 200 K (right). Each spectrum was taken consecutively every 4 minutes. Inset shows the 1182 and 1527 cm ⁻¹ peaks with a different intensity scale. The FWHM and area of the 3319 cm ⁻¹ peak are all included. All spectra were collected at 260 K.	lso 28
Figure 3.5	TPR spectra of $p(2\times2)$ -N layer on Pt(111) exposed to (left) 1.0×10^{-2} and (right) 1.0×10^{-1} Torr H ₂ at 120 K for 30 mins with a heating rate of 2 K/s. Note the incorrect fragmentation ratio for masses 15, 16, and 17 of ammonia with mass 16 more intense than the parent mass 17. This was due to mass bleeding and mass drifting issues in the mass spectrometer. This issue was later resolved as outlined in Appendix A3.	29
Figure 3.6	TPRS spectra for mass 17 of 0.1 L NH ₃ adsorbed on a clean Pt(111) without (black) and with 40 L H ₂ (red).	out H ₂ 31
Figure 4.1	Possible reaction pathways for acrolein.	34
Figure 4.2	TPR spectra of 0.1 L (left) and 1.0 L (right) acrolein on Ru(001); m/e = 31, 58, 57, 56, 28, and 2 represent 1-propanol, propanal, 2-propenol, acrolein, carbon monoxide, and hydrogen, respectively. Different intensity scales were used for the spectra in the two panels.	39
Figure 4.3	TPR spectra for 1.0 L of acrolein on clean Ru(001). Left panel shows spectra before (dotted lines) and after (solid lines) deconvolution. Right panel shows spectra after deconvolution with an expanded intensity scale. Masses shown are for $m/e = 31$ (1-propanol), 58 (propanal), and 57 (2-propenol).	39
Figure 4.4	Corrected TPR spectra for 0.1 L of acrolein on bare (left) and 10 L H_2 pre-covered (right) Ru(001). Only the hydrogenation products and molecular acrolein desorption spectra are shown.	40
Figure 4.5	Plots of the integrated TPRS areas for (clockwise from top left) propanal, 2-propenol, and 1-propanol against H_2 /acrolein exposures shown in the figure.	41

Figure 4.6	RAIR spectra taken at 90 K of 0.6 L acrolein adsorbed on the bare Ru(001) surface and 1.0 L of acrolein adsorbed on bare and 3.0 L H_2 pre-exposed Ru(001) surface.	44
Figure 4.7	Change in geometry at different coverage regimes. As the coverage increases, the C=O bond tilts away from the surface while the angle between the surface and the C=C bond decreases.	45
Figure 4.8	Left, highest yield TPRS traces of propanal obtained from 1.0 L acrolein on bare (black) and 3.0 L H ₂ (red) pre-exposed Ru(001); and right, RAIR spectra for 1.0 L acrolein taken at 90 K and then annealed to the indicated temperatures for 1 minute. The annealed spectra were obtained at 160 K. Topmost spectrum is for 1.0 L of pure propanal taken at 150 K.	46
Figure 4.9	RAIR spectra of 1.0 L acrolein on a Ru(001) spectra pre-exposed to 3.0 L H_2 taken at 160 K after annealing to the indicated temperatures and held there for 1 minute.	46
Figure 4.10	Left, highest yield TPRS traces of 1-propanol obtained from 1.0 L acrolein on bare (black) and 3.0 L H ₂ (red) pre-exposed Ru(001); and right, RAIR spectra of 1.0 L acrolein taken at 90 K and then annealed to the indicated temperatures for 1 minute. The annealed spectra were obtained at 250 K. Topmost spectrum is for 0.1 L of pure 1-propanol taken at 90 K.	ı 49
Figure 4.11	RAIR spectra of 1.0 L acrolein on a Ru(001) surface pre-exposed to 3.0 L H_2 taken at 250 K after annealing to the indicated temperatures and held there for 1 minute.	49
Figure 4.12	CO TPRS results for 1.0 L acrolein on bare (black) and 3.0 L H_2 precovered (red) Ru(001).	51
Figure 5.1	Deconvoluted TPRS traces for desorption of (clockwise from top left) masses 57, 58, 31, 30, 2, and 28 corresponding to 2-propenol, propanal, 1-propanol, formaldehyde, H_2 , and CO, respectively, from three separate TPRS experiments of 1.0 L of 2-propenol (black lines), 1.0 L of propanal (red lines), and 1.0 L of 1-propanol (blue lines).	60
Figure 5.2	Deconvoluted TPRS trace for propene from 1.0 L of 2-propenol.	62
Figure 5.3	RAIR spectra of 1.0 L of 2-propenol on Ru(001) taken at 90 K after annealing to the indicated temperatures.	64
Figure 5.4	RAIR spectra of 1.0 L of propanal on Ru(001) taken at 90 K after annealing to the indicated temperatures.	66

Figure 5.5	RAIR spectra of 1.0 L of 1-propanol on Ru(001) taken at 90 K after annealing to the indicated temperatures.	70
Figure 5.6	Raw and deconvoluted TPR spectra for masses 57 (2-propenol), 31 (1-propanol), and 58 (propanal) after exposing the Ru(001) surface to 0.2 L of 2-propenol.	72
Figure 5.7	RAIR spectra of 0.1 – 1.0 L propanal at 90 K on clean Ru(001).	76
Figure 5.8	The possible pathways following acrolein hydrogenation on Ru(001).	77
Figure 6.1	Image of the previous evaporator setup showing the (a) power feedthrough and (b) W filament with a Pt wire tightly wrapped around it.	80
Figure 6.2	Auger electron spectra of a clean Ru(001) surface and different Pt/Ru(001 surfaces grown using the old evaporator design. The platinum coverages were estimated from the Pt N ₇ VV peak at 64 eV and the Ru MNN peak at 273 eV as described in the text.) 81
Figure 6.3	Images of (a) infrared pyrometer used to measure filament temperature during deposition and (b) inside the UHV chamber during deposition showing the distance between evaporator and substrate.	83
Figure 6.4	Images of (a) the type C thermocouple feedthrough housed in a stainless steel support ready to be coupled to a UHV linear translator, (b) close-up showing the W filament connected to the insulated Cu electrodes and the thermocouple wires, and (c) view inside the UHV chamber during deposition.	85
Figure 6.5	Evidence of reproducibility. Left, Auger spectra of clean Ru(001) and Pt/Ru(001) surfaces and, right, RAIR spectra of 5.0 L CO taken on those Pt/Ru(001) surfaces.	85
Figure 6.6	Auger spectra of bare Ru(001) and Pt/Ru(001) surfaces with estimated Pt coverages shown in the figure.	86
Figure 6.7	LEED images of clean Ru(001) and selected Pt/Ru(001) surfaces. All images were taken with beam energy of 240 eV at 300 K.	87
Figure 6.8	RAIR spectra taken at 90 K (left) and TPD spectra from 100 to 700 K (right) for different Pt/Ru(001) NSAs each exposed to a saturated CO coverage (5.0 L). The platinum coverages are indicated in the figure. RAIR and TPD spectra from the clean Ru(001) surface are also included for comparison.	88

Figure 6.9	RAIR spectra of saturated CO (5.0 L) coverage on 3.0 MLE Pt/Ru(001) NSA taken at 90 K after annealing to the indicated temperature for 1 minute.	90
Figure 7.1	Deconvoluted TPR spectra for (clockwise from left) acrolein, propanal, 2-propenol, and 1-propanol obtained after exposure of 1.0 L of acrolein to Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K). The acrolein panel contains a spectrum (black) from the clean Ru(001) surface for comparison.	96
Figure 7.2	Deconvoluted TPR spectra for (clockwise from left) acrolein, propanal, 2-propenol, and 1-propanol obtained after exposure of 1.0 L of acrolein to 3.0 L H ₂ pre-covered Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K).	97
Figure 7.3	Deconvoluted TPR spectra for (clockwise from left) CO, H_2 , propylene, and ethylene obtained after exposure of 1.0 L of acrolein to Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K). The CO and H_2 panels contain spectra (black) from the clean Ru (001) surface for comparison.	98
Figure 7.4	Deconvoluted TPR spectra for (clockwise from left) CO, H_2 , propylene, and ethylene obtained after exposure of 1.0 L of acrolein to 3.0 L H_2 pre-covered Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K).	100
Figure 7.5	RAIR spectra taken at 90 K for the indicated exposures of acrolein on 1 ML Pt/Ru(001).	101
Figure 7.6	RAIR spectra of 5.0 L acrolein on 1 ML Pt/Ru(001) surface taken at 90 K after annealing to the indicated temperatures for 1 minute.	102
Figure 7.7	RAIR spectra showing the free CO stretch region only all taken at 90 K. Top two spectra were taken after $1.0 L$ acrolein was exposed to a clean Ru(001) surface at 90 K and annealed to the indicated temperatures. Bottom spectrum was taken after $0.1 L$ CO was exposed to a 1.6 MLE Pt/Ru(001) NSA at 90 K.	110

Figure 8.1	LEED images of epitaxial single layer graphene grown on a Ru(001) substrate. The images were taken at different regions of the Ru(001) surface by moving the sample across the LEED electron gun (with $x = 0.510$ being the center spot). All images were taken with beam energy of 70 eV at 300 K.	114
Figure 8.2	Left, Auger spectra of the clean Ru(001) surface and single layer graphene grown (SLG) on Ru(001) with the ratio of the positive (+ve) to the negative (-ve) portions of the 273 eV peak included. Right, LEED image taken at 300 K after annealing the surface to 600 K for 1 minute.	115
Figure 8.3	TPD spectra of 5.0 L CO (saturation coverage) on (bottom) clean and (top) single layer graphene-covered Ru(001) surface.	116
Figure 8.4	Auger spectra of different Pt/SLG/Ru(001) surfaces with the platinum monolayer equivalent (MLE) coverage indicated on each spectrum.	119
Figure 8.5	RAIR (left) and TPD (right) spectra of saturated (5.0 L) CO on Pt/SLG/Ru(001) with coverages as indicated.	120
Figure 8.6	Left, RAIR spectra taken at 90 K on 0.85 MLE Pt/SLG/Ru(001) (solid line) and 0.87 Pt/Ru(001) (dashed line) at different CO exposures indicated in the figure. Right, TPD spectra of saturated CO exposure (5.0 L) at 90 K on the same surfaces (spectrum from SLG/Ru(001) surface is included for comparison).	124
Figure 8.7	Left, Auger spectra of different SLG/Ru(001) surfaces, as indicated in the figure, showing a reduction in the intensity of the 64 eV Pt peak. All Auger spectra were collected at the same regions on the surface. Right, RAIR spectra of saturated (5.0 L) CO on the Pt/SLG/Ru(001) surfaces shown in the left panel.	125
Figure 8.8	TPD spectra collected after exposing saturated (5.0 L) CO, at 90 K, to 0.30 MLE Pt/SLG/Ru(001) surface. Run 1 spectrum was collected immediately after deposition while Runs 2 and 3 were collected after Runs 1 and 2, respectively. The integrated TPD area for each spectrum is also included.	126
Figure A1	Cracking patterns of (clockwise from top left) acrolein, propanal, 1-propanol, and 2-propenol taken after leaking in 5×10^{-8} Torr of each compound into the chamber. Each plot is an average of over 50 scans.	131
Figure A2	Left, RAIR spectra taken at 90 K after saturated (5.0 L) CO is exposed to the Ru(001) surface after several sputtering cycles as indicated in the	

	figure. The peak/shoulder at 2088 cm ⁻¹ is from platinum atoms remaining on the surface. Right, RAIR spectrum of 5.0 L CO on clean Ru(001) with a single, sharp peak at 2056 cm ⁻¹ with over 4% intensity and no shoulder due to platinum or any other contaminants on the surface.	136
Figure A3	Auger spectra (left) and LEED image (right) of a clean Ru(001) surface. Both were collected at room temperature with beam energy of 70 eV for the LEED image.	137
Figure A4	Data collected in 2009, with the Pfeiffer-Vacuum QMS 200, showing the incorrect fragmentation pattern for pure ammonia gas. The correct fragmentation pattern taken from the NIST Chemistry WebBook is shown and is reproduced with permission.	138
Figure A5	Mass fragmentation pattern of pure ammonia gas collected after the mass bleed and mass drift problems in the Pfeiffer-Vacuum QMS 200 were resolved. The intensity ratios are now in agreement with the values from the NIST WebBook shown in Figure A4.	139

List of Abbreviations

AES	Auger electron spectroscopy
CHA	Concentric hemispherical analyzer
СМА	Cylindrical mirror analyzer
DFT	Density functional theory
FTIR	Fourier-transform infrared
FWHM	Full width at half maximum
HREELS	High resolution electron energy loss spectroscopy
IR	Infrared
IRAS	Infrared reflection absorption spectroscopy
IRRS	Infrared reflection spectroscopy
L	Langmuir (1 L = 1×10^{-6} Torr \cdot s)
LEED	Low energy electron diffraction
МСТ	Mercury-cadmium-telluride (HgCdTe)
ML	Monolayer
MLE	Monolayer equivalent
NSA	Near surface alloy
PD	Polarization dependent
PM	Polarization modulated
QMS	Quadrupole mass spectrometer
RAIRS	Reflection absorption infrared spectroscopy

REF	RAIR enhancement factor
RFA	Retarding field analyzer
SAA	Single atom alloy
SFG	Sum frequency generation
SLG	Single layer graphene
STM	Scanning tunneling microscopy
TPD	Temperature-programmed desorption
TPRS	Temperature-programmed reaction spectroscopy
UHV	Ultra-high vacuum
XPS	X-ray photoelectron spectroscopy

Summary

Over the last few decades, surface science studies have proven important in understanding the chemistry involved in many heterogeneous catalytic reactions and in the design of better catalysts. Recently, such studies have been conducted on model systems under ambient pressure conditions to facilitate the reconciliation of the insights from surface science and industrial catalysis.

Here, different selective hydrogenation reactions on single metal and bimetallic surfaces have been studied using a combination of common surface science techniques including RAIRS, TPRS, AES, and LEED. On Pt(111), a $p(2\times2)$ -N layer was grown by oxydehydrogenation of ammonia, and the resulting nitrogen layer was hydrogenated to NH, NH₂, and NH₃ under ambient pressures of hydrogen. This result was in contrast to what was observed under UHV conditions where hydrogenation did not proceed beyond NH formation.

Under UHV conditions, it was shown that acrolein adsorbs on the Ru(001) surface at 90 K, mostly via the C=O bond, and completely decomposes to CO around 460 K at low coverages. With increasing coverage, adsorption via the C=C bond predominates with most of the acrolein either desorbing molecularly or decomposing to CO, H_2 , and surface carbon. Also, a small amount of acrolein self-hydrogenates to yield 2-propenol, propanal, and 1-propanol with propanal being the major product. Furthermore, it was found that the low yield of 2-propenol might be due to its isomerization, on the surface, to propanal around 180 K before it desorbs molecularly at 200 K. While propanal does not isomerize to 2-propenol on the Ru(001) surface, it seems to undergo a reversible hydrogenation-dehydrogenation reaction with 1-propanol around 200 to 320 K.

Summary (continued)

These acrolein adsorption and hydrogenation reactions were further studied on wellcharacterized Pt/Ru(001) bimetallic surfaces to investigate the possibility of enhanced selectivity on the Ru(001) surface due to the presence of the platinum atoms. The Pt/Ru(001) bimetallic surfaces were prepared using a homemade evaporator and a fully optimized physical vapor deposition process. It was shown that the 1 ML pseudomorphic Pt/Ru(001) surface can hydrogenate acrolein to propanal with 100% selectivity, whereas other Pt/Ru(001) surfaces at submonolayer or multilayer coverages display no hydrogenation activity. However, all the Pt/Ru(001) surfaces were shown to readily reduce acrolein to propylene around 130 K with higher temperature (> 300 K) propylene desorption observed for surfaces with higher platinum coverages. The presence of even a small amount of platinum was found to completely alter the catalytic properties of the Ru(001) substrate, and at coverages above 3 ML, the Pt/Ru(001) surface behaved effectively like Pt(111). However, the 1 ML Pt/Ru(001) surface displayed properties that are distinct from those of Pt(111) or Ru(001). Additionally, isolated platinum nanoclusters deposited on a single layer of epitaxial graphene grown on Ru(001) were found to exhibit an infrared enhancement effect with up to a 4-fold increase in the infrared response.

The results in this thesis present examples of novel properties and reactions that can be seen at ambient pressure conditions and on well-defined bimetallic surfaces that contribute to the understanding of similar processes in real catalytic systems.

1. Introduction

In the design of better heterogeneous catalysts, understanding the key principles governing the activity and selectivity of a catalyst is desirable. However, industrial catalysts are often solids consisting of a mixture of different components interacting to yield very complex morphologies. Furthermore, the operating conditions for industrial catalysts often involve high temperatures and pressures at which different chemistries, including new adsorbate structures and interactions, might come into play. Thus, a thorough investigation and understanding of the physico-chemical phenomena involved on the surface of industrial catalysts during a reaction can be very difficult to achieve.

Whereas earlier surface science studies focused on well-defined single crystal surfaces including stepped and defect-rich surfaces under ultra-high vacuum (UHV) conditions, the results obtained are often difficult to correlate with industrial catalytic processes. This discrepancy between real catalysis and surface science studies is commonly referred to as the *material and pressure gaps*. To narrow these gaps and facilitate a better understanding of real catalytic systems, modern surface science has seen increased focus on studies of model systems that mimic, as much as possible, the catalytic systems of interest using surface-sensitive techniques operating under comparable reaction conditions. The earlier studies on single crystal surfaces have been enhanced by studies of model systems such as: supported metal catalysts using oxide single crystals or thin oxide films as support materials, and bimetallic systems consisting of two catalytically active metals or a catalytically active metal dispersed in the surface layer of a noble metal host. These model systems incorporate some of the complexities of industrial catalytic systems, including particle size effects and adsorbate-support interactions, but are still well-defined enough to facilitate their study using surface science techniques. Furthermore,

techniques that can be operated at pressures above UHV conditions have also been developed, such as high-pressure scanning tunneling microscopy (HP-STM), high-pressure X-ray photoelectron spectroscopy (HP-XPS), sum frequency generation (SFG), and polarization-modulation or polarization-dependent infrared spectroscopy (PM-RAIRS or PD-RAIRS).¹⁻³ The last two techniques, SFG and PD-RAIRS, are vibrational spectroscopies but the latter has some advantages including shorter acquisition times, a wider spectral range, and a relatively cheaper operating cost. This technique, PD-RAIRS, is used in our group to study different reaction systems at ambient pressure conditions.

In this thesis, some of the work done to bridge both the pressure and material gaps will be presented albeit with more emphasis on the latter. Standard surface science techniques including reflection absorption infrared spectroscopy (RAIRS), temperature programmed reaction spectroscopy (TPRS), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED) have been utilized to study different reactions, especially selective hydrogenation reactions, on Pt(111), Ru(001), Pt/Ru(001) surfaces. On Pt(111), the growth and ambientpressure hydrogenation of a p(2x2) nitrogen layer to form ammonia was investigated. Previous works from our group have shown that a p(2x2)-N layer can be prepared from ammonia either by electron-induced dissociation⁴ followed by annealing to 450 K or from a reaction with preadsorbed molecular oxygen at 85 K followed by a 400 K anneal.⁵ These studies also show that the hydrogenation of the p(2x2)-N layer, in UHV, does not proceed beyond the formation of the NH species. However, since all the steps in the sequential addition of H atoms to N atoms to form NH₃ are in equilibrium,⁶ pushing the reaction beyond NH might be facilitated by an increase in the hydrogen pressure. This hypothesis was tested by exposing the nitrogen atoms to higher pressures of hydrogen in the ambient-pressure chamber. On Ru(001) and Pt/Ru(001), the selective hydrogenation of acrolein, the smallest α , β -unsaturated aldehyde, was studied extensively. The aim was to observe the partial hydrogenation of the C=O bond to form the unsaturated alcohol, an important process in the fine chemicals and pharmaceutical industries.⁷⁻⁹ The reaction was studied on the Ru(001) surface to investigate its activity and selectivity for the unsaturated alcohol. Thereafter, several Pt/Ru(001) near surface alloys (NSAs) were prepared and thoroughly characterized using AES, LEED, CO-TPD, and CO-TPRS. Based on the higher hydrogenation activity of Pt relative to Ru and the unique properties of bimetallic surfaces,^{10, 11} the acrolein hydrogenation reaction was also investigated on Pt/Ru(001) NSAs. In addition, the growth and characterization of graphene on Ru(001) was studied with LEED, AES, CO-RAIRS, and CO-TPD to verify the formation of a single layer graphene (SLG). Thereafter, isolated platinum nanoclusters were fabricated on the SLG/Ru(001) surface and studied with CO-RAIRS for possible enhancement of the IR intensity by utilizing the plasmonic properties of the platinum nanoclusters.

Chapter 2 begins with a brief introduction to the fundamentals of vibrational spectroscopy, especially Fourier-transform infrared spectroscopy, and then focuses on reflection absorption infrared spectroscopy (RAIRS), which is one of the main techniques employed in the works presented here. The fundamentals of the other techniques used, including temperature programmed reaction spectroscopy (TPRS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) are also briefly discussed followed by descriptions of the experimental setups and the design of the evaporator used in the platinum deposition experiments. More specific experimental methods used in a particular experiment, presented in a given chapter, are described in an "Experimental" section for that chapter. Chapter 3 presents the results obtained from the growth and ambient-pressure hydrogenation of a p(2x2)-N layer on

Pt(111). The RAIRS and TPRS results that point to the possible formation of ammonia at ambient hydrogen pressures are also discussed. In chapter 4, the results obtained from the adsorption and hydrogenation of acrolein on Ru(001) are presented. The need for deconvolution of TPR spectra by collecting the fragmentation pattern of the corresponding pure compounds and the evidence for the formation of propanal and 1-propanol will be discussed in detail. Chapter 5 continues the work from the previous chapter but focuses on the surface chemistry of the acrolein hydrogenation compounds, namely propanal, 2-propenol, and 1-propanol. Isomerization between these compounds and a detailed discussion of their RAIR spectra are presented. The preparation and characterization of Pt/Ru(001) bimetallic surfaces using the combination of AES, LEED, CO-TPD, and CO-TPRS are dealt with in chapter 6. These well-characterized Pt/Ru(001) surfaces were then used to study the acrolein hydrogenation reaction, and the results are presented in Chapter 7. In Chapter 8, the fabrication of isolated platinum nanoclusters on single layer graphene grown on Ru(001), and the observation of an enhanced infrared response on these nanoclusters will be discussed. Chapter 9 is the conclusion that summarizes the main results from all the work presented in this thesis and provides an outlook. The Appendix contains information on the deconvolution of TPRS data, cleaning of platinum layers from the Ru(001) substrate, and a procedure to prevent "mass drift" and "mass bleed" problems in the Pfeiffer Vacuum QMS 200.

2. Experimental Methods

2.1 Introduction to Infrared Spectroscopy

Vibrational spectroscopy is one of the most powerful and important tools available to gather information about the molecular adsorbates that form on metal surfaces. There are different vibrational spectroscopic techniques available, including but not limited to infrared, Raman, and high-resolution electron energy loss spectroscopies. Of these, infrared (IR) spectroscopy is probably the most suitable to study catalytically relevant adsorbate-surface interactions, especially since the advent of Fourier-transform infrared spectroscopy (FTIR). This is due to its relatively higher resolution ($< 0.1 \text{ cm}^{-1}$ is now possible), high sensitivity (typically 0.1% of a CO monolayer is detectable), and usability on a variety of surfaces (from single crystals to bimetallic surfaces and complex real catalysts) both under ultra-high vacuum (UHV) and ambient pressure conditions. The principle of infrared spectroscopy is based on the vibrational transitions in molecules caused by absorption of infrared radiation. This infrared radiation can be divided into three regions: $13000 - 4000 \text{ cm}^{-1}$ (Near IR or NIR), $4000 - 200 \text{ cm}^{-1}$ (Mid IR or MIR), and $200 - 200 \text{ cm}^{-1}$ 10 cm⁻¹ (Far IR or FIR). All spectra contained in this thesis were collected in the MIR region, specifically from 4000 - 800 cm⁻¹. The information contained in the resultant spectra is related to the chemical nature of the adsorbate molecules and the adsorbate-substrate and adsorbateadsorbate interactions. Information from IR spectra often requires complementary information from other techniques so as to provide a more complete understanding of the system under consideration.

2.1.1 Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier-transform infrared spectrometers were developed in the mid-twentieth century to replace diffraction grating-based spectrometers. They were based on the Michelson interferometer which splits an incoming beam of radiation into two paths and then recombines them after a path difference has been introduced, resulting in an *interference*. The variation in the intensity of the emergent beam is thus measured as a function of the path difference, or retardation (δ), by a detector. Figure 2.1 shows a simple form of the Michelson interferometer. It consists of two mutually perpendicular mirrors – one fixed and the other able to move along its perpendicular plane axis. Bisecting the two mirrors is a *beamsplitter* that partially transmits a collimated beam of radiation from an external source to the moving mirror (at point B) and partially reflects the beam to the fixed mirror (at point A). When the beams return to the beamsplitter, they *interfere* before being partially reflected (towards the source) and partially transmitted (towards the sample before reaching the detector). Because of this *interference*, the intensity of each beam returning to the source or passing through the sample to the detector depends on the retardation (δ) between the beams in the two arms of the interferometer.



Figure 2.1 A simple schematic of the Michelson interferometer. The solid line shows the median ray while the dashed lines show the extremes of the collimated beam

When the optical path difference is zero or an integer multiple of the wavelength, that is $\delta = 0$ or $n\lambda$, the two beams are in phase upon recombination at the beamsplitter resulting in *constructive interference*. Thus, all the incident radiation passes through the beamsplitter to the sample and then the detector. However, if the retardation equals an integer multiple of one-half the wavelength, that is $\delta = n\lambda/2$, the two beams are out of phase on recombination at the beamsplitter resulting in *destructive interference*, whereby all the incident radiation returns to the source and none passes through the sample (see Figure 2.2). If the mirror is moved at a constant velocity, the signal at the detector will be seen to vary sinusoidally. The modulated (ac) component of this sinusoid is referred to as the *interferogram*. In practice, the amplitude of the interferogram is proportional to the intensity of the source, beamsplitter efficiency, varying response of the detector at different wavenumbers, and detector amplifier characteristics.

Constructive Interference



Figure 2.2 Constructive (top) and destructive (bottom) interference resulting from electromagnetic waves from fixed (solid line) and moving (dashed) mirrors at different retardation (δ) values

The advantages of FTIR spectrometry over dispersive spectrometry include the (a) *multiplex or Felgett's advantage* which is a result of the fact that the spectral information from all wavelengths can be measured simultaneously, (b) *throughput or Jacquinot's advantage* arising from that fact that more radiation can be passed between the source and the detector for each resolution element resulting in a higher signal-to-noise ratio for a given resolution and wavelength, and (c) *the wavelength accuracy or Connes' advantage* which arises from the fact that the wavelength scale is calibrated by a laser beam of known wavelength (often HeNe laser) passing through the interferometer instead of the mechanical movements of diffraction gratings thus creating a more stable and accurate measurement.

2.1.2 Reflection Absorption Infrared Spectroscopy (RAIRS)

One of the most powerful surface vibrational spectroscopic techniques is reflection absorption infrared spectroscopy (RAIRS) which also goes by the acronyms IRRS (IR reflection spectroscopy) and IRAS (IR reflection absorption spectroscopy). A RAIR spectrum is a vibrational spectrum of a molecule chemisorbed or physisorbed on a surface, often a metal surface, and contains information about the identity, structure, and orientation of the adsorbed species. Since metals are not transparent to infrared radiation, reflection mode as opposed to transmission mode is involved in this technique. Also, as a result of the relatively low IR intensities used, the interaction with the adsorbate layer is linear in the electric field, and for the most part, a RAIR spectrum can be compared with the conventional absorption spectrum of the same molecule.¹²

In RAIRS, infrared radiation is reflected off a metal surface and passes through an adsorbate layer. The intensity of the reflected light is related to phase shift, δ . Upon reflection, the intensity of s-polarized light (electric field direction is perpendicular to the plane of incidence) is almost cancelled by reflection at grazing incidence whereas for p-polarized light (electric field direction is parallel to the plane of incidence), it is almost doubled at grazing incidence (until very grazing situations). As a consequence, at high incidence angle, only the p-polarized component of the radiation can be reflected from the surface (see Figure 2.3).



Figure 2.3 Schematic of the components of the electric vector when infrared radiation strikes a metal surface at high incidence (or grazing) angle (θ_I)

Thus, only vibrations with component dynamic dipole moment aligned perpendicular to the plane of the surface can interact with the (p-polarized) radiation. This is referred to as the *surface selection rule*. In the language of group theory, it means a vibrational state can be accessed by an electric dipole transition from the ground vibrational state if the upper state belongs to the same irreducible representation as the surface normal. This can also be seen clearly from the *image effect* shown in Figure 2.4 which arises due to the fact that when a molecule is adsorbed on a substrate, the molecule induces *opposite image charges* in the substrate and the total dipole moment can either be zero or doubled depending on the orientation of the dipole on the surface.



Figure 2.4 Schematic of the image dipole effect on metal surfaces

The RAIR spectrum, also called the differential reflectance spectrum, can thus be represented mathematically as shown in equation 2.1:

$$\frac{\Delta R_p}{R_p^0} = \frac{R_p^0 - R_p}{R_p^0}$$
(2.1)

where R_p and R_p^0 are the p-polarized reflectance with and without the adsorbate respectively. The relationship between *reflectance* (*R* or ρ ,) which is the fraction of incident radiant power reflected from a surface, *absorptance* (α) which is the ratio of the *absorbed to the incident* radiant power, and *transmittance* (τ) which is the ratio of the transmitted to the incident radiant power, is given by:¹³

$$\rho + \alpha + \tau = 1 \tag{2.2}$$

It is instructive to quickly highlight the difference between *absorptance (a)* and *absorbance (A)*. Whereas the former is as defined above, the latter is the common logarithm of the ratio of the *incident to the transmitted* radiant power through a sample. Since *absorptance* (hence, also reflectance) is proportional to the square of the electric field intensity¹⁴ (E²) and the area of surface sampled increases as $1/\cos\theta_I$, the sensitivity of RAIRS increases as $E^2/\cos\theta_I$. From the work of Greenler^{15, 16} and Chesters¹⁷, the optimum angle of incidence (θ_I) for most metal surfaces is $85 \pm 3^\circ$.



Figure 2.5 Sample RAIR spectrum of CO on a Ru(001) surface with (a) a double sided, forwardbackward interferogram of a SiC MIR source, (b) single-beam spectrum of background (blue) and sample (black), and (c) double-beam spectrum in transmittance mode obtained from the ratio of sample to background simple-beam spectra using a liquid-nitrogen cooled MCT detector

A typical interferogram from a broadband MIR source (globar or SiC) is shown in Figure 2.5a. It contains information over the entire MIR region to which the detector (usually a photoconductive MCT detector) is responsive. A Fourier transformation converts the interferogram (a time domain spectrum showing intensity against retardation within the mirror scan) to the final IR spectrum (the more familiar frequency domain spectrum showing intensity against frequency). Unlike double-beam grating spectrometers, most FTIR spectrometers are single-beam instruments and thus do not obtain transmittance or absorbance IR spectra in real time. Instead a background single-beam spectrum, which takes account of the combined performance of the source, interferometer, detector, and any other contributions along the optical path, is first collected as shown in Figure 2.5b (blue line). Next, a single-beam sample spectrum is collected (Figure 2.5b, black line) which contains information from the sample and the background spectrum (Figure 2.5b, black line) results in a "double-beam" spectrum of the sample shown in Figure 2.5c.

2.2 Temperature-Programmed (Desorption) Reaction Spectroscopy (TPD or TPRS)

Temperature-programmed reaction spectroscopy, also known as temperature-programmed desorption, is another UHV technique that provides information that is often complementary to that obtained from RAIRS. It is based on the fact that adsorbed particles will desorb from a surface at different temperatures due to differences in energetics (activation energy) and kinetics (order and rate constant) of the desorption reaction. The process involves the exposure of molecules to a clean substrate, under vacuum, at low temperature. After adsorption, the surface is heated up by ramping the temperature at a constant rate while the desorbing species are monitored by a quadruple mass spectrometer (QMS). The resulting pressure versus time (which

12

can be converted to temperature) curve is referred to as a "desorption spectrum".¹⁸ In our lab, the temperature (measured with a K-type thermocouple spot-welded to the substrate) is ramped using a programmable temperature controller and the output voltage from the controller is then used as auxiliary input into the QMS while the latter is simultaneously collecting the pressure for a given mass of the species of interest. However, due to some limitations to the input voltage values acceptable by the Hiden HAL201/3F QMS, a "×10 gain" is applied to the output voltages from the temperature controller before they are inputted into the QMS. The resulting voltages, which are linear in time, can then be converted to temperature using the NIST temperature-voltage table for a K-type thermocouple.¹⁹ The desorption spectrum provides valuable information, including the identity of the desorbing species, their coverage, the adsorption sites present on a surface, the difference between physisorbed, chemisorbed, and condensed species, and the nature of the reaction occurring on the surface (when applicable). Other information that can be deduced from desorption spectra include the order of the desorption reaction and the activation energy of desorption.

2.3 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy, named after Pierre Auger, is another common surface analytical technique that can provide elemental composition and quantitative information about all elements in the periodic table except H and He.²⁰ It is based on the emission of low kinetic energy electrons (10 - 2000 eV) from atoms with a hole in their inner shell during the deexcitation process. Since the mean free path of electrons in solids is on the order of a few atomic distances, the low kinetic energy of the Auger electron is thus the main reason for the surface sensitivity of this technique. Also, because of the dependence of this kinetic energy on the

binding energy of the electrons in the shells of the excited atom, it carries chemical information including the elemental composition and sometimes the oxidation states of the species.

Various methods have been used to generate the inner hole but the most common is electron or photon impact with energies of about 1 - 20 keV. The hole generated in one of the inner shells (K) of the excited atom is filled by an electron from an outer shell (V), and the energy involved in that process can either be released in the form of an emitted photon (fluorescence transition) or it can be transferred to another electron in an outer shell (V), which is then ejected from the atom. This ejected electron is called an *Auger electron*, as shown in Figure 2.6 for the KLL transition.



Figure 2.6 Schematic representation of the KLL Auger process in a solid. In the ground state, the atom is excited by photon or electron impact leading to a hole in the K shell. This hole is filled by an L electron during transition and the excess energy is transferred to another L electron that is then ejected from the atom. The final state is a doubly ionized atom

Thus, the kinetic energy of the Auger electron is given by:

$$E_{kin} = E_K - E_V - E_V \tag{2.3}$$

Since E_{kin} only depends on the energy of the three energy levels involved, and each element has a unique binding energy, each element has a characteristic pattern of Auger emission lines.

For the Auger process, the energy of the excitation source does not influence the kinetic energy of the ejected electron. Thus, for an X-ray excitation source, varying the primary energy is an easy way to distinguish between photoelectron and Auger electron signals since the energy of photoelectrons depend on the excitation energy (this is useful in X-ray photoelectron spectroscopy, XPS, where both photoelectrons and Auger electrons are present in the XPS spectrum).

The emitted Auger electrons are characterized by their energy and intensity thus, the task of an Auger analyzer-detector system is to distinguish between electrons of different energies and to convert the incoming electrons into a signal that is proportional to the number of electrons. The two main types used are the retarding field analyzer (RFA) and the cylindrical mirror analyzer (CMA). The concentric hemispherical analyzer (CHA) is also used in systems that combine XPS and AES. For both the RFA and the CMA, it is necessary to differentiate the response signal to get the first derivative of the Auger spectrum so as to enhance the Auger signal from the noisy background electrons. This is achieved by using a computer or by modulating the detector voltage and using a phase-sensitive amplifier. In the RFA, the response signal has to be differentiated twice by phase-sensitive detection of twice the modulation frequency (2ω) , whereas in the CMA, the response signal is differentiated once by phase-sensitive detection of the fundamental frequency (ω). This essentially means that while the RFA acts as a high-pass filter the CMA can be seen as a band-pass filter. Thus, the shot noise in a CMA is drastically reduced compared to a RFA by a factor of ~ 100 .²⁰ A disadvantage of the CMA is its sensitivity to the sample position, but its good signal-to-noise ratio, better resolution, and comparable

transmittance favors it over the RFA for most applications.²¹ A CMA analyzer was used to obtain all the AES data presented here.

Equation (2.3) has to be corrected to account for the work function of the analyzer, ϕ_A :

$$E_{kin} = E_X - E_Y - E_Z - \phi_A \tag{2.4}$$

While AES has a lot of advantages and a very good surface sensitivity of 0.4 - 2 nm depth (or 0.1 - 1% of a monolayer with a CMA), it has a few disadvantages including the possibility of surface damage especially to adsorbates, induced chemistry in sensitive materials from the large electron flux, and difficulty working with insulating samples (charging problems).

2.4 Low Energy Electron Diffraction (LEED)

Low energy electron diffraction (LEED) is another useful surface sensitive technique in UHV studies. It is used to check the crystallographic quality of a surface by allowing relatively low kinetic energy electrons (20 - 250 eV) to impinge on the surface at a 90° incident angle. These energies correspond, as shown in equation 2.5, to electrons with de-Broglie wavelengths of 2.74 - 0.77 Å, which are of the same order of magnitude as interatomic distances.

de Broglie wavelength, $\lambda = h/mV$

For an electron, $\lambda = h/mV = \sqrt{150/E_e}$ where λ is in Å and E_e is in eV

For
$$E_e = 20 - 250 \text{ eV}$$
, then $\lambda = \sqrt{150/E_e} = 2.74 - 0.77 \text{ Å}$

(2.5)
At these low energies, the electrons interact strongly with the surface atoms resulting in an inelastic mean free path of only a few Å. Thus, the diffraction signal arises predominantly from the topmost layer. The direction of these diffracted electron beams can be obtained using the Ewald construction method. However, an approach using a 2D lattice analogous to an optical grating will suffice to a first approximation as follows:

Constructive interference, i.e. enhancement of intensity, only occurs in certain direction according to Bragg's equation:

$$n\lambda = a \sin\theta$$

where θ is the constructive interference angle and d is the lattice constant. For a 2D lattice, scattering conditions have to be fulfilled in both directions. Thus, if the lattice constant(s) a_1 (or a_2) increase, the scattering angle for the corresponding beam h (or k) decreases. This is the basis of the real and the *reciprocal* lattice space. For real space vectors \hat{a}_i and \hat{a}_j there is a corresponding and mutually perpendicular reciprocal space vector \hat{a}_i^* and \hat{a}_j^* , respectively. If the angle between \hat{a}_i and \hat{a}_i^* is φ , then the relationship between the real and reciprocal space vectors is given by:

$$\hat{a}_i^* = \frac{1}{(\hat{a}_i \sin \varphi)} \text{ and } \hat{a}_j^* = \frac{1}{(\hat{a}_j \sin \varphi)}$$
(2.7)

Thus, the observed 2D LEED pattern is a representation of the reciprocal lattice space of the real space structure. A retarding field analyzer equipped with a phosphor screen is used to detect the diffracted electrons. Thus, as elastic electrons with the appropriate energy pass through the grids

in the RFA they strike the screen and light is emitted at that spot. The relative positions of these spots on the phosphor screen show the crystallographic structure of the surface. These diffracted spots also move and increase in number as the energy of the incident electrons is increased. Also, the presence of adsorbates on the surface can result in overlayer structures (superstructures) with relatively more complex LEED patterns.

Quantitative information can also be obtained from LEED data by comparing the measured intensity of each diffraction spot as a function of the incident electron energy (dynamic I-V curve analysis) and with theoretical calculations based on the assumption of a particular model.²²

2.5 Setup of Ultra High Vacuum (UHV) system

All the experimental results in this thesis were collected from two chambers, with most of the work performed in the chamber shown in Figure 2.7a. My introduction to UHV studies and first project utilized the ambient-pressure chamber (Figures 2.7b and c) described elsewhere.²³



Figure 2.7 (a) Chamber where most of the work in this thesis was performed, (b) ambientpressure chamber, with (c) enlarged view of the IR cell, mirror boxes, and IR detector

The two chambers are similar in design, with the main difference being the addition of an ambient-pressure IR cell to the latter. The schematic of the chamber is shown in Figure 2.8. The setup of the chamber has been described elserwhere in detail.^{24, 25} Briefly it is a 24 liter UHV stainless steel chamber pumped by a turbomolecular pump (Leybold-Heraeus TMP 360 CSV, 345 liter/s) which is backed by a dual-stage mechanical pump (Leybold Trivac D2A, 1.5 L/s). After a 48 h bakeout at 150 – 200 °C, the base pressure typically reaches 1×10^{-10} Torr as monitored by a Bayard-Alpert nude ion gauge (Granville-Phillips, series 274).



Figure 2.8 Schematic of the front and back view of the UHV chamber shown in Figure 2.7a. The chamber is equipped with a FTIR spectrometer, AES, QMS, LEED, ion sputtering gun, and a homemade evaporator

The chamber is equipped with a Bruker IFS 66v/S FTIR spectrometer for RAIRS measuremnts, a PHI 10-155 cylindrical mirror analyzer for AES, PHI 15-120 optics for LEED, a Hiden HAL201/3F quadrupole mass spectrometer (QMS) for TPRS, and a homemade evaporator for physical vapor deposition. The gas manifold is pumped by a small turbomolecular pump (Leybold-Heraeus TMP 50, 50 L/s) backed by a dual-stage mechanical pump (Leybold Trivac D2A, 1.5 L/s). The pressure of the manifold is monitored by a thermocouple gauge and is kept at 1×10^{-3} Torr.

A disc-shaped Pt(111) single crystal, 14 mm in diameter and ~1 mm in thickness, was used in the ambient-pressure experiments while a rectangular-shaped Ru(001) single crystal, 16×12 mm, was used for all the other experiments. Both crystals can be liquid-nitrogen cooled to 85 K as measured with a K-type thermocouple spot-welded to the top of the crystals to monitor the temperature. The Pt(111) crystal can be resistively heated to 1200 K, whereas the Ru(001) crystal can be resistively heated to only 900 K. For temperatures above 900 K (up to 1500 K), a thoriated tungsten filament mounted behind the crystal was used for electron beam heating with the crystal under a 600 V positive bias.

3. Preparation and Ambient-Pressure Hydrogenation of p(2×2)-N on Pt(111)

3.1 Preface

The work presented in this chapter served as my introduction to working with an ultra-high vacuum chamber. Gas handling, chamber maintenance, proper sample preparation, troubleshooting and resolution of issues with analytical tools, and data analysis, processing, and presentation were all part of the skills and techniques I learnt and developed working on this project. However, due to time constraints and scheduling issues, the project was not completed but the data collected and what is required to complete the project are presented below.

3.2 Introduction

The Haber-Bosch process, whereby nitrogen is hydrogenated to form ammonia, is one of the most important catalytic processes. While iron-based catalysts are mostly used in industry for this reaction,²⁶ other metals have also shown some promise with ruthenium²⁷ shown to have relatively higher activity. Furthermore, the kinetics of this reaction and the properties of atomic nitrogen on several metal surfaces have been studied extensively.²⁸⁻³⁰ One of these surfaces is platinum which is used as a catalyst in the reduction of NO_x in automotive exhaust and in nitric oxide synthesis via the catalytic oxidation of ammonia.⁵ Thus, understanding the properties of atomic nitrogen, including its hydrogenation activity, on platinum surfaces is relevant to several industrial processes.

For the nitrogen hydrogenation reaction, it is believed that the elementary steps involved are similar on most metal surfaces.⁶ On Fe surfaces these have been shown to be:

Step 1
$$N_2 \rightarrow 2N(ads)$$
,

Step 2 $H_2 \leftrightarrows 2H(ads),$ Step 3 $N(ads) + H(ads) \leftrightarrows NH(ads),$ Step 4 $NH(ads) + H(ads) \leftrightarrows NH_2(ads),$ Step 5 $NH_2(ads) + H(ads) \leftrightarrows NH_3(ads),$ Step 6 $NH_3(ads) \leftrightarrows NH_3(g)$

where (ads) refers to an adsorbed state. In addition, the first step has been shown to be the ratedetermining step while the other reaction steps are in equilibrium.³¹

Our group has previously prepared a $p(2\times2)$ overlayer of atomic nitrogen on Pt(111) by the electron-induced dissociation⁴ of ammonia followed by annealing to 450 K and by the oxydehydrogenation⁵ of ammonia at 400 K with the latter process found to yield a higher coverage of nitrogen atoms. These N atoms in the $p(2\times2)$ -N layer were found to readily hydrogenate to NH but there was no evidence for the formation of NH₂ or NH₃ with hydrogen exposures up to 160 L.⁵ This means that the reaction does not proceed beyond step 3. However, since steps 3 – 6 are in equilibrium, increased hydrogen pressure (and thus, higher H coverage) should, in principle, push the reaction beyond NH to yield NH₃, the complete hydrogenation product. This hypothesis was tested by studying the reaction using the ambient-pressure system where pressures of up to 10 Torr can be readily achieved.

3.3 Experimental

As mentioned, the experiments were performed in the ambient-pressure system consisting of a UHV chamber with a base pressure of 2×10^{-10} Torr coupled to an IR cell with a base pressure of 5×10^{-10} Torr, and both can be isolated from each other during experiments via a gate valve. The Pt(111) crystal was cleaned by Ar⁺ ion sputtering at room temperature (1.0 kV, 5.0 μ A, 10

minutes), followed by annealing to 1200 K for 5 minutes and then exposing the surface to 2×10^{-7} Torr of O₂ for 1 hour at 850 K. Afterwards, the sample is further annealed to 1200 K for 2 minutes to desorb any remaining O₂ and ensure a well-ordered surface. AES and LEED images collected at room temperature were used to confirm that the surface is clean and well-ordered. All the gas exposures are in Langmuir (1 L = 1×10^{-6} Torr \cdot s).

RAIR spectra between 800 to 4000 cm⁻¹ were obtained using p-polarized light and a MCT detector cooled with liquid nitrogen. Each spectrum was obtained with 1024 scans and a resolution of 4 cm⁻¹. For the TPRS experiments, a heating rate of 2 K/s was used as the temperature was ramped from 300 to 1000 K. Ammonia (99.99%, Matheson) and oxygen (99.998%, Matheson) were purified by several freeze-pump-thaw cycles and their purity checked with a mass spectrometer prior to use. Hydrogen (99.999%, Matheson) was used as supplied.

3.4 Results and Discussion

3.4.1 Preparation of p(2×2)-N layer

A $p(2\times2)$ -N layer was prepared by oxydehydrogenation of ammonia following the recipe developed by Herceg and coworkers,⁵ but using relatively higher gas exposures. As shown in Figure 3.1, exposing the clean Pt(111) surface to 3.0 L of O₂, at 85 K, leads to a peak at 874 cm⁻¹ that can be readily assigned to the v(O-O) of molecular oxygen.³² Exposing this surface to 1.0 L NH₃ results in the development of new features with the disappearance of the 874 cm⁻¹ peak suggesting that the O₂ coverage has been reduced beyond the RAIRS detection limit. These peaks match those observed by Herceg and coworkers⁵ and thus the reader is referred to their work for extensive discussions about the peak assignments.



Figure 3.1 RAIR spectra of the thermal evolution of Pt(111) exposed to 3.0 L O₂ and 1.0 L NH₃ at 85 K. All spectra were collected at 85 K after annealing to the indicated temperatures Annealing the surface to 200 K results in the disappearance of most of the peaks except the ammonia symmetric deformation mode at 1236 cm⁻¹ with a shoulder at 1174 cm⁻¹. This disappearance can be attributed to desorption and reaction with coadsorbed oxygen. At 250 K, there seems to be an intensity transfer between the $\delta_s(NH_3)$ modes with a more intense peak at 1186 cm⁻¹ and a smaller peak at 1227 cm⁻¹. A peak at 3319 cm⁻¹ corresponding to v(NH) can also be seen. As temperature is increased, the $\delta_s(NH_3)$ modes are blueshifted to 1198 and 1230 cm⁻¹ respectively with increasing intensity except for the latter. After annealing to 380 K, there is a huge diminution in the intensity of the $\delta_s(NH_3)$ peaks with the noticeable increase in the intensity

of the NH stretch peak at 3319 cm⁻¹. In agreement with Herceg and coworkers⁵, annealing above this temperature results in the dissociation of the NH species to form surface N atoms in a $p(2\times 2)$ pattern as shown in the LEED image in Figure 3.2



Figure 3.2 LEED image of $p(2 \times 2)$ -N atoms on Pt(111) surface at room temperature



3.4.2 Hydrogenation of p(2×2)-N layer – RAIRS Results

Figure 3.3 RAIR spectra of the p(2×2)-N layer exposed to 1.0×10^{-2} Torr H₂ at 120 K and subsequent annealing to the indicated temperatures for 1 minute

To minimize contamination and/or interference from molecular ammonia during the hydrogenation experiments, the $p(2\times2)$ -N layer was prepared in the main chamber with the gate valve to the IR cell closed. Afterwards, the chamber is evacuated before the sample is transferred to the IR cell for the RAIRS experiments.

The p(2×2)-N layer was exposed to 1.0×10^{-2} Torr of H₂ at 120 K followed by annealing, for 1 minute, to the different temperatures shown in Figure 3.3. Prior to the exposure of H₂, a background spectrum was collected at 120 K and all subsequent spectra were taken at this temperature

As seen in Figure 3.3 after exposing the nitrogen atoms to 1.0×10^{-2} Torr of hydrogen at 120 K. a peak at 3321 cm⁻¹ which can be readily assigned to the v(NH) mode of NH(ads), appeared immediately. Annealing this surface to 230 K, for 1 minute, results in an increase in the intensity of this peak with the appearance of another peak at 1188 cm⁻¹. This latter peak can be readily assigned to the symmetric deformation (umbrella) mode of ammonia. Further annealing to higher temperatures results in increase in the intensities of both peaks and the appearance of another peak at 1527 cm⁻¹ around 250 K, which can either be assigned to the asymmetric or degenerate deformation mode³³ of ammonia or the δ_s (HNH) mode³⁴⁻³⁶ of adsorbed NH₂. An HREELS study by Sun et al.³⁶ on Pt(111) assigned a loss observed at 1555 cm⁻¹ to the δ_s (HNH) mode of NH₂ which suggests that the 1527 cm⁻¹ mode is more likely coming from adsorbed NH₂. In agreement with the argument of Bassignana and coworkers³⁴ in their HREELS work on Ni(110), the intensity of the NH peak relative to the two other peaks preclude the definite assignment of these peaks to the same species. Thus, it is very likely that the surface is composed of a mixture of NH, NH₂, and possibly NH₃ since the frequencies of ammonia molecular fragments are very sensitive to their chemical environments.³³ The intensity of these peaks is at its highest after annealing to 260 K. Above this temperature, there is a decrease in the peak intensities with the simultaneous disappearance of the 1527 cm⁻¹ peak (most likely below the RAIRS detection limit).



Figure 3.4 RAIR spectra showing the time evolution of the p(2x2)-N layer on Pt(111) exposed to 1.0×10^{-2} Torr H₂ at 120 K (left) and 1.0×10^{-1} Torr H₂ at 200 K (right). Each spectrum was taken consecutively after every 4 minutes. Inset shows the 1182 and 1527 cm⁻¹ peaks with a different intensity scale. The FWHM and area of the 3319 cm⁻¹ peak are also included. All spectra were collected at 260 K

To further understand how the surface species changes over time, the experiment was repeated with the surface kept at 260 K (since this is the temperature at which the peaks were the most intense). The three peaks at 1182, 1527, and 3319 cm⁻¹ can be seen in the spectra (left panel) shown in Figure 3.4 with similar intensities to those in Figure 3.3. The positive peak observed around 1182 cm⁻¹ after 16 minutes suggests that the species responsible for that peak has been displaced into the gas phase. This observation supports the initial suggestion that these three peaks arise from different species on the surface and this is further buttressed by increasing the hydrogen pressure to 1.0×10^{-1} Torr, in a separate experiment. As seen in the right panel of Figure 3.4, the increased pressure has no appreciable effect on the peak positions of the 1527 and 3319 cm⁻¹ but, again, there is a positive peak around 1182 cm⁻¹. However, the peak area for the 3319 cm⁻¹ peak changes with increased H₂ pressure. At 0.01 Torr of H₂, the peak area increases

with time from 1.4×10^{-2} to of 3.8×10^{-2} after 16 minutes whereas at a higher hydrogen pressure (0.1 Torr), the peak area stays constant around 3.8×10^{-2} before decreasing to 3.2×10^{-2} after 16 minutes. This can be attributed to partial desorption into the gas phase at these relatively higher pressures. These values are higher than the value of 2.6×10^{-2} observed by Herceg et al.⁴ after exposing the nitrogen layer to 20 L H₂ under UHV conditions. Also, the FWHM values for this peak show that they are narrower than the FWHM of 11.2 - 12.8 observed by Herceg et al.⁴ in their work on the reversible hydrogenation of surface N atoms to NH on Pt(111) in UHV. This suggests that even under much higher hydrogen pressures, the NH species on surface are in a relatively more ordered environment.



3.4.3 Hydrogenation of p(2×2)-N layer – TPRS Results

Figure 3.5 TPR spectra of $p(2\times2)$ -N layer on Pt(111) exposed to (left) 1.0×10^{-2} and (right) 1.0 $\times 10^{-1}$ Torr H₂ at 120 K for 30 mins with a heating rate of 2 K/s. Note the incorrect fragmentation ratio for masses 15, 16, and 17 of ammonia with mass 16 more intense than the parent mass 17. This was due to mass bleeding and mass drifting issues in the mass spectrometer. This issue was later resolved as outlined in Appendix A3

Several TPRS experiments were also conducted to verify the RAIRS results. To avoid contamination/interference from molecular ammonia during the TPRS experiments in the UHV chamber, the opposite approach to that used in the RAIRS experiments was employed in preparing the $p(2\times2)$ -N layer. Here, the $p(2\times2)$ -N layer was prepared in the IR cell, with the cell isolated from the UHV chamber with the aid of three differentially pumped sliding seals, after which the cell was evacuated to remove any unreacted O₂ and NH₃. The $p(2\times2)$ -N layer was then exposed to different amounts of H₂ (1.0×10^{-2} and 1.0×10^{-1} Torr H₂) at 120 K for 30 minutes after which the IR cell was evacuated before the sample was slowly moved up to the main chamber where TPR spectra from ~300 to 800 K were collected as shown in Figure 3.5. Masses 2, 17, and 28 were monitored to follow the desorption of H₂, NH₃, and CO/N₂ respectively. Masses 15 and 16 were also monitored to further follow NH₃ desorption, while masses 12 and 14 were monitored to distinguish between CO desorption from the background and the desorption of N₂ from NH₃ decomposition and from unreacted N atoms.

 NH_3 is very sticky, thus the low temperature NH_3 desorption (masses = 15, 16, and 17) around 300 K in both panels is likely due to desorption of molecular NH_3 adsorbed on the sample holder and manipulator at 85 K from the oxydehydrogenation reaction. However, the ammonia peak centered around 470 K is from the hydrogenation of N atoms on the surface. The relatively high desorption temperature might be due to the effect of the excess hydrogen. That is, as seen in the H_2 and NH_3 peaks in Figure 3.5, ammonia desorption begins only after all of the H_2 has desorbed. The slight bump around 470 K in the H_2 desorption trace is clearly from the fragmentation of NH_3 in the ionizer of the mass spectrometer. As shown in Figure 3.6, a similar peak centered around 470 K was also observed in a separate TPRS experiment where a Pt(111) surface precovered with 0.1 L NH_3 was exposed to 40 L H_2 . This peak was absent when the

experiment was repeated without H_2 co-adsorption. N_2 desorption from ammonia decomposition and/or unreacted N atoms peaks at 514 K while the peak at 450 K for masses 12 and 28 are from the desorption of CO adsorbed from the background.



Figure 3.6 TPRS spectra for mass 17 of 0.1 L NH₃ adsorbed on a clean Pt(111) without H₂ (black) and with 40 L H₂ (red)

The observation of NH₃ formation from the TPRS and RAIRS results contradicts previous results by Herceg et al.^{4, 5} where they showed that, in UHV, hydrogenation of the N atoms of Pt(111) does not proceed beyond NH formation. However, in their experiments, the p(2x2)-N layer was either exposed to H₂ at 300 K and the surface annealed to 380 K, or the H₂ was exposed at 380 K before the surface was cooled to 80 K where the spectra were collected. Here, the H₂ exposure was done at 80 – 200 K depending on the hydrogen pressure. This difference in

the temperature at which the surface was exposed to H_2 seems important with regards to having sufficient amount of H atoms on the surface such that the equilibrium,

Step 4
$$NH(ads) + H(ads) \leftrightarrows NH_2(ads),$$

is pushed to the right. That is, the relatively higher temperature for H_2 exposure in their work precludes the formation of sufficient amounts of $NH_2(ads)$ since most of the H atoms would have desorbed at those temperatures (see TPRS trace for mass 2 in Figure 3.5). Thus, the formation of copious amounts of $NH_2(ads)$ on the surface seems to be the most important step in the formation of ammonia from surface N atoms on Pt(111). This can be achieved by using higher H_2 pressures (using an ambient-pressure cell) and exposing H_2 at lower temperatures.

3.5 Conclusion

A p(2x2) layer of N atoms has been successfully prepared by the oxydehydrogenation of ammonia. Using RAIRS and TPRS, the N atoms in the p(2x2) layer were shown to be readily hydrogenated to NH, NH₂, and then NH₃ at hydrogen pressures of up to 1.0×10^{-1} Torr. The TPRS results suggest that NH₃ desorption is delayed by the desorption of unreacted hydrogen atoms resulting in a relatively high NH₃ peak desorption temperature of 470 K. Further experiments, using AES, TPRS and CO-RAIRS, to estimate the coverage of N atoms in the p(2x2) layer and the amount of unreacted N atoms after hydrogenation are necessary.

4. Adsorption and hydrogenation of acrolein on Ru (001)

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• <u>Dominic A. Esan</u>, Yuan Ren, Xu Feng, and Michael Trenary, Adsorption and hydrogenation of acrolein on Ru(001), *J. Phys. Chem. C.*, **2017**, 121 (8), pp 4384 – 4392

4.1 Introduction

The partial hydrogenation of α , β -unsaturated aldehydes is an important step in several synthetic industrial processes, especially in the fine chemicals and pharmaceutical industries.^{7,8,9} Generally, it has been established that the thermodynamics of the catalytic hydrogenation of α , β unsaturated aldehydes favor the formation of saturated aldehydes via hydrogenation of the C=C bond, while the manipulation of the kinetics of the process may yield the desired unsaturated alcohol product via the hydrogenation of the carbonyl bond.^{37,38}

Several studies have reported the hydrogenation of these α , β -unsaturated aldehydes with the goal of forming the unsaturated alcohol.^{39,40,41,42} Most of these studies have been on acrolein (CH₂=CH–CHO), the simplest α , β -unsaturated aldehyde. As shown in Figure 1 below, there are different pathways open to the acrolein molecule following thermal activation on the surface. It can undergo partial hydrogenation to form propanal via hydrogenation of the C=C bond, or 2-propenol via hydrogenation of the C=O bond and complete hydrogenation to the saturated alcohol (1-propanol). It can also follow the decarbonylation pathway to yield CO and ethylene, and the latter can further decompose to produce surface carbon and hydrogen.



Figure 4.1. Possible reaction pathways for acrolein

De Jesus and Zaera^{40, 43} have studied the surface chemistry of acrolein on Pt(111) using temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). Their results show that acrolein mostly decomposes to carbon monoxide (CO), hydrogen (H₂), and surface carbon with the simultaneous formation of small amounts of ethylene, propylene, and ketene, but no hydrogenation products were reported. Similar results were obtained by Brown and Barteau on Rh(111).⁴⁴ Murillo and Chen⁴² used TPD and high resolution electron energy loss spectroscopy (HREELS) to show that, on a multilayer Ni(111) film on Pt(111), acrolein yields mostly propanal following thermal activation with very slight traces of 2-propenol, but 1-propanol was completely absent. On Ag(111), Brandt et al.³⁹ observed the formation of all three hydrogenation products when acrolein was co-adsorbed with hydrogen. Using X-ray photoelectron spectroscopy, near edge X-ray absorption spectroscopy, and TPD, they also observed that the coverage of the coadsorbed hydrogen affected the product distribution with the unsaturated alcohol (2-propenol) desorbing at low hydrogen coverages while the saturated alcohol desorbs at high hydrogen coverages. This was attributed to the orientation of the C=C bond of 2-propenol, which is almost parallel to the surface at high hydrogen coverages and thus undergoes hydrogenation to the saturated alcohol. Davis and Barteau⁴⁵ reported a combined TPD and HREELS study where the thermal activation of acrolein

on Pd(111) follows the decarbonylation pathway to yield mostly ethylene and CO with small amounts of propanal and surface carbon. However, Dostert et al.⁴⁶ in a combined pulsed molecular beam and in-situ RAIRS study of acrolein hydrogenation on Pd(111) under isothermal conditions, showed that the formation of 2-propenol with nearly 100% selectivity was possible. This, however, requires the presence of an overlayer of a spectator oxopropyl species formed from the addition of one H atom to the C=C bond of acrolein.

All these possible reaction pathways have been generally interpreted to depend on the initial acrolein adsorption geometry,^{42,40,44} and the changes in those geometries with increasing temperature.^{45,46} This interpretation has also been supported by several theoretical studies on different metal surfaces^{47,48,49,50} where the initial adsorption geometry was shown to influence the reaction pathway of the adsorbed acrolein and the resulting product distribution. On Pt(111),⁴⁷ density functional theory (DFT) and HREELS was used to show that the initial adsorption geometry consisted of a mixed phase of η_3 -cis (C,C,O) and η_4 -trans (C,C,C,O) structures at low coverages, whereas a mixed η_2 -cis and η_2 -trans geometry where the adsorption is only by the C=C bond occurs at higher coverages. Loffreda et al.⁴⁸ used DFT calculations to show that the product selectivity in acrolein hydrogenation on Pt(111) is controlled by the balance between the hydrogenation of the C=O bond to yield 2-propenol is favored, but desorption of the C=O bond-containing-hydrogenation product, propanal, is much easier. Thus, the kinetics of the reaction controls the selectivity.

Other groups have tried to use bimetallic catalysts to manipulate the kinetics of the reaction to form 2-propenol. Murillo et al.⁵¹ showed that the selectivity and activity for the formation of 2-

propenol from acrolein was enhanced on the subsurface Pt-Ni-Pt(111) system, with similar results reported for the subsurface Pt-Co-Pt(111) system.⁵²

Platinum and ruthenium have long been suggested as suitable catalysts for the selective hydrogenation of α , β -unsaturated aldehydes with the latter having a lower cost but comparable catalytic properties.^{53,54} However, to the best of our knowledge, there have been no prior studies of acrolein hydrogenation on the Ru(001) surface. Our aim is to establish the behavior of acrolein on the bare, and hydrogen-covered, Ru(001) surface and to determine the extent to which it can react to form the three possible hydrogenation products – propanal, 2-propenol, and 1-propanol – using both TPRS and RAIRS to estimate the yields of these products.

4.2 Experimental

The experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr described earlier (Chapter 2.5). The chamber is equipped with a PHI 10-155 cylindrical mirror analyzer for Auger electron spectroscopy (AES), PHI 15-120 optics for lowenergy electron diffraction (LEED), and a Hiden HAL201/3F quadrupole mass spectrometer for temperature-programmed reaction spectroscopy (TPRS). The chamber is coupled to a Bruker IFS-66v/S Fourier-transform infrared (FTIR) spectrometer for RAIRS measurements. The incident and reflected IR beams enter and exit the UHV chamber through differentially pumped, O-ring-sealed KBr windows.

The rectangular (15×10 mm) Ru(001) crystal had a thickness of 1.5 mm and was purchased from Princeton Scientific, Corp. with a specified orientation of less than 0.1° degree from the (001) plane and was polished to a roughness of less than 0.1 micron. The mounting of the Ru(001) single crystal has been described elsewhere.⁵⁵ The crystal was cleaned by Ar⁺ ion

sputtering and annealing to 1500 K, followed by a second Ar^+ ion sputtering and annealing to 850 K. The surface order and cleanliness were verified with LEED and AES. Because the C KLL Auger peak overlaps with the Ru MNN peak at 273 eV, TPRS was also used to check and quantify small amounts of carbon contamination that cannot be detected by AES; the absence of a recombinative CO desorption peak between 500 and 600 K after O₂ exposure indicates the absence of surface carbon. Further verification of the cleanliness of the surface is done by taking a RAIR spectrum of a saturated CO layer; a sharp and intense single peak at ~2056 cm⁻¹ confirms the cleanliness of the surface.

Acrolein (96%, stabilized with hydroquinone, Alfa Aesar), 2-propenol (\geq 99%, Aldrich Chemistry), propanal (\geq 99%, Acros organics), and 1-propanol (\geq 99.5%, Sigma Aldrich) were all purified, prior to use, by successive freeze-pump-thaw cycles and their purity was checked in situ by mass spectrometry. Hydrogen (99.999%, Specialty Gases of America) was used as supplied.

RAIR spectra between from 800 to 4000 cm⁻¹ were obtained using a liquid nitrogen (LN₂)cooled MCT (HgCdTe) detector and a SiC IR source. Each spectrum was obtained with 1024 scans and 4 cm⁻¹ resolution. A linear heating rate of 2 K/s was used for the TPRS experiments and the temperature was ramped from about 100 to 600 K. Desorption of hydrogen (H₂), carbon monoxide (CO), acrolein (CH₂=CHCH=O), propanal (CH₃CH₂CH=O), 2-propenol (CH₂=CHCH₂OH), and 1 propanol (CH₃CH₂CH₂OH) were monitored at m/e 2, 28, 56, 58, 57, and 31, respectively. Prior to each experiment, the clean Ru(001) surface was flash annealed to 600 K after cooling below 160 K, and then allowed to cool to 90 K before gas exposures.

4.3 TPRS Results

4.3.1 Acrolein on Ru(001)

The clean Ru(001) surface at 90 K was exposed to 0.1 to 1.0 L of acrolein, and the temperature was ramped linearly at 2 K/s from 100 to 600 K. From the TPR spectra in Figure 4.2 for the 0.1 L exposure, the decarbonylation pathway dominates resulting in desorption of only H₂ and CO. For the 1.0 L exposure, molecular desorption of acrolein at 172 K accompanies decarbonylation. Furthermore, some of the acrolein also self-hydrogenates to yield all possible hydrogenation products – propanal (m/e = 58), 2-propenol (m/e = 57), and 1-propanol (m/e = 31). This pattern was also observed for acrolein exposures of 0.2 L and above. However, to remove extraneous contributions to the TPRS traces, they were deconvoluted by subtracting contributions to a particular mass in proportion to the relative intensities of the different masses in the cracking pattern of a given molecule. The details of the deconvolution procedure, including the cracking patterns for each molecule, are included in Appendix A1.

Following deconvolution, the TPRS traces can be confidently attributed to each hydrogenation product as shown in Figure 4.3, with peak desorption temperatures at ~183, 208, and 290 K corresponding to propanal, 2-propenol, and 1-propanol, respectively.



Figure 4.2 TPR spectra of 0.1 L (left) and 1.0 L (right) acrolein on Ru(001); m/e = 31, 58, 57, 56, 28, and 2 represent 1-propanol, propanal, 2-propenol, acrolein, carbon monoxide, and hydrogen, respectively. Different intensity scales were used for the spectra in the two panels



Figure 4.3 TPR spectra for 1.0 L of acrolein on clean Ru(001). Left panel shows spectra before (dotted lines) and after (solid lines) deconvolution. Right panel shows spectra after deconvolution with an expanded intensity scale. Masses shown are for m/e = 31 (1-propanol), 58 (propanal), and 57 (2-propenol)

4.3.2 Coadsorption of H₂



Figure 4.4 Corrected TPR spectra for 0.1 L of acrolein on bare (left) and 10 L H_2 pre-covered (right) Ru(001). Only the hydrogenation products and molecular acrolein desorption spectra are shown

The effect of coadsorbed H_2 on the reaction was observed by exposing varying amounts of acrolein to a Ru(001) surface pre-exposed to 10.0 L of H_2 . This effect is most evident at low exposures as shown in Figure 4.4 where the bare (left) and hydrogen pre-exposed (right) Ru(001) surface were exposed to 0.1 L of acrolein. At low coverage, acrolein decomposes completely to CO on the bare Ru(001) surface with no detectable desorption of acrolein or any of the hydrogenation products. This suggests that the decarbonylation and decomposition pathways dominate. However, on the 10.0 L H_2 pre-exposed surface, molecular desorption and hydrogenation also occur along with the production of CO. This indicates that the presence of hydrogen on the surface increases the yield of the hydrogenation products. This same effect of H_2 pre-exposure was observed for acrolein exposures of 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and for 1.0 L.

The yield of each of the hydrogenation products varies with the amount of H_2 pre-exposure, as shown in Figure 4.5 where the integrated TPRS areas for each hydrogenation product are plotted against the H₂/acrolein exposures. The yields, as represented by the integrated TPRS areas, for both the 0.4 and 1.0 L acrolein exposures are effectively saturated for a H₂ pre-exposure of 2.0 L for propanal and 2-propenol, while the 1-propanol yield is saturated after 3.0 L H₂ exposure.



Figure 4.5 Plots of the integrated TPRS areas for (clockwise from top left) propanal, 2-propenol, and 1-propanol against H_2 /acrolein exposures shown in the figure

Ru (001) surface			TPRS yield ($\times 10^{-3}$ ML)		
H ₂ exposure (L)	acrolein exposure (L)	initial coverage (\times 10 ⁻³ ML) with CH ₂ CHCHO (acrolein)	CH ₃ CH ₂ CHO (propanal)	CH ₂ CHCH ₂ OH (2-propenol)	CH ₃ CH ₂ CH ₂ OH (1-propanol)
-	0.1	123	0	0	0
10.0		102	2.25	0.20	0.13
-	0.2	197	1.67	0	0.22
10.0		104	7.60	0.41	0.30
-	0.3	169	1.98	0	0.095
10.0		111	10.1	0.48	0.35
-	0.4	209	2.98	0	0.14
2.0		115	12.8	0.92	0.53
3.0		109	11.5	0.61	1.04
5.0		105	9.65	0.49	0.30
10.0		121	11.7	0.74	0.46
-	0.6	253	6.79	0.23	0.20
10.0		137	14.3	0.87	0.52
-	0.8	266	7.28	0.25	0.27
10.0		152	14.0	0.65	0.47
-	1.0	273	6.84	0.37	0.32
2.0		156	18.3	1.04	0.79
3.0		180	18.0	0.98	2.36
5.0		157	12.9	0.71	0.40
10.0		166	12.8	0.70	0.44

Table 4.1 Calculated TPRS yields, relative to CO, for varying acrolein and H_2 /acrolein exposures on Ru(001)

NB: The relatively high initial acrolein coverage obtained for the 0.2 L acrolein exposure is attributed to an excess amount of CO in the chamber during that TPRS run

Table 4.1 lists the TPRS yields for different acrolein and H_2 /acrolein systems, relative to CO, for each hydrogenation product and for the molecularly desorbed acrolein. The yields were calculated, as described in Appendix A2, following the empirical method developed by Ko et al.⁵⁶ The TPRS yield of the hydrogenated products calculated here is defined in relation to the *high temperature CO TPRS peak as a whole* since it's difficult to separate the contributions to this peak coming from each individual species (acrolein, propanal, 2-propenol, and 1-propanol). While the yields of each product generally increase with increasing acrolein exposure, the yields do not show a simple monotonic variation with hydrogen exposure, suggesting a complex interplay between various reaction channels.

4.4 **RAIRS Results**

To gain further insights into the TPRS results, RAIRS experiments were carried out on both the bare and H_2 pre-exposed Ru(001) surfaces. The RAIR spectra of the hydrogenation products were also collected to help identify the presence of related species on the surface as intermediates in the acrolein hydrogenation reactions.

4.4.1 Adsorption of acrolein on bare and H₂-covered Ru(001)

The 0.6 L acrolein (bottom) spectrum at 90 K, in Figure 4.6, shows most of the characteristic acrolein modes including v(C-C), v(C=C) and v(C=O) at 1180, 1631 and 1689 cm⁻¹, respectively.^{57,58} The CH stretch modes appear in the 0.6 L spectrum at 2697, 2760, and 2806 cm⁻¹ and were assigned to $v_s(CH)_{aldehyde}$, $v_s(=CH_2)$, and $v(CH)_{vinyl}$, respectively, based on the gas phase trans acrolein spectra obtained by Hamada et al.⁵⁹ Background CO adsorbs on the surface but is displaced by acrolein, which results in the positive peak around 2000 cm⁻¹ accompanied by the smaller negative v(CO) peak that is slightly red-shifted for the CO that remains on the surface along with the adsorbed acrolein. This spectral region is excluded in all subsequent spectra.

Previous RAIR spectra by Bournel et al.⁵⁷ of multilayer acrolein on Pt(111) do not show any peaks in the CH stretch region while RAIR spectra of multilayer acrolein on Pt(111) by de Jesus and Zaera⁴⁰ show a very weak peak at 2810 cm⁻¹ for the v_s (CH)_{aldehyde} mode.



Figure 4.6 RAIR spectra taken at 90 K of 0.6 L acrolein adsorbed on the bare Ru(001) surface and 1.0 L of acrolein adsorbed on bare and 3.0 L H_2 pre-exposed Ru(001) surface

Figure 4.6 reveals a strong hydrogen and acrolein coverage dependence on the intensities of the v(C=C) and v(C=O) modes. At low exposures (0.6 L), the v(C=C) mode at 1631 cm⁻¹ is largest whereas at higher exposure (1.0 L) the v(C=O) mode is blue-shifted to 1694 cm⁻¹ and becomes more intense relative to the v(C=C) mode, which is red-shifted to 1628 cm⁻¹. These shifts in frequency and changes in intensity of the two modes suggests a change from the η_4 -trans (C,C,C,O) planar adsorption geometry⁴⁷ of acrolein at low exposures where both the C=C and C=O bonds interact weakly with the surface to a η_2 -trans geometry at higher exposures, where the bonding to the surface is mostly via the C=C bond. Thus, at high exposures, the angle

between the C=C bond and the surface decreases as the C=O bond tilts away leading to the increased intensity for the CO stretch mode, in agreement with the surface selection rules.^{32,60} This change in geometry (Figure 4.7) as the surface gets more crowded is even more pronounced in the presence of co-adsorbed hydrogen where the relative intensity of the v(C=O) peak (blue-shifted to 1695 cm⁻¹) over the v(C=C) peak (red-shifted to 1626 cm⁻¹) is even larger. This is in contrast to what occurs on the Ag(111) surface where Brandt et al.³⁹ observed that the C=C bond tilts away from the surface at higher acrolein coverages making it less susceptible toward reaction with the hydrogen adatoms and thus favoring the formation of the unsaturated alcohol.



Figure 4.7 Change in geometry at different coverage regimes. As the coverage increases, the C=O bond tilts away from the surface while the angle between the surface and the C=C bond decreases

4.4.2 Acrolein hydrogenation at 160 K

In Figure 4.8, a series of RAIR spectra collected after the bare Ru(001) surface was exposed to 1.0 L of acrolein at 90 K is shown. The lowest spectrum was collected at 90 K. Thereafter, the surface was annealed to the indicated temperatures and held there for 60 s before it was cooled to 160 K where the subsequent spectra (except the topmost spectrum) were collected. The RAIR spectra were obtained at 160 K because this corresponds to the onset of propanal desorption, as shown in the left panel of Figure 4.8.



Figure 4.8 Left, highest yield TPRS traces of propanal obtained from 1.0 L acrolein on bare (black) and 3.0 L H₂ (red) pre-exposed Ru(001); and right, RAIR spectra for 1.0 L acrolein taken at 90 K and then annealed to the indicated temperatures for 1 minute. The annealed spectra were obtained at 160 K. Topmost spectrum is for 1.0 L of pure propanal taken at 150 K



Figure 4.9 RAIR spectra of 1.0 L acrolein on a Ru(001) spectra pre-exposed to 3.0 L H₂ taken at 160 K after annealing to the indicated temperatures and held there for 1 minute

The 1.0 L acrolein spectrum at 90 K is similar to that shown previously in Figure 4.6. Annealing this surface to 160 K shows pronounced changes in the CH stretch region with new peaks at 2888, 2943, and 2974 cm⁻¹. These are easily assigned to the $v_s(CH_3)$, $v_{as}(CH_2)$, and $v_{as}(CH_3)$ modes of propanal. Similarly, the presence of the CO stretch, CH₃ antisymmetric deformation, CH₂ wag, CH₃ rock, and antisymmetric CCC stretch modes of propanal at ~1665, 1458, 1343, 1080, 992 cm⁻¹, respectively, confirms the formation of propanal on the surface. The intensity of these modes indicates that the amount of propanal produced on the surface is considerably higher than estimated from the TPRS experiments. These propanal modes, which can also be seen in the topmost spectrum for 1.0 L of propanal collected at 150 K, were assigned in agreement with the HREELS study of propanal on Rh(111) by Brown and Barteau⁶¹ and the gas phase study by Köroğlu et al.⁶² The presence of propanal persists on the surface until 210 K,⁶³ which is just above the peak desorption temperature. At higher temperatures most of the propanal either desorbs, hydrogenates to the saturated alcohol (see below), or decomposes to CO and hydrogen. Repeating the experiment on a Ru(001) surface pre-exposed to H_2 did not yield significantly different results from those obtained on the bare Ru(001) surface. The RAIR spectra of Figure 4.8 do not reveal any 1-propanol even though the 1.0 L TPRS results in Figure 4.3 show some 1propanol desorption in this temperature range (160 - 210 K).

4.4.3 Acrolein hydrogenation at 250 K

Similar RAIRS experiments were conducted to verify the formation of 1-propanol at higher temperatures. Again, the bare Ru(001) surface was exposed to 1.0 L of acrolein at 90 K, and the lowest spectrum in the right panel of Figure 4.10 was collected at 90 K. The surface was then annealed to the indicated temperatures and held there for 60 seconds before it was cooled to 250

K where all the subsequent spectra, except the topmost spectrum, were collected. A temperature of 250 K was chosen because it corresponds to the onset of desorption of 1-propanol, as shown in the TPRS results in the left panel of Figure 4.10. The topmost spectrum in the right panel is for 0.1 L of pure 1-propanol taken at 90 K.

In Figure 4.10, the 1.0 L of acrolein spectrum obtained at 90 K (lowest spectrum) is similar to that described earlier. Annealing to 250 K shows the CH stretches for 1-propanol at 2884, 2945, and 2983 cm⁻¹, which were assigned to the $v_s(CH_2)$, $v_s(CH_3)$, and $v_{as}(CH_3)$ modes of 1-propanol. The peak at 1463 cm⁻¹, which is red-shifted at higher temperatures to 1459 cm⁻¹ was assigned to the $\delta(CH_2)$ mode of 1-propanol.

The characteristic v(OH) mode of 1-propanol at 3400 cm⁻¹ appears after annealing the surface to 300 and 320 K and was gone by 350 K. The similarity in intensity, frequency, and shape of this OH stretch peak is comparable to that of 0.1 L 1-propanol directly adsorbed on the surface, implying that the coverage and structure is similar in the two cases. Although the large width and red-shift from the frequency of an isolated O-H stretch implies the presence of hydrogenbonding, there is insufficient information to further speculate on the structure of the adsorbed 1-propanol. At these higher temperatures, especially at 320 K, the CH stretch modes are no longer visible in the spectrum but the CH₂ bend mode at 1459 cm⁻¹ persists. The assignment of these 1-propanol modes, which can also be seen in the 0.1 L 1-propanol spectrum (topmost spectrum), is in agreement with the gas phase spectrum obtained by Fukushima and Zwolinski⁶⁴ and the HREEL spectra on Rh(111) of Brown and Barteau.⁶¹

Similar results (Figure 4.11) were obtained when the experiments were repeated on the H₂precovered Ru(001) surface except the v(OH) mode shifts from 3400 cm⁻¹ to 3380 cm⁻¹, which suggests a higher yield of 1-propanol on the H₂-precovered Ru(001) surface. This mode also persists on the surface up to 350 K above which the 1-propanol has either completely desorbed or decomposed to CO and H₂.



Figure 4.10 Left, highest yield TPRS traces of 1-propanol obtained from 1.0 L acrolein on bare (black) and 3.0 L H₂ (red) pre-exposed Ru(001); and right, RAIR spectra of 1.0 L acrolein taken at 90 K and then annealed to the indicated temperatures for 1 minute. The annealed spectra were obtained at 250 K. Topmost spectrum is for 0.1 L of pure 1-propanol taken at 90 K



Figure 4.11 RAIR spectra of 1.0 L acrolein on a Ru(001) surface pre-exposed to 3.0 L H₂ taken at 250 K after annealing to the indicated temperatures and held there for 1 minute

4.5 Discussion

4.5.1 Evidence for Propanal

The corrected TPR spectra of 1.0 L of acrolein in the left panel of Figure 4.8 reveals the formation of propanal (m/e = 58) with a peak desorption temperature at 183 K. The leading edge of the propanal trace, at 160 K, is thus used as the base temperature for the series of RAIR spectra for 1.0 L of acrolein shown in Figure 4.8 (right). At 160 K, the CH region suggests the formation of propanal on the surface with peaks at 2888, 2943, and 2974 cm⁻¹ that were assigned to the $v_s(CH_3)$, $v_{as}(CH_2)$, and $v_{as}(CH_3)$ modes of propanal, which persists up to 210 K. These frequencies agree with those obtained in a separate experiment where 1.0 L of propanal was exposed to the Ru(001) surface at 90 K and the surface annealed to 150 K as shown in the topmost spectrum of Figure 4.8. For propanal directly adsorbed on $Ru(001)^{63}$, the RAIR spectra show a strong dependence on temperature, especially in the 800 - 1800 cm⁻¹ region, which necessitates obtaining acrolein spectra at a higher temperature than 90 K in order to interpret the spectral features attributable to propanal formed from acrolein. In the 160 K spectrum, the formation of propanal on the surface is further supported by the presence of the propanal v(CO)mode at 1665 cm⁻¹, which is slightly blue shifted from 1661 cm⁻¹ for the directly adsorbed propanal at 150 K. This mode is gone by 210 K. The disappearance of the v(CO) mode above 200 K was also observed in the spectra for directly adsorbed propanal.⁶³ The CH₂ deformation mode at 1458 cm⁻¹ and the broad peak centered at 1343 cm⁻¹ and assigned to the CH₂ wag both persist up to 210 K, indicating formation of propanal from acrolein. The peak at 908 cm⁻¹, assigned to the CH₃ rocking mode, sharpens from 160 to 210 K and is one of the most striking features of propanal formed from acrolein. The corresponding peak for directly adsorbed propanal appears at 912 cm⁻¹ in Figure 4.8. These 160 - 210 K RAIR spectra support the formation of propanal and subsequent decomposition to CO at temperatures above 210 K as suggested by the TPR spectra. The decomposition of propanal to CO at temperatures around 250 K and the subsequent observation of desorption-limited CO were confirmed in a series of RAIR and TPR spectra collected for directly adsorbed propanal on Ru(001).⁶³



Figure 4.12 CO TPRS results for 1.0 L acrolein on bare (black) and 3.0 L H_2 precovered (red) Ru(001)

Figure 4.8 (left panel) shows that more propanal desorbs from the hydrogenation of acrolein when the surface is first exposed to H₂. However, a higher coverage of propanal is not observed in the corresponding RAIR spectra (Figure 4.9). This implies that once propanal is formed from acrolein hydrogenation, a higher fraction desorbs rather than decomposes when coadsorbed hydrogen is present. This is consistent with the comparison of TPRS results in Figure 4.12, which show that less CO (0.10 ML) desorbs following acrolein adsorption on hydrogen precovered than on clean Ru(001) (0.23 ML). Although the decomposition of acrolein, propanal, 2-propenol, and 1-propanol each contribute to CO desorption, it is reasonable to assume that the

reduced amount of CO corresponds to a reduced amount propanal decomposition as RAIRS implies that more of the acrolein is hydrogenated to propanal. This competition between desorption and decomposition of the hydrogenation product has also been reported for Pt(111) by Loffreda et al.⁴⁸ In addition, some of the propanal produced on both the bare and H₂ pre-exposed Ru(001) surface can further hydrogenate to 1-propanol as seen in the lower temperature peak in Figure 4.10 (left panel). This was also observed in our experiments with pure propanal on the Ru(001) surface.⁶³

4.5.2 Evidence for 1-Propanol

The formation of 1-propanol (m/e = 31) on the surface and subsequent desorption can be deduced from the corrected TPR spectra obtained from 1.0 L of acrolein on both the bare and H_2 pre-exposed Ru(001) surface as shown in the left panel of Figure 4.10. The spectra show two desorption peaks for 1-propanol at 188 and 271 K, suggesting that it forms by two distinct pathways. In experiments with directly adsorbed 1-propanol, 1-propanol was found to desorb molecularly with two peaks at similar temperatures as seen in Figure 4.10.63 This indicates that neither 1-propanol desorption peak in Figure 4.10 is necessarily reaction-limited; the 1-propanol may form at a lower temperature than it desorbs. The low temperature peak is attributed to hydrogenation of propanal. Hydrogenation to 1-propanol was also seen in the results of our TPRS experiments with propanal, 2-propenol, and 1-propanol on the Ru(001) surface.⁶³ In contrast, the high temperature peak most likely arises from the hydrogenation of 2-propenol (peak desorption temperature of 203 K in Figure 4.3) to 1-propanol on the surface and its subsequent desorption. This attribution is also supported by our TPRS results following 2propenol adsorption on the Ru(001) surface where 1-propanol desorption was seen at 235 and 271 K at low coverages.⁶³ The leading edge of the higher temperature 1-propanol TPRS peak in
Figure 4.10 is around 250 K and was thus the temperature used to collect the series of RAIR spectra shown in the right panel of Figure 4.10 because the temperature range of the lower temperature TPRS peak was initially used to detect the higher yield of propanal with RAIRS, which showed no evidence of 1-propanol. At 250 K, the modes in the CH stretch region and the CH₂ deformation mode at 1463 cm⁻¹ are best assigned to propanal. The RAIR spectra of 2propenol show that its signature modes disappear above 150 K which explains why no peaks attributable to it are seen in the right panel of Figure 4.10.⁶³ However, the appearance of the v(OH) mode as a broad peak around 3400 cm⁻¹, after the 300 K anneal, combined with the persistence of the CH₂ deformation mode (redshifted to 1459 cm⁻¹) confirms the presence of 1propanol, which remains on the surface until around 320 K. Above this temperature, the alcohol begins to decompose to CO and H₂. However, on the H₂ pre-exposed Ru(001) surface (Figure 4.11) the alcohol persists on the surface until about 350 K, above which it begins to decompose. This behavior of the alcohol on both the bare and H₂ pre-exposed surface is in agreement with the trailing edges of the TPR spectra seen in Figure 4.10. The v(OH) mode for the reactionproduced 1-propanol and that of the 0.1 L pure 1-propanol spectra in Figure 4.10 have quite similar intensities and hence similar coverages. We can make a semi-quantitative estimate of this coverage as follows. Based on similarly sized molecules, we estimate the ion gauge sensitivity for 1-propanol to be a factor of 4 higher than for N_2 ,⁶⁵ for which our ion gauge is calibrated. Therefore, the actual 1-propanol pressure would be a factor of 4 lower. Using this reduced pressure and a molar mass of 60 g mol⁻¹ to estimate that the actual exposure was 6.5×10^{12} cm⁻² and the Ru atom density on the Ru(001) surface of 1.6×10^{15} cm⁻², we estimate a 1-propanol coverage in the top spectrum of Figure 4.10 of 0.004 ML. This is based on the reasonable assumption of a unit sticking coefficient for 1-propanol on the 90 K surface. This is an order of magnitude higher than the amount of 1-propanol (0.00037 ML) formed from acrolein hydrogenation as estimated from TPRS.

4.5.3 Implications for Selective Acrolein Hydrogenation

While most studies on selective hydrogenation of unsaturated aldehydes have concluded that the initial adsorption geometry plays a key role in determining the product distribution, our results suggest that the desorption energetics and reactivity of the desired product are also very important in understanding the product distribution. The low yield of 2-propenol observed here, as estimated by TPRS, can be partly attributed to the high reactivity of 2-propenol on the Ru(001) surface. In separate experiments, we have shown that on Ru(001),⁶³ 2-propenol follows several pathways; it readily isomerizes to propanal around 170 K, partly desorbs molecularly around 200 K, with the remaining adsorbed 2-propenol hydrogenating to 1-propanol at 220 K. This suggests that the barrier for 2-propenol desorption is relatively high compared to isomerization to propanal, in agreement with the DFT results of Loffreda et al.⁴⁸ on Pt(111) where they found that the barrier for desorption of propanal is much lower than for 2-propenol but the barrier for the first hydrogenation step for adsorbed acrolein is lower at the C=O bond than at the C=C bond. Furthermore, while Brandt et al.³⁹ found that the desorption of 2-propenol is dependent on the coverage of coadsorbed atomic hydrogen with a low H_{ads} coverage facilitating 2-propenol desorption, we did not observe such dependence on Ru(001) and we suspect this might be due to the higher activity of Ru(001) relative to Ag(111). Thus, varying the hydrogen coverage does not appear to be a viable route to increasing the selectivity towards 2propenol. Although the bare Ru(001) surface is effective in promoting the hydrogenation of acrolein to propanal and to 1-propanol, as revealed by RAIRS, these products undergo significant decomposition rather than desorption. If the surface could be modified to enhance the

desorption of the products without suppressing their formation, it might be possible to increase the hydrogenation activity of Ru. However, it seems less likely that such modification would lead to selectivity to 2-propenol.

4.6 Conclusion

The results reported here demonstrate that acrolein can be hydrogenated on the Ru(001) surface to desorb all possible hydrogenation products – 2-propenol, propanal, and 1-propanol– although the desorption yields are very small as most of the acrolein either desorbs molecularly or eventually decomposes to CO and H_2 . The highest desorption yield of the hydrogenation products is propanal with the desired product, 2-propenol, desorbing in only minute quantities. In contrast to the TPRS results, RAIRS shows significant hydrogenation to propanal and 1propanol. This indicates that the reaction steps involved in hydrogenating acrolein to propanal and 1-propanol readily occur on Ru(001) but that the rate of decomposition of these products is higher than their rates of desorption. This suggests that modifying the surface in a way that promotes desorption of the hydrogenation products over their decomposition could lead to effective Ru hydrogenation catalysts.

5. Surface Chemistry of Propanal, 2-Propenol, and 1-Propanol on Ru(001)

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5.1 Introduction

In this chapter, we continue our studies of C_3 oxygenates with the surface chemistry of propanal, 2-propenol, and 1-propanol, which are all hydrogenation products of acrolein as shown in the previous chapter. To provide a better understanding of the hydrogenation pathways of acrolein, a comparative study of the adsorption and thermal chemistry of these hydrogenation products is necessary.

The C₃ oxygenates – propanal, 2-propenol, and 1-propanol – have been studied extensively. On Rh(111), Brown and Barteau⁶¹ used temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) to show that both propanal and 1-propanol decompose to form CO, H₂, and surface carbon with the former also yielding some ethane. This difference was attributed to the η^2 (C,O) geometry of the propanal around 145 K, which enhances decarbonylation. A similar result for propanal was obtained on Pd(111).⁶⁶ The formation of an allyl alkoxide was reported⁴⁵ after the adsorption of 2-propenol on Pd(111), which resulted in two different reaction pathways after annealing to 200 K – decarbonylation to yield CO and H₂ and dehydration to yield propylene and water. An allyl alkoxide intermediate was also reported on Rh(111) after adsorption of 2-propenol.⁴⁴ However, only the decarbonylation pathway to yield CO, H₂, and surface carbon was observed. At low coverages

on $Pd(110)^{67}$, 2-propenol was shown to decompose to CO, H₂, and carbonaceous species with small amounts of ethylene and ethane also produced. The desorption of propanal (235 K) was observed at near saturation coverages while molecular desorption of 2-propenol occurs only after saturation coverages.

In contrast to what was observed on Rh(111), a TPD study⁶⁸ on Pd(111) showed that the decomposition of 1-propanol also produced ethane in addition to CO, H₂, and surface carbon. On $Pt(111)^{69}$, 1-propanol was shown to desorb molecularly around 160 K (multilayer desorption) and 230 K (monolayer desorption). The remaining 1-propanol decomposes to CO (450 K), H₂ (320 and 450 K), and surface carbon via the decomposition of the ethylidyne intermediate produced after adsorption.

In addition to these studies on single metals, Murillo and $Chen^{70}$ used TPD and HREELS to study the adsorption and reaction of these C₃ oxygenates on Pt(111), Ni(111) thin film, and Ni/Pt(111) bimetallic surfaces. They found that 2-propenol can undergo isomerization to propanal on both Pt(111) and Pt-Ni-Pt(111) surfaces and can also self-hydrogenate to 1-propanol on the Ni(111) film. For propanal, the decarbonylation pathway was dominant on all the surfaces with the production of small amounts of ethylene. However, unlike both 2-propenol and propanal, 1-propanol mainly desorbs molecularly on all three surfaces.

A recent report by Dostert et al.⁷¹ used RAIRS and TPD to follow the adsorption geometry at different coverages and the thermal activity of propanal and 2-propenol on Pd(111). They identified three coverage regimes for propanal – sub-monolayers characterized by the red-shifted v(CO) at 1663 cm⁻¹, monolayers with a second v(CO) at 1693 cm⁻¹ that grows and saturates with increasing coverage into the multilayer regime, which is characterized by a third unperturbed

v(CO) at 1728 cm⁻¹ similar to its value in the gas phase. For 2-propenol, only a few C-H stretches are observed, which precludes identification and characterization of the adsorbed species at low coverages but for multilayers, spectra similar to that of the gas phase are observed. This difference was attributed to the flat geometry adopted by 2-propenol on the Pd(111) surface in contrast to the tilted geometry of propanal which interacts primarily with the surface via the C=O bond. The TPD results for both compounds show molecular desorption with decomposition to H₂ and CO at higher temperatures.

In a separate study, Dostert et al.⁴⁶ showed in a pulsed multimolecular beam study that an oxopropyl spectator species forms on Pd(111) during acrolein hydrogenation. Once the surface is covered by oxopropyl the selectivity towards 2-propenol increases to 100%. Although they identified the oxypropyl with RAIRS,⁴⁶ they do not mention observing it in their later combined RAIRS and TPD study of acrolein, 2-propenol, and propanal adsorption on Pd(111).⁷¹ As the methods used in the latter study are quite similar to our methods, it is perhaps not surprising that we also do not observe the oxopropyl species from either acrolein or 2-propenol adsorption on Ru(001).

Here, we have utilized the high resolution of RAIRS to identify the adsorbates on the surface from low to high coverages and the surface intermediates produced with increasing temperature when these C_3 oxygenates are adsorbed on Ru(001). An understanding of the surface chemistry of the possible products of acrolein hydrogenation provides useful insights into the reaction pathways of this simplest α , β -unsaturated aldehyde.

The chamber setup and the experimental details are as described in chapter 4.

5.2 TPRS Results

Propanal, 2-propenol, and 1-propanol produce very similar mass fragments, which makes unique identification of the desorbing species difficult. Thus, the fragmentation ratios for each of the pure compounds (propanal, 2-propenol, and 1-propanol) was collected and these enabled us to select the best mass fragment to use in monitoring the desorption of a particular compound and thereafter deconvolute the resulting raw TPR spectra to remove any extraneous contributions. The mass fragment ratios and the detailed deconvolution process can be found in Appendix A1.

The clean Ru(001) surface was separately exposed to 2-propenol, propanal, and 1-propanol at 90 K and the temperature was linearly ramped at 2 K/s from 100 to 700 K. Product desorption from the surface was followed by monitoring 2, 26, 27, 28, 30, 31, 39, 57, and 58 amu. Mass 60 was also monitored to provide a unique identifier for 1-propanol desorption. Figure 5.1 shows the deconvoluted TPRS traces for different masses arising from 1.0 L each of 2-propenol (black lines), propanal (red lines), and 1-propanol (blue lines). For each compound, a 1.0 L exposure yields approximately a saturated monolayer coverage because at higher exposures multilayer desorption peaks are observed with TPRS.

5.2.1 Desorption of 2-propenol, propanal, and 1-propanol

The 57 amu panel shows that molecular 2-propenol only desorbs, around 200 K, when the Ru(001) surface is directly exposed to 2-propenol but does not form following exposure to propanal or 1-propanol. This suggests that neither the isomerization of propanal to 2-propenol nor the dehydrogenation of 1-propanol to 2-propenol occurs on the Ru(001) surface. In the 58 amu panel the desorption of propanal from the Ru(001) surface was observed for all three starting compounds. 2-propenol, after exposure to the surface at 90 K, isomerizes around 180 K

to propanal. This is similar to the low temperature molecular propanal desorption peak, at 175 K, from the propanal TPRS experiment. Molecular propanal also desorbs at a higher temperature of 277 K. Two peaks centered at 224 and 316 K show that propanal was also produced from the dehydrogenation of 1-propanol.



Figure 5.1 Deconvoluted TPRS traces for desorption of (clockwise from top left) masses 57, 58, 31, 30, 2, and 28 corresponding to 2-propenol, propanal, 1-propanol, formaldehyde, H₂, and CO, respectively, from three separate TPRS experiments of 1.0 L of 2-propenol (black lines), 1.0 L of propanal (red lines), and 1.0 L of 1-propanol (blue lines)

The 31 amu panel shows desorption of 1-propanol from the Ru(001) surface during the three TPRS runs. 2-propenol hydrogenates to 1-propanol and desorbs around 220 K. Similarly,

propanal hydrogenates to 1-propanol and desorbs at a higher temperature of 256 K, whereas 1propanol desorbs molecularly at 227 and 298 K. The relative TPRS areas also suggest that the hydrogenation of the C=C bond (in 2-propenol) is more facile on the Ru(001) surface relative to the C=O bond (in propanal).

5.2.2 Desorption of other species

The CO (28 amu panel) desorption begins around 350 K for both propanal and 2-propenol with a peak desorption temperature of 446 K, whereas the onset of CO desorption for 1-propanol is slightly delayed (ca. 390 K) with peak desorption temperature of 467 K. The 2-propenol TPRS run also shows CO and H_2 desorption just above 600 K. Since CO desorbs molecularly from the clean surface around 450 K, the peak desorption temperatures for CO observed here indicate that it follows desorption-limited kinetics.

The onset of H_2 desorption (2 amu panel) from the three compounds varies significantly. Whereas H_2 desorption from 2-propenol begins around 240 K, it begins at 270 and 300 K for propanal and 1-propanol, respectively. The lowest peak desorption temperature (316 K) for H_2 from 1-propanol also coincides with the higher peak desorption temperature of propanal (316 K) from the dehydrogenation of 1-propanol. These observations suggest that both reaction- and desorption-limited kinetics contribute to the H_2 peaks. The last panel shows desorption of a 30 amu species from the three TPRS runs, which we suspect to be H_2CO after eliminating the possibility of hydrocarbons with similar mass fragments, such as ethane, by comparing the peak desorption temperatures to that of CO from each of the three TPRS runs.

The desorption of propene (39 amu) was also observed around 130 and 160 K, as shown in Figure 5.2, during the 2-propenol TPRS run. In addition to the species shown in Figures 5.1 and

5.2, other hydrocarbon species – C_2H_4 (26 and 27 amu) and C_2H_6 (28 and 30 amu) – were also monitored during all the TPRS runs. However, no desorption of any of these hydrocarbon species was observed.



Figure 5.2 Deconvoluted TPRS trace for propene from 1.0 L of 2-propenol

5.2.3 TPRS yields

Table 5.1 Yields in units of $\times 10^{-3}$ ML of the products observed with TPRS following exposure to 2-propenol, propanal, and 1-propanol

Compound	Exposure (L)	Product and Yield $\times 10^{-3}$ ML						
		СО	2-Propenol	Propanal	1-Propanol	Propene		
2-Propenol	1.0	50.0	11.0	13.9	7.13	12.7		
Propanal	1.0	60.30	0	18.8	0.22	0		
1-Propanol	1.0	58.5	0	11.1	150	0		
1								

Using the method described in Chapter 4 and fully outlined in Appendix A2, the TPRS yields, relative to CO, were calculated and presented in the table below for all the desorption products except H_2 from the different TPRS runs.

5.3 **RAIRS Results**

To further understand the adsorption geometries and nature of the intermediates during the thermal activation of these compounds, several RAIR spectra were collected at 90 K using similar coverages as those in the TPRS experiments.

5.3.1 2-Propenol

Figure 5.3 shows a series of RAIR spectra obtained after exposing the Ru(001) surface at 90 K to 1.0 L of 2-propenol and after annealing to the indicated temperatures. All spectra were collected at 90 K. The vibrational modes observed at 90 K are compared in Table 5.2 to the frequencies in the liquid phase and on other surfaces. The positive peak around 2000 cm⁻¹ is due to background CO, which adsorbs on the surface but is displaced and shifted following 2-propenol adsorption.

The peaks listed in Table 5.2 persist even after annealing to 150 K with the v(OH) mode redshifted to 3276 cm⁻¹ with decreased intensity. After the 200 K anneal the v(OH) mode disappears, while the changes in the frequencies in the CH stretch region coupled with the disappearance of v(C=C) at 1647 cm⁻¹ suggests the presence of a different species on the surface. Annealing to 300 K results in the formation of adsorbed CO with v(CO) at 1994 cm⁻¹. The v(CO) mode is blueshifted to 2004 cm⁻¹ with increased intensity upon further annealing to 400 K. Above this temperature, the CO begins to desorb.



Figure 5.3 RAIR spectra of 1.0 L of 2-propenol on Ru(001) taken at 90 K after annealing to the indicated temperatures

Vibrational mode	Liquid ⁷²	Pd(111) ⁴⁵	Rh(111) ⁴⁴	Si(111)-7x7 ⁷³	This work
ν(OH)	3400	3380	3365		3323
$v_{as}(=CH_2)$	3092	3135	3110	3102	3098
v_s (=CH)				3012	3012
$v_s(=CH_2)$					2987
$v_{as}(CH_2)$					2922
$v_s(CH_2)$	2923	2950	2885	2976	2861
v(C=C)	1603	1610	1675	1657	1647
$\delta(CH_2), \delta(CH)$	1371-1457	1390	1450	1422	1456
δ(ΟΗ)	1324	n.r.	n.r.	1288	1286
τ(CH ₂)					1238
v(C–C)				1131	1119
v _a (CCO)	1103	1000	1020		1022
ω(=CH ₂)	962	1000	1020	932	997
v _s (CCO)	910, 885	905	945		
ρ (=CH ₂)					929
γ(=CH)	n.r.	815	750		
n.r. = not resolved					

Table 5.2 Comparison of vibrational assignments for 2-propenol (CH₂=CHCH₂OH)

5.3.2 Propanal

Similarly, Figure 5.4 shows RAIRS results after 1.0 L of propanal was exposed to the Ru(001) surface at 90 K and annealed to the indicated temperatures for 60 s and then cooled to 90 K where all the spectra were collected. The assigned vibrational modes for the 90 K spectrum are listed in Table 5.3 along with liquid and gas phase data.



Figure 5.4 RAIR spectra of 1.0 L of propanal on Ru(001) taken at 90 K after annealing to the indicated temperatures

Vibrational mode	Liquid ⁷⁴	Liquid ⁷⁵	Gas ⁶²	This work	
$v_{as}(CH_3)$	2980	2979	2981	2979	
$v_{as}(CH_2)$	2941	2942	2954	2943	
$v_{s}(CH_{3})$	2880	2883	2906	2885	
ν(CH), FR 2δ(CH)	2820	2835	2818	2829	
$\delta(CH_2)+\delta(CH)$	2770			2770	
2δ(CH), FR ν(CH)	2720	2736	n.r.	2718	
ν(C=O), FR 2ρ(CH ₃)	1728	1733	1754	1730, 1658	
2ρ(CH ₃), FR ν(C=O)	1690	1693	1693	1688	
$\delta_{as}(CH_3)$	1452	1455	1459	1455	
δ(CH ₂)	1416	1414	1423	1409	
δ(CH ₃)	1392	1392	1395	1389	
δ(CH)	1378	1377	1380	1364	
ω(CH ₂)	1338	1340	1338	1342	
ρ(CH ₃)	1065	1093	1098	1095, 1076	
$v_{as}(CCC)$		1014	1010	1001	
ρ(CH ₃)	898	899	892	911	
ρ(CH ₃)	876	876		871	
n.r. = not resolved; FR = Fermi Resonance					

Table 5.3 Comparison of vibrational assignments for propanal (CH₃CH₂CHO)

The 90 K spectrum shows peaks in the CH stretch region at 2718 and 2829 cm⁻¹, which correspond to the well-known Fermi doublet^{76,74} arising from the resonance between the $v(CH)_{aldehyde}$ and the first overtone of the $\delta(CH)_{aldehyde}$ modes, respectively. The other assignments are listed in Table 5.3 with the peaks at 1658 and 1730 cm⁻¹ representing another

case of Fermi resonance between the v(CO) and the first overtone of the CH₃ rocking mode at 871 cm⁻¹, respectively.⁷⁴

The 120 K spectrum is similar to that at 90 K except for the slight shifts in the CH stretch frequencies. In the spectrum at 150 K, the symmetric and antisymmetric CH₃ stretches are redshifted to 2879 and 2968 cm⁻¹, respectively, while the antisymmetric CH₂ stretch is blueshifted to 2937 cm⁻¹ but the Fermi doublets at 2829 and 2718 cm⁻¹ have disappeared. The CO stretch and the first overtone of ρ (CH₃) at 1661 and 1730 cm⁻¹, respectively, show a loss of intensity while the 1688 cm⁻¹ peak has disappeared. This suggests that the C=O bond is tilted more towards the surface resulting in stronger interaction with the metal atoms. The same loss of intensity can be seen for the other peaks at lower frequencies except for the CH₃ deformation modes at 912 and 1080 cm⁻¹ and the v(CCC) mode at 1001 cm⁻¹, which have become more intense. The 200 K spectrum is very similar to that at 150 K except for the complete disappearance of all the modes in the CO stretch region, which suggests, in accordance with the surface selection rules,³² that the C=O bond is parallel to the surface. These two spectra at 150 and 200 K are similar to the spectra we obtained from annealing 1.0 L of acrolein at 160 – 210 K,⁷⁷ as shown in the previous chapter.

The 250 K spectrum is similar to the 200 K spectrum with the appearance of two new peaks at 1223 and 1774 cm⁻¹, which we tentatively attribute to the $\rho(CH_2)$ and $\nu(CO)$ modes of physisorbed formaldehyde (H₂CO).^{78,79} Annealing to 300 K reveals the presence of unidentified hydrocarbon species and adsorbed CO with $\nu(CO)$ at 1992 cm⁻¹. This mode persists to 400 K with increasing intensity and a slight blue-shift to 2010 cm⁻¹. Further annealing above 400 K leads to CO desorption from the surface.

5.3.3 1-Propanol

1.0 L of 1-propanol was also exposed to the Ru(001) surface at 90 K and annealed to the indicated temperatures for 60 s, and then cooled to 90 K where all the RAIR spectra, shown in Figure 5.5, were collected. Table 5.4 shows the assigned vibrational modes for the 90 K spectrum in comparison with data from the liquid and gas phase and on other single crystal surfaces. The 90 and 120 K spectra are essentially the same with a few shifts in frequencies, especially the blue-shift of the OH stretch from 3280 to 3292 cm⁻¹. Annealing to 150 K results in a further blue-shift of the v(OH) band to 3307 cm^{-1} with significantly reduced intensity. At 200 K, the v(OH) mode is completely gone with additional modes visible in the CH stretch region at 2856 and 2935 cm^{-1} , with the previous bands at 2880, 2941, and 2970 cm^{-1} now shifted to 2878, 2954, and 2974 cm⁻¹, respectively. A new mode also appears at 939 cm⁻¹ that persists to 250 K. The CH stretch region after the 250 K anneal is similar to the 200 K spectrum but the 2935, 2954, and 2974 cm⁻¹ peaks are now combined into a broad peak centered at 2936 cm⁻¹. Further annealing to 300 K leaves the surface with some carbonaceous species and adsorbed CO with a v(CO) band at 2002 cm⁻¹ that grows in intensity and is blue-shifted to 2013 cm⁻¹ with increasing temperature.



Figure 5.5 RAIR spectra of 1.0 L of 1-propanol on Ru(001) taken at 90 K after annealing to the indicated temperatures

Vibrational mode	Liquid ⁸⁰	Gas ⁶⁴	Rh(111) ⁶¹	Cu(111) ⁸¹	This work
ν(OH)	3333	3687	3205	3275	3280
$v_{as}(CH_3)$	2963	2978	2970	2965	2966
$v_{as}(CH_2)$	2937			2937	2942
$v_s(CH_2)$	2878	2892		2877	2881
$\delta(CH_2)$ -sciss	1467	1464	1495	1475	1458
ω(CH ₂)	1346	1393	1390	1365	1382
τ(CH ₂)	1271	1300	n.r.	1294	1292
δ(COH)		1218	n.r.	1239	1228
ρ(CH ₂)	1132				1136
$\rho(CH_3) + \nu(CC)$	1100, 1069	1066	1040	1103, 1074	1105, 1061
$v_{as}(CCC)$		1013		1023	1009
$v_{as}(CCO), v_{as}(CO)$	969	971		972	971
n.r. = not resolved					

Table 5.4 Comparison of vibrational assignments for 1-propanol (CH₃CH₂CH₂OH)

5.4 Discussion

5.4.1 2-Propenol TPRS and RAIRS data

The TPRS data of 1.0 L of 2-propenol in Figure 5.1 shows that it desorbs molecularly at 200 K. However, in addition to desorption, some of the 2-propenol isomerize at 175 K to propanal and some hydrogenate to 1-propanol with a peak desorption temperature of 222 K. Both isomerization to propanal and hydrogenation to 1-propanol are also observed following a 0.2 L exposure of 2-propenol (see Figure 5.6). The TPRS intensities are quite low, suggesting that decomposition to CO and H_2 is more likely at the lower coverage, as was observed for acrolein on Ru(001) in Chapter 4. Isomerization of 2-propenol to propanal is supported by the RAIRS results. The 2872, 2922, and 2955 cm⁻¹ peaks in the 200 K RAIR spectrum of 2-propenol shown in Figure 5.3 can be assigned to the $v_s(CH_3)$, $v_{as}(CH_2)$, and $v_{as}(CH_3)$ of propanal, respectively.



Figure 5.6 Raw and deconvoluted TPR spectra for masses 57 (2-propenol), 31 (1-propanol), and 58 (propanal) after exposing the Ru(001) surface to 0.2 L of 2-propenol

Similarly, the peaks at 1104 and 1489 cm⁻¹ can also be assigned to the CH_3 rock and CH_2 deformation modes of propanal, respectively. The justification for these assignments, apart from the TPRS result, can be seen by comparing this spectrum with the 200 K spectrum of propanal in

Figure 5.4 where similar frequencies appear in the CH stretch region, although they are blueshifted in Figure 5.4 relative to their values in Figure 5.3 due to the coverage dependence of the propanal frequencies (see Figure 5.7 below for RAIR spectra of propanal at lower coverages). This formation of propanal via isomerization of 2-propenol was reported earlier by Shekhar and Barteau on Pd(110)⁶⁷ to occur at 235 K. The TPRS results also show that 2propenol can be hydrogenated to yield 1-propanol with peak desorption temperature around 220 K. However, in the 200 to 300 K RAIR spectra of 2-propenol, no peaks attributable to 1propanol are evident. This might be due to the relatively small yield of 1-propanol as seen by comparing the TPRS peak area for the isomerization product (propanal) and the hydrogenation product (1-propanol). A somewhat surprising result was the formation of propene (Figure 5.2) as revealed by the TPRS peak at 134 K, which suggests a low temperature dehydration route for 2propenol on the Ru(001) surface. Propene desorption was also observed by Davis and Barteau on Pd(111)⁴⁵ but at a higher temperature of 260 K, possibly due to the higher adsorption temperature of 170 K used in that experiment. Desorption of other hydrocarbons (C₂H₄ and $C_{2}H_{6}$) was not observed. The hydrogen desorption spectrum shows two peaks at 298 and 315 K with a long trailing edge, which supports our attribution of the 30 amu peaks to H_2CO with its peak desorption temperature also coinciding with that of CO. The peak desorption temperature for CO at 446 K is consistent with it being desorption-limited since the RAIRS results show the presence of adsorbed CO by 300 K.

5.4.2 Propanal TPRS and RAIRS data

The TPRS results for propanal show that it desorbs molecularly with TPRS peaks at 175 and 277 K but also hydrogenates to 1-propanol with peak desorption temperature at 256 K. However, there was no evidence of isomerization to 2-propenol from the TPRS data. Hydrocarbon

desorption was also not detected in the TPRS experiments, which suggests that hydrogenation and decomposition are the only available pathways for propanal on the Ru(001) surface. The H₂ desorption spectrum shows a peak at 289 K with shoulders at 327 and 369 K and a long tail. The RAIR spectra at 200 K shows the disappearance of the v(CO) mode at 1730 cm⁻¹. This is accompanied by the disappearance of the first overtone of the $\rho(CH_3)$ mode with which it is in Fermi resonance suggesting a stronger interaction between the C=O bond and the surface, which makes the bond more susceptible to hydrogenation. This might be the likely route for the formation and desorption of 1-propanol from the surface above 200 K. However, no v(OH) mode is observed in the RAIR spectra, which is consistent with what was observed in the 1-propanol RAIR spectra (Figure 5.5) where the v(OH) mode disappears above 150 K. Thus it's difficult to unambiguously verify, with RAIRS, the presence of 1-propanol on the surface from the hydrogenation of propanal. At 250 K, new peaks at 1223 and 1774 cm⁻¹ appear and are tentatively assigned to the $\rho(CH_2)$ and $\nu(CO)$ modes of physisorbed H₂CO^{78,79} as the relatively higher frequency of the CO stretch mode suggests very weak interaction with the surface. Most of the propanal modes persist to 300 K, consistent with the TPRS results. At this temperature, the presence of CO on the surface is also evident with the sharp peak for v(CO) at 1992 cm⁻¹. The increase in the intensity of this mode with a blue-shift to 2010 cm⁻¹ is consistent with an increase in the CO coverage with increasing temperature.

5.4.3 1-Propanol TPRS and RAIRS data

The 1-propanol TPRS results show that desorption of molecular 1-propanol occurs in two peaks centered at 227 and 298 K. It also dehydrogenates to yield propanal with two propanal desorption peaks centered at 224 and 316 K, but no 2-propenol desorption was observed. The H_2 desorption spectrum shows a peak at 316 K with a shoulder at 334 K and a slight bump around

481 K. The 316 K H₂ desorption peak corresponds to the high temperature peak for propanal desorption, which suggests that it is produced during the dehydrogenation process. Similar to our conclusions from the TPRS results for 2-propenol and propanal, we attribute the 30 amu desorption spectrum to H₂CO with peak temperatures at 230 and 302 K. Although these temperatures are similar to those for desorption of molecular 1-propanol at 227 and 298 K, we are confident they are not from the fragmentation of the desorbing 1-propanol because they persist even after several careful deconvolution steps. The broad peak in this spectrum at 467 K, which coincides with the peak for desorption-limited CO, supports our assignment to H₂CO instead of ethane (C₂H₆). The 1-propanol modes in the 90 K RAIR spectrum persist on the surface until 150 K. After annealing to 200 K the v(OH) mode has disappeared and the peak at 2970 cm⁻¹ assigned to v_{as} (CH₃) has blueshifted to 2974 cm⁻¹ with a much reduced intensity. The v_{as} (CH₂) mode also shifted to a higher frequency at 2954 cm⁻¹. Three new peaks appear in this spectrum with two in the CH stretch region at 2856 and 2935 cm⁻¹ and a sharp peak at 939 cm⁻¹. Since the TPRS results shows the onset of propanal desorption around this temperature, we assigned these peaks at 939, 2856 and 2935 cm⁻¹ peaks to the $\rho(CH_3)$, $v_s(CH_3)$ and $v_{as}(CH_2)$ modes of propanal. These peaks are also present in the 250 K spectrum but the CH₂ and CH₃ antisymmetric stretches in 1-propanol at 2954 and 2974 cm⁻¹ have disappeared. These RAIRS observations and the TPRS results suggest that the Ru(001) surface is covered with a complex mixture of molecular fragments between 200 and 250 K and thus definitive assignments of the IR peaks is not feasible. The sharp peak at 2002 cm⁻¹ with a slight bump at 1894 cm⁻¹ in the 300 K spectrum are both assigned to v(CO) of CO molecules residing in different environments on the surface. These peaks increase in intensity with increasing temperature and above 400 K, the CO molecules begin to desorb.



Figure 5.7 RAIR spectra of 0.1 - 1.0 L propanal at 90 K on clean Ru(001)

5.5 Conclusion

The TPRS and RAIRS results presented here show the complex chemistries exhibited by 2propenol, propanal, and 1-propanol upon separate adsorption on the Ru(001) surface. The results show that, although 2-propenol can molecularly desorb from the surface, it is highly reactive on the surface and undergoes dehydration, isomerization, hydrogenation, and decomposition. This might explain the relatively low yields of 2-propenol during acrolein hydrogenation experiments on Ru(001) seen in the previous chapter. The formation of propanal from 1-propanol and vice versa suggests that the hydrogenation of propanal to 1-propanol is a reversible process on the Ru(001) surface. All these observations are presented in the figure below which shows the pathways following acrolein hydrogenation on the Ru(001) surface.



Figure 5.8 The possible pathways following acrolein hydrogenation on Ru(001)

6. Preparation and Characterization of Pt/Ru(001) Bimetallic Surfaces

6.1 Introduction

In this and subsequent chapters, the work done with and on Pt/Ru(001) bimetallic systems, as we attempt to address the *materials gap*, mentioned earlier in Chapter 1, will be described in detail. We begin, in this chapter, with the growth of pseudomorphic platinum layers on a Ru(001) substrate and subsequent characterization using AES, LEED, CO-TPD and CO-RAIRS.

As discussed in Chapter 1, modifying a catalyst for improved performance involves either altering its structure, its composition, or both. Fundamental understanding of the effect of these modifications can be achieved with the use of bimetallic surfaces because they are simple enough to enable a systematic study of the relationship between their microscopic structure and their activity and/or selectivity. Additionally, a wide variety of possible surface structures and compositions, with varying degrees of complexity, can be prepared and studied via the architecture of bimetallic surfaces.^{82, 83} Several bimetallic systems are also well-known catalysts in their own right.^{11, 84}

Two types of bimetallic surfaces are of particular interest: single atom alloys (SAAs) and near surface alloys (NSAs). In SAAs, single and isolated atoms of catalytically active metals are dispersed on the surface layer of a noble metal host. Examples of catalytic reactions on the surfaces of SAAs include the selective hydrogenation of styrene and acetylene on Pd/Cu(111) facilitated by the presence of isolated Pd atoms that lower the energy barrier to both hydrogen uptake on and subsequent desorption from the Cu(111) surface.^{85, 86} The bonding properties of these isolated Pd atoms on the Cu(111) substrate were further elucidated in a recent work.⁸⁷ Similarly, isolated Pt atoms were shown to enable the 100% selective hydrogenation of

butadiene to butenes with stable activity in a Pt/Cu(111) SAA system.⁸⁸ Pd/Au(111) and Ni/Au(111) are other SAA systems that have been recently reported to exhibit interesting catalytic properties.^{89, 90}

NSAs, on the other hand, are defined as bimetallic systems consisting of a solute (usually catalytically active) present near the surface of another usually catalytically active host metal in a composition different from the bulk composition.^{10, 91} These solutes can either be on the surface (known as overlayer NSAs) or below the surface of the host metal (known as subsurface NSAs). For example, the decomposition of ethylene was found to be significantly reduced on Ni/Pt(111) in comparison to Ni(111) or Pt(111).⁹² The subsurface Ni/Pt(111) bimetallic surface was also recently shown to be active in the hydrogenation of acrolein to yield both the allyl alcohol (2propenol) and propanal with the latter being the main product. This hydrogenation activity was absent on Pt(111) while a very low hydrogenation activity was observed on Ni(111).^{42, 70} The subsurface Co/Pt(111) bimetallic system was also found to be active towards the hydrogenation of acrolein, though the activity is lower than that observed on the subsurface Ni/Pt(111) system.⁵² The Ni/Pd(111) bimetallic surface has been shown to have a higher activity for the hydrogenation of 1,3-butadiene than its monometallic counterparts, with the bimetallic surface also displaying very good selectivity for the 1-butene product.⁹³ An increased CO uptake was observed on several Pt/Ru(001) bimetallic surfaces⁹⁴⁻⁹⁸ and the saturation coverage was found to be higher than the previously established saturation coverage on the Ru(001) surface. The relationship between CO adsorption characteristics and the morphology of the Pt/Ru(001) surfaces was used to partly explain the enhanced CO tolerance shown by PtRu bimetallic anodes in a direct methanol fuel cell.99 The Cu/Ru(001) bimetallic NSA was also shown to enable increased hydrogen uptake relative to Ru(001) due to the presence of the Cu layer.¹⁰⁰

For the Pt/Ru(001) NSA, the atomic distances within the close packed Pt and Ru surfaces are very similar, with M – M bond lengths of 2.77 and 2.70 Å, respectively. Since the uppermost layer of virtually all transition metals experience tensile stress, it has been shown that the platinum atoms can grow pseudomorphically – that is adopt the lattice structure of the underlying Ru substrate – up to four Pt layers.⁹⁴ The electronic and lateral strain within these pseudomorphic Pt layers and the modification of their electronic structure induced by the substrate-overlayer interaction⁹⁶ renders this bimetallic system an interesting candidate for investigation of its possible unique catalytic properties.

The chamber setup and the experimental details are as described in Chapter 4 with the description of the evaporator added here.



6.2 Old Evaporator Design and its Limitations

Figure 6.1 Image of the previous evaporator setup showing the (a) power feedthrough and (b) W filament with a Pt wire tightly wrapped around it

The previous evaporator setup (Figure 6.1) was designed by a former graduate student, Dr. Yuan Ren, and a postdoctoral researcher, Dr. Ira Waluyo. It consists of a 15 amp, 4-pin power

feedthrough with Cu electrodes, insulated by a ceramic tube in the vacuum side, mounted on a 2.75 inch CF flange. The Cu electrodes are connected to a W bridge by a Be/Cu inline barrel connector (Figure 6.1a). An omega-shaped W filament with a thin Pt wire (0.5 mm diameter, 99.99%) tightly wrapped around it (Figure 6.1b) was spot-welded to this W bridge. Resistively heating this W filament above 1500 K by applying current to the Cu electrodes results in the evaporation of platinum atoms and subsequent deposition on the Ru(001) substrate as shown by the Auger spectra in Figure 6.2, after annealing to 750 K for 1 minute.



Figure 6.2 Auger electron spectra of a clean Ru(001) surface and different Pt/Ru(001) surface grown using the old evaporator design. The platinum coverages were estimated from the Pt N_7VV peak at 64 eV and the Ru MNN peak at 273 eV as described in the text

The platinum coverages were estimated using the ratio of the peak-to-peak heights of the 64 eV Pt N_7VV peak to that of the 273 eV Ru MNN peak after normalization to account for overlap of

any C KLL peak present. The normalization of the 273 eV peak to remove any carbon contamination was done by using, as a basis, the ratio of the positive to the negative parts of the 273 eV peak, which is ~0.80 for a clean Ru(001) surface free of carbon.¹⁰¹ A secondary check was also done by taking the ratio of the peak-to-peak height of the 231 eV peak, which is unaffected by carbon, to that of the 273 eV peak. A value of ~2.0 is obtained for clean Ru(001),¹⁰² and the 273 eV peak can then be normalized against that value.

A closer look at the Auger spectra in Figure 6.2 shows that there are several problems with the deposition process. From the bottom, comparing the second (red) and third (blue) spectra, the estimated platinum coverage for the former is 0.70 while that of the latter is 0.20 even though the former was deposited at a lower temperature (1520 to 1593 K) using the same deposition time. Similarly, the topmost spectrum (green) also shows a lower Pt coverage of 0.58, relative to the second spectrum, for double the deposition time (80 to 40 minutes) at a higher temperature (1608 to 1520 K). Clearly, these estimated coverages are problematic. Other issues that were discovered include the entrainment of background CO molecules during platinum deposition and the inability to reproduce Pt/Ru(001) surfaces with similar platinum coverages despite using similar growth conditions/parameters.

After extensive work, the reasons for the aforementioned issues were identified as:

a) Poor temperature measurement – due to the design of the evaporator setup, the only way to measure the temperature during deposition was to use an infrared pyrometer (Figure 6.3a). The pyrometer relies on matching the color of an internal filament to the color of the filament under measurement as observed through a lens. This invariably introduces significant errors during temperature measurement, which affects reproducibility.

- b) Distance between evaporator and substrate as shown in Figure 6.3b, there is a distance of more than 10 cm between the evaporator and the Ru(001) substrate thus the background pressure rises by over two orders of magnitude during deposition. Also, very long deposition times are required to have appreciable amounts of Pt on the Ru(001) surface, which means the probability of entraining background CO during deposition is extremely high.
- c) Incomplete removal of Pt layers As outlined in Appendix A3, the removal of platinum from the Pt/Ru(001) surfaces requires a longer and more thorough cleaning process than the previous approach to cleaning the Ru(001) surface, when mostly organic species or simple molecules were adsorbed on the surface. This insufficient cleaning process resulted in the presence of some Pt atoms on the surface prior to any subsequent deposition, leading to the incorrect coverage estimates as shown in Figure 6.2.



Figure 6.3 Images of (a) infrared pyrometer used to measure filament temperature during deposition and (b) inside the UHV chamber during deposition showing the distance between evaporator and substrate

6.3 Evaporator Redesign and Optimization

To correct these problems, the evaporator setup was redesigned using a type C thermocouple feedthrough consisting of two Cu electrodes and two thermocouple leads all insulated by a ceramic tube in the vacuum side and mounted on a 2.75 inch CF flange. The omega-shaped W filament, shown in Figure 6.1b, was spot-welded to two W wires that were connected via a Be/Cu inline barrel connector to the Cu electrodes while very thin type C thermocouple wires were spot-welded to the W filament. As shown in Figure 6.4, the feedthrough is housed in a homemade stainless steel tube to provide support for the Cu electrodes and thermocouple wires. It is attached to a UHV linear translator (VG Scienta), which enables the evaporator and Ru(001) substrate to come in close proximity during deposition (Figure 6.4c). This minimizes the deposition time, increase in background pressure, and excessive platinum coating of other components in the UHV chamber during deposition. A new cleaning procedure was also developed (see Appendix A3).

This new design was tested for reproducibility and control of deposition parameters by twice depositing platinum at source temperatures above 1500 K. As shown in the Auger spectra of Figure 6.5, a 20 minutes deposition at a source temperature of 1540 K, followed by annealing the crystal at 750 K for 1 minute, results in a platinum coverage of 0.20 monolayer equivalent (MLE) that was readily reproduced using the same parameters. This reproducibility was also confirmed by the RAIR spectra of 5.0 L CO on these surfaces. As shown in Figure 6.5 (right panel), the three peaks at 2044, 1840, and 2073 cm⁻¹ corresponding to v(CO) of CO molecules located at Pt-free Ru, bridge-bonded, and on-top Pt sites respectively, confirm the presence of platinum on the surface. The similar intensities and frequencies of these peaks show that the deposition is indeed reproducible.



Figure 6.4 Images of (a) the type C thermocouple feedthrough housed in a stainless steel support ready to be coupled to a UHV linear translator, (b) close-up showing the W filament connected to the insulated Cu electrodes and the thermocouple wires, and (c) view inside the UHV chamber during deposition



Figure 6.5 Evidence of reproducibility. Left, Auger spectra of clean Ru(001) and Pt/Ru(001) surfaces and, right, RAIR spectra of 5.0 L CO taken on those Pt/Ru(001) surfaces

6.4 Optimization of Deposition Process – Growth and Characterization at Varying Platinum Coverages Using AES, LEED, CO-RAIRS & CO-TPD

To fully optimize the deposition process, platinum was deposited at varying temperatures (below the platinum melting point of 2045 K) and deposition time. It was found that depositing platinum at temperatures between 1840 – 1890 K, with the Ru(001) substrate at \leq 340 K, results in a deposition rate of ~4 × 10⁻³ ML/s leading to the growth of pseudomorphic platinum layers from submonolayer to multilayer coverages. After deposition, annealing the surface to 750 K for 1 minute allows the formation of larger platinum islands, whereas annealing to, and above, 850 K results in the formation of PtRu surface alloy.^{95, 96}



Figure 6.6 Auger spectra of bare Ru(001) and Pt/Ru(001) surfaces with estimated Pt coverages shown in the figure

Using this method, several Pt/Ru(001) near surface alloys were grown and fully characterized with Auger, LEED, CO-RAIRS and CO-TPD. The Auger spectra of clean Ru(001) and the Pt/Ru(001) NSAs are shown above, with the platinum coverages estimated using the same method as described earlier (Section 6.2). From the figure, the 64 eV platinum peak can be seen at 0.12 MLE coverage, and it increases in intensity with increasing platinum coverage. At a coverage of 0.63 MLE, a second platinum peak at 94 eV appears and continues to grow in intensity along with the 64 eV peak with increasing platinum coverage.

If the growth of the platinum on the Ru(001) substrate is indeed pseudomorphic, we expect to see no differences in the LEED patterns of the clean Ru(001) and the Pt/Ru(001) surfaces. This is confirmed by the LEED images shown in Figure 6.7.



Figure 6.7 LEED images of clean Ru(001) and selected Pt/Ru(001) surfaces. All images were taken with beam energy of 240 eV at 300 K

To further characterize these Pt/Ru(001) NSAs and to, especially, verify the estimated platinum coverages, RAIRS and TPD experiments were performed using CO as a probe molecule. The CO-RAIR spectra also enabled us to compare these Pt/Ru(001) NSAs with other Pt/Ru(001) bimetallic systems previously reported in the literature.



Figure 6.8 RAIR spectra taken at 90 K (left) and TPD spectra from 100 to 700 K (right) for different Pt/Ru(001) NSAs each exposed to a saturated CO coverage (5.0 L). The platinum coverages are indicated in the figure. RAIR and TPD spectra from the clean Ru(001) surface are also included for comparison

In the RAIR spectra (left panel), the bottom spectrum from clean Ru(001) shows a single, sharp peak at 2056 cm⁻¹ for the v(CO) mode. For the Pt/Ru(001) surface, three peaks corresponding to v(CO) of CO molecules located at Pt-free Ru, bridge-bonded, and on-top Pt sites can be seen at 2048, 1842, and 2073 cm⁻¹, respectively, for submonolayer platinum coverages (see also Figure 6.5, right panel). As the platinum coverage increases, the peak corresponding to on-top Pt sites gradually increases in intensity and is blueshifted to 2087 cm⁻¹, while the peak corresponding to
Pt-free Ru sites concurrently decreases in intensity as it is slightly blueshifted to 2050 cm⁻¹. The relative sharpness of these peaks suggests a high degree of order in the Pt islands and the Pt-free Ru sites on the surface. As the platinum coverage goes above 1 ML, only modes corresponding to platinum sites at 1836 and 2081 cm⁻¹ can be seen on the surface, while the peak corresponding to Pt-free Ru sites has vanished completely. This shows that the surface is, by now, completely covered with platinum. Similarly, the TPD spectra from the clean Ru(001) surface shows two peaks at 390 and 446 K that gradually decreases in intensity as platinum is deposited on the surface. For the 0.12 ML Pt/Ru(001) NSA, three peaks at 330 K corresponding to desorption from Pt sites and at 397 and 456 K corresponding to desorption from Pt-free Ru sites were observed. As the platinum coverage increases, there is a gradual decrease in intensity of peaks corresponding to desorption from Pt-free Ru sites along with simultaneous increase in desorption from Pt sites. Around 0.70 ML, the low temperature peak from Ru sites has disappeared, while an extra peak appears around 230 K corresponding to desorption from Pt sites. Above 1 ML, and similar to the RAIR results, the peaks corresponding to desorption from Pt-free Ru sites have vanished completely with peaks at 232, 273, and 383 K corresponding to desorption from Pt sites. These results suggest that above 1 ML, the Ru(001) surface is completely covered with Pt.

These results differ slightly from those of Behm et al.⁹⁷ who observed peaks corresponding to CO bonded to on-top platinum sites *only* (no peak belonging to bridge-bonded CO) at or above one ML platinum coverage. This might be due to the different deposition conditions since they deposited at a much faster rate (0.1 ML/s) using a commercial evaporator (Omicron EFM3). Similarly, the results of Jakob and Schlapka⁹⁴ also differ slightly from ours since they did not observe any peak corresponding to bridge-bonded CO until a platinum coverage of 0.80 ML in their RAIR spectra. However, at 1.1 ML platinum coverage, they observed modes corresponding

to CO on both bridge-bonded and on-top Pt sites *and* Pt-free Ru sites suggesting that even at platinum coverages above 1 ML, the Ru(001) substrate in their study is not completely covered with platinum atoms. Again, these differences might be due to their higher substrate temperature (600 K) and a slightly slower deposition rate (3×10^{-4} ML/s). Thus, the morphology of the platinum layers depends on the growth conditions, including the deposition method, deposition rate, and substrate temperature during deposition.



Figure 6.9 RAIR spectra of saturated CO (5.0 L) coverage on 3.0 MLE Pt/Ru(001) NSA taken at 90 K after annealing to the indicated temperature for 1 minute

It is worthwhile to include here the CO-RAIR spectra collected on a Pt/Ru(001) NSA with a Pt coverage of 3 MLE. As shown in Figure 6.9, there are clearly no peaks from Pt-free Ru sites, suggesting that the surface is completely covered with platinum. However, in the 90 K spectrum, there are two peaks corresponding to CO adsorbed at on-top sites of platinum at 2089 and 2108 cm^{-1} and for CO adsorbed at platinum bridge sites, there is a peak at 1861 cm^{-1} with a shoulder at

1895 cm⁻¹. Annealing to 175 K for 1 minute (CO molecules become mobile on the surface above 150 K), the shoulder at 1895 cm⁻¹, redshifted to 1900 cm⁻¹, is sharper and more intense while the other peaks seem unchanged. These dual peaks arising from similar sites suggest there are different local atomic geometries in the platinum layer, with the 2089 cm⁻¹ peak arising from adsorption at step sites, while the 2108 cm⁻¹ peak corresponds to adsorption at terraces.¹⁰³

6.5 Conclusion

A homemade evaporator has been designed and optimized for physical vapor deposition of different metals onto a substrate. Platinum was successfully and reproducibly deposited on a Ru(001) substrate, with the resulting Pt/Ru(001) NSAs fully characterized with AES, LEED, CO-RAIRS, and CO-TPD. It was shown that platinum can be grown pseudomorphically on a Ru(001) substrate, with CO-RAIRS results also suggesting the presence of different local atomic geometries in the platinum layers at higher platinum coverages.

7. Selective Hydrogenation of Acrolein to Propanal on a Pseudomorphic Pt/Ru(001) Bimetallic Surface

7.1 Introduction

As discussed in Chapter 4, it has long been established that the hydrogenation of the C=C double bond in acrolein is more thermodynamically favorable while the manipulation of the reaction kinetics can be used to tilt the reaction towards the production of the desired unsaturated alcohol.^{37, 38} Thus, the unique kinetic effects observed on bimetallic surfaces^{11, 42, 84, 93} makes them suitable candidates as model catalytic systems in studying this selective hydrogenation reaction.

Platinum and ruthenium have long been suggested as suitable catalysts for the selective hydrogenation of α , β -unsaturated aldehydes, with the latter having a lower cost but comparable catalytic properties.^{53, 54} In Chapter 4, we showed that on the Ru(001) surface, acrolein mostly desorbs molecularly or decomposes to carbon monoxide (CO), hydrogen (H₂), and surface carbon but a small amount also self-hydrogenates to yield all possible hydrogenation products – propanal, 2-propenol, and 1-propanol – with propanal having the highest yield. On Pt(111), de Jesus and Zaera used temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) to show^{40, 43} that acrolein mostly decomposes to CO, H₂, and surface carbon with the simultaneous formation of small amounts of ethylene, propylene, and ketene, but no hydrogenation products were reported. However Loffreda et al.,⁴⁸ using density functional theory (DFT) calculations, reported that the product selectivity in acrolein hydrogenation of Pt(111) is controlled by the balance between the hydrogenation step and the desorption of the partially hydrogenated products. They found that the hydrogenation of the C=O bond to yield 2-propenol is favored but the desorption barrier of the saturated aldehyde,

propanal, is much lower. Thus, they concluded that the kinetics of the reaction controls reactivity.

The surface chemistry of acrolein and other C_3 oxygenates on Ru(001) and the work done on the growth and characterization of Pt/Ru(001) bimetallic surfaces were discussed in detail in previous chapters. Combining elements from those chapters, we report here on the adsorption and hydrogenation of acrolein on pseudomorphic Pt/Ru(001) NSAs with different platinum coverages from submonolayer to multilayer using temperature-programmed reaction spectroscopy (TPRS) and reflection absorption infrared spectroscopy (RAIRS). The aim is to probe the catalytic properties of the Pt/Ru(001) bimetallic surfaces and to verify whether the well-reported unique kinetic properties of bimetallic systems could possibly be utilized to promote the selective hydrogenation of the C=O double bond in acrolein and the subsequent desorption of the unsaturated alcohol product.

The chamber and evaporator setup and the experimental details are as described in previous chapters.

7.2 Results – Choice of Platinum Coverages

The acrolein hydrogenation experiments were conducted on four different Pt/Ru(001) surfaces based on the pattern observed from the characterization experiments discussed in Chapter 6. Submonolayer coverage with 0.28 ML Pt, monolayer coverage with 1.1 ML Pt, and multilayer coverage with 3.7 ML Pt were prepared and annealed to 750 K for 1 minute after deposition around 340 K to yield an overlayer Pt/Ru(001) NSA. The fourth Pt/Ru(001) surface studied has a submonolayer Pt coverage of 0.67 ML but was annealed to 1000 K, for 1 minute after deposition, to yield a PtRu/Ru(001) surface alloy. For this surface alloy, the LEED images before and after annealing to 1000 K showed no discernible differences. Also, the intensity of the 64 eV Pt AES peak before and after annealing to 1000 K stays the same whereas the intensity of the 273 eV Ru peak increased by ~ 10% after annealing. This suggests a degree of surface mixing with incorporation of Pt atoms into the top Ru layer. Although the amount of Pt in the subsurface cannot be readily estimated, substantial platinum dissolution into the bulk is expected after annealing the surface above 1250 K.⁹⁶ This surface was prepared to study the effect, if any, of surface mixing and the presence of the platinum atoms in the subsurface of the Ru(001) substrate on acrolein hydrogenation.

7.3 TPRS Results

Several TPR spectra were collected after 1.0 L acrolein was adsorbed on the clean and 3.0 L H₂precovered Pt/Ru(001) surfaces at 90 K and the temperature ramped linearly at 2 K/s from 100 to 700 K. The desorption of hydrogen, ethylene, carbon monoxide, 1-propanol, propylene, acrolein, 2-propenol, and propanal was monitored at 2, 26, 28, 31, 39, 56, 57, and 58 amu, respectively. Other masses, 27 amu for ethylene and 60 amu for 1-propanol, were also monitored to differentiate and identify these desorption products. Because most of these masses are present as fragments of acrolein, a deconvolution procedure described in Appendix A1 was applied to each of the TPR spectra shown below (except for acrolein and hydrogen). However, due to the inexact nature of this deconvolution process, there were incomplete cancellations in some of the resulting deconvoluted TPR spectra. These incomplete cancellations can, however, be clearly identified in each spectrum, and thus have no effect on the interpretation of results presented here.

7.3.1 Acrolein and its hydrogenation products

Figure 7.1 shows the deconvoluted TPR spectra of acrolein and its hydrogenation products – propanal, 2-propenol, and 1-propanol. Similar to what was observed on Ru(001), acrolein mainly desorbs molecularly from all the Pt/Ru(001) surfaces around 170 K. The 0.28 ML Pt surface shows additional acrolein desorption at 220 and 270 K, while the alloyed (0.67 ML Pt) and multilayer Pt surfaces show slight peaks around 240 and 280 K. These extra desorption peaks could not be resolved on the monolayer Pt surface but it instead shows a long-tailed desorption to about 350 K. It is noteworthy that the amount of molecular acrolein desorbing from these surfaces is much less than what was observed on the Ru(001) surface (\times 1/10 intensity factor), an effect that is clearly due to the platinum.



Figure 7.1 Deconvoluted TPR spectra for (clockwise from left) acrolein, propanal, 2-propenol, and 1-propanol obtained after exposure of 1.0 L of acrolein to Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K). The acrolein panel contains a spectrum (black) from the clean Ru(001) surface for comparison

The desorption of propanal was not observed from any of the surfaces except the monolayer platinum surface, where desorption is seen around 330 K. The peaks seen in the propanal panel for the 0.28, 3.7, and alloyed 0.67 ML platinum surfaces are due to incomplete cancellation during deconvolution but it can clearly be seen that these peaks are coming from the acrolein. No other hydrogenation product was observed to desorb from any of the Pt/Ru(001) surfaces as revealed by the absence of any peaks in the 1-propanol and 2-propenol panels. These suggests

that the hydrogenation pathway for acrolein is mostly suppressed by the presence of platinum on the Ru(001) substrate.



Figure 7.2 Deconvoluted TPR spectra for (clockwise from left) acrolein, propanal, 2-propenol, and 1-propanol obtained after exposure of 1.0 L of acrolein to 3.0 L H₂ pre-covered Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K)

Similar results, shown in Figure 7.2, were obtained when these Pt/Ru(001) surfaces were precovered with 3.0 L H₂ prior to the adsorption of acrolein. For the 0.67 ML subsurface system, the peaks in the 1-propanol panel are due to miscancellation during deconvolution. Similarly, in the propanal panel, all the peaks are due to miscancellation except for the peak at 339 K for the 1.1 ML surface.



7.3.2 Other desorption products

Figure 7.3 Deconvoluted TPR spectra for (clockwise from left) CO, H_2 , propylene, and ethylene obtained after exposure of 1.0 L of acrolein to Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K). The CO and H_2 panels contain spectra (black) from the clean Ru (001) surface for comparison

CO desorption was observed around 430 K for the 0.28 ML platinum surface, and with increasing platinum coverage, the CO desorption temperature reduces to 365 K for the 1 ML platinum surface and 356 K for the multilayer platinum surface. For the PtRu surface alloy (0.67 ML), two desorption peaks occur at 321 and 420 K, which might suggest CO desorption from Pt-rich and Pt-deficient sites, respectively. This similarly applies to the H₂ desorption spectrum from this PtRu alloy system with the 288 K peak attributed to Pt-rich sites while the 373 K peak

can be attributed to Pt-deficient sites. The hydrogen desorption spectra from the 1.1 and 3.7 ML platinum systems both show a low temperature peak centered around 290 K. However, the high temperature peak is at 414 K for the 1 ML platinum surface compared to 511 K for the multilayer platinum surface. The submonolayer (0.28 ML) surface shows H_2 desorption peaks at 304 and 365 K, which are slightly lower than their corresponding peaks on the Ru(001) surface.

Desorption of hydrocarbons was also monitored by following masses 26, 27, and 39 for ethylene and propylene. In the ethylene panel (mass 26), all the peaks below 300 K are from the fragmentation of molecular acrolein. They are present due to incomplete cancellation during the deconvolution procedure. Thus, ethylene desorption was not observed on any of the submonolayer platinum surfaces. The 1.1 ML platinum surface shows some ethylene desorption with a broad peak centered around 420 K. However, the multilayer platinum surface shows clear ethylene desorption with a relatively large peak at 348 K and a slight shoulder at 492 K. Low temperature propylene desorption was observed at 130 K on all the Pt/Ru(001) surfaces. Again, the 150 – 280 K peaks on all the surfaces are from the fragments of molecular acrolein that were not completely removed during deconvolution. Thus there is no high temperature propylene desorption begins to appear in the TPR spectra. The 1.1 ML platinum surface shows propylene desorption at 375 K while on the 3.7 ML platinum surface, propylene desorbs around 340 K and at 348 K for the PtRu alloy system.

When these Pt/Ru(001) surfaces were pre-exposed to 3.0 L H₂ followed by acrolein adsorption, similar results were observed as shown in Figure 7.4.



Figure 7.4 Deconvoluted TPR spectra for (clockwise from left) CO, H_2 , propylene, and ethylene obtained after exposure of 1.0 L of acrolein to 3.0 L H_2 pre-covered Pt/Ru(001) surfaces with Pt coverages of (red) 0.28 ML, (blue) 1.1 ML, (green) 3.7 ML, and (magenta) 0.67 ML (annealed to 1000 K)

7.4 RAIRS Results

From the TPRS results, the 1.1 ML Pt/Ru(001) surface was the only surface to show any appreciable hydrogenation activity with the desorption of propanal at 330 K. To confirm this result, the adsorption characteristics and hydrogenation of acrolein on a 1 ML Pt/Ru(001) surface were studied via a series of RAIRS experiments.



Figure 7.5 RAIR spectra taken at 90 K for the indicated exposures of acrolein on 1 ML Pt/Ru(001)

Figure 7.5 shows a series of RAIR spectra obtained at 90 K after different amounts of acrolein were exposed to a 1 ML Pt/Ru(001) NSA at 90 K. At lower exposures (≤ 1.0 L), the RAIR spectra show the characteristic acrolein modes but the modes in the CH stretch region only begin to appear at exposures ≥ 2.0 L. The 5.0 L spectrum shows all the modes seen on the clean Ru(001) surface (see Figure 4.6) but a weak peak at 1793 cm⁻¹, not present on the clean Ru(001) surface, can be seen here and it shifts to lower wavenumbers with increasing acrolein coverage. At 5.0 L exposure, this peak is split into two components at 1729 and 1786 cm⁻¹. In the 5.0 L spectrum, the very intense v(C=O) peak at 1699 cm⁻¹ suggests that on the 1 ML platinum surface, acrolein adopts a geometry with the C=O bond perpendicular to the surface whereas the C=C bond is almost parallel to the surface (hence the small v(C=C) peak at 1651 cm⁻¹). This

adsorption geometry likely renders the C=C bond more susceptible to attack by H adatoms on the surface thus resulting in propanal as the hydrogenation product. This was confirmed by annealing the 5.0 L surface to higher temperatures for 1 minute and then cooling it down to 90 K before taking the spectra shown in Figure 7.6.



Figure 7.6 RAIR spectra of 5.0 L acrolein on 1 ML Pt/Ru(001) surface taken at 90 K after annealing to the indicated temperatures for 1 minute

Annealing to 150 K results in the appearance of a new peak in the CH stretch region at 2937 cm⁻¹, which was not present in the 90 K acrolein spectra in Figure 7.5. This peak can be readily attributed to v_{as} (CH₂) of propanal and the v(C=O) peak at 1655 cm⁻¹ can also be assigned to propanal (see Figure 4.8). Whereas the asymmetric CH₂ stretch mode can be seen up to 250 K without any shift in frequency, the C=O stretch mode persists on the surface to 300 K and is gradually blueshifted to 1672 cm⁻¹. Similarly, the peak at 1736 cm⁻¹, which persists up to 300 K can also be tentatively assigned to the v(C=O) of propanal formed on a platinum site with a

different local atomic geometry (see Discussion section below). These peaks have been assigned to propanal since they coincide with the desorption of propanal from the ~1 ML platinum surface (as shown in the top right panel of Figure 7.1, the leading edge of the TPR spectra is around 150 K). The right panel shows the corresponding v(C=O) region for adsorbed CO. At 150 and 200 K, the peaks seem to arise from poor cancellation of background CO displaced after adsorption of acrolein since there are no peaks in that region in their corresponding single beam spectra. The 2067 cm⁻¹ peak in the 250 – 400 K spectra is adsorbed CO produced from the decarbonylation of acrolein.

7.5 Discussion

7.5.1 Comparison of TPRS results on Pt/Ru(001) with Pt(111) and Ru(001) surfaces

The inactivity of all the Pt/Ru(001) surfaces studied, with the exception of the 1.1 ML platinum surface, towards acrolein hydrogenation suggests that the platinum atoms have a very strong effect on the properties of the Ru(001) surface even at low coverages. As shown in Chapter 4, the bare Ru(001) surface is active for the hydrogenation of acrolein to yield all possible hydrogenation products with propanal being the major one. De Jesus and Zaera, on the other hand, have shown that Pt(111) is inactive towards acrolein hydrogenation but undergoes decarbonylation to yield mostly carbon monoxide and small amounts of ethylene, propylene, and ketene.⁴⁰ Thus, comparing our results on the Pt/Ru(001) surfaces with those obtained on Ru(001) and Pt(111) should reveal the influence of the platinum atoms on the catalytic properties of the Ru(001) substrate.

As shown in Figure 2, the 0.28 ML platinum surface shows no appreciable hydrogenation activity even though most of the Ru(001) substrate is free of platinum. Similarly, the difference

in the CO and H_2 TPR spectra from this surface and those from the clean Ru(001) surface suggests that the presence of even small amounts of platinum on the Ru(001) surface is enough to alter its surface chemistry. The submonolayer (0.67 ML) PtRu alloy system also shows no hydrogenation activity but the CO and H₂ TPR spectra are different from what was observed on both the 0.28 ML Pt/Ru(001) and clean Ru(001) surfaces. The influence of the surface mixing can be seen in the noticeable peak at 321 K in the CO spectrum, a temperature that is even lower than what was observed on Pt(111).⁴³ This influence is also noticeable in the H₂ spectra with two distinct peaks at 288 and 373 K corresponding to desorption from platinum-rich (or alloyed) and platinum-free sites, respectively. The estimated CO yield from both the surface platinum and submonolayer PtRu alloy systems are, however, similar and are about three times smaller relative to what was estimated from the clean Ru(001) surface. Whereas both the surface platinum and submonolayer PtRu alloy systems are completely inactive towards ethylene formation, low temperature propylene desorption around 135 K was observed on both surfaces. This was also observed on clean Ru(001) around the same temperature after adsorption of 2propenol (see Figure 5.2). However, it was neither observed on Ru(001) nor on Pt(111) during acrolein TPRS experiments. The high temperature propylene desorption observed from the PtRu alloy system at 348 K is likely not a subsurface effect but the result of the higher platinum coverage (0.67 ML) relative to the 0.28 ML platinum system since the amount of propylene desorbing at higher temperatures (above 300 K) increases with increasing platinum coverage. The effect of the Ru(001) substrate still is relatively more noticeable on these submonolayer surfaces.

Similar to the submonolayer systems, the multilayer (3.7 ML) platinum surface shows no appreciable acrolein hydrogenation activity. However, the decarbonylation pathway leading to

the formation of CO and hydrocarbons is more pronounced on this surface. This is completely different from what was observed on Ru(001) (see Chapter 4). The CO desorption peak at 356 K is much lower compared to the 455 K observed on Ru(001) but much closer to the CO peak desorption temperature on Pt(111) at 403 K.43 Similarly, the estimated CO yield on this multilayer surface is about 2.5 times smaller relative to the yield from the Ru(001) surface. The peak shape and peak desorption temperatures for H₂ from this multilayer surface are also very similar to what was observed by de Jesus and Zaera on Pt(111).⁴³ The H₂ peak at 290 K seems to be from acrolein decarbonylation to ethylene, whereas the higher temperature peak at 511 K can be attributed to the formation of surface carbon via dehydrogenation of hydrocarbon moieties left on the surface. On Pt(111), ethylene desorption was observed at 330 K while propylene was observed to desorb with a broad peak centered at 335 K.⁴³ Similarly, on the multilayer (3.7 ML) platinum surface, ethylene desorbs with a sharp peak at 348 K and an additional small but broad peak centered around 490 K. High temperature propylene desorption at 340 K occurs along with low temperature propylene desorption around 130 K, which was also observed on all other Pt/Ru(001) NSAs studied. This reduction of acrolein to propylene has previously been reported on platinum electrodes in acid media.¹⁰⁴ The formation of propylene via acrolein dimerization as proposed by de Jesus and Zaera⁴⁰ can be ruled out here since this requires the concurrent formation of ketene, which was not observed. A plausible mechanism for propylene formation might be the formation of an allyl alkoxide via the interaction of the acrolein C=O bond with the surface. C-O scission and allyl hydrogenation (not necessarily in that order) would yield propylene and surface oxygen.⁴⁵ The oxygen could then be removed from the surface by hydrogenation to H₂O, which was observed to desorb when allyl alcohol (propenol) was adsorbed on Pd(111).⁴⁵

All the data presented above suggests that this 3.7 ML Pt/Ru(001) surface is effectively acting like a Pt(111) surface. In their work⁹⁴ on the growth of platinum layers on Ru(001) using CO as a probe molecule, Jakob and Schlapka concluded that at platinum coverages \geq 3 ML, the substrate effect is negligible and the properties of the Pt/Ru(001) surface gradually approach those of Pt(111). We reach the same conclusion based on the similarities in the TPRS results presented here on the 3.7 ML Pt/Ru(001) surface and those reported for Pt(111).⁴³

The TPRS results obtained on the 1.1 ML platinum surface shows it is active for acrolein hydrogenation to propanal with a peak desorption temperature of 332 K (see Figure 7.1). The CO and H_2 desorption spectra (Figure 7.3) show broad desorption peaks that are distinct from the relatively sharp peaks observed on the other Pt/Ru(001) surfaces and their single crystal counterparts.

On all the Pt/Ru(001) NSAs studied, the amount of molecular acrolein that desorbs is much less than what was observed on the clean Ru(001) surface, as shown in Table 7.1 below. Similarly, less CO desorbs from all the NSAs relative to clean Ru(001). Estimates of the CO yield on all the surfaces from the integrated TPRS areas suggest that the multilayer (3.67 ML) NSA gave the most CO desorption, which is still about 2.6 times less than the amount that desorbs from Ru(001). Thus, since there is no significant hydrogenation activity on almost all the NSAs and the hydrocarbon yield is relatively small, the decomposition of these hydrocarbons to yield surface carbon seems most likely. This conclusion was corroborated by AES spectra taken after each TPRS run with the amount of surface carbon left over estimated to be > 15% from the increase in the Ru MNN and C KLL Auger peaks which overlap at 273 eV.

	TPRS Yield (×10 ⁻³ ML)			
Surface	CH ₂ CHCHO (acrolein)	СО	CH ₃ CH ₂ CHO (propanal)	
bare Ru(001)	249	227	6.84	
0.28 MLE Pt/Ru(001)	21.4	70.9	0	
0.67 MLE PtRu alloy	17.8	56.8	0	
1.1 MLE Pt/Ru(001)	47.8	27.2	4.59	
3.7 MLE Pt/Ru(001)	15.1	87.2	0	

Table 7.1 Yields in units of $\times 10^{-3}$ ML of acrolein, CO, and propanal desorbing from the indicated surfaces during TPRS experiments after exposure to 1.0 L of acrolein at 90 K. The yields were calculated as described in Appendix A2

7.5.2 TPRS and RAIRS results on ~1 ML pseudomorphic Pt/Ru(001) NSA – deviation from Pt(111) and Ru(001) surfaces

Compared to the submonolayer and multilayer systems discussed above, the 1.1 ML pseudomorphic Pt/Ru(001) surface displays properties that deviate from those of either Pt(111) or Ru(001). Whereas the Pt(111) surface shows no acrolein hydrogenation activity,⁴⁰ the 1.1 ML Pt/Ru(001) NSA is active towards acrolein hydrogenation and gives propanal as the only hydrogenation product, unlike Ru(001) where all possible hydrogenation products were observed though propanal had the highest yield as shown in Chapter 4. Also of note is the higher temperature (332 K) desorption of propanal on the 1.1 ML platinum surface compared to the propanal peak desorption temperature of 180 K on Ru(001) (Figure 4.3) though the propanal

yield, as estimated from the integrated TPRS areas, is about 35% less on the 1.1 ML Pt/Ru(001) surface. On the 1.1 ML Pt/Ru(001) NSA, hydrocarbon desorption was also observed with relatively small amounts of ethylene and propylene desorption at higher temperatures compared to Pt(111). In Figure 7.3, ethylene desorbs with a small but broad peak centered around 420 K, while propylene desorption is centered at 375 K whereas on Pt(111), these molecules desorb at 330 and 335 K, respectively.⁴³ No hydrocarbon desorption was observed from Ru(001) as discussed in Chapter 4. The CO TPR results for the 1.1 ML platinum surface shows a very broad peak centered at 365 K with the yield an order of magnitude less than that from the clean Ru(001) surface.

The formation of propanal on the ~1 ML Pt/Ru(001) NSA was also verified by RAIRS as shown in Figure 7.6. The 1655 and 2937 cm⁻¹ peaks, in the 150 K spectrum, assigned to v(CO) and v_{as} (CH₂) of propanal respectively, suggest that propanal is present on the surface and it is noteworthy that in the TPR spectra for propanal on the ~1 ML Pt/Ru(001) surface, the onset of propanal desorption is also around 150 K. The propanal CO stretch peak persists up to 300 K albeit with reduced intensity and a blue shift to 1672 cm⁻¹, which is indicative of a weakened interaction between the propanal, particularly the C=O group, and the metal surface. This weakened interaction is to be expected since the rate of propanal desorption is increasing around those temperatures as seen in the TPRS trace in Figure 7.1. This gradual desorption of propanal from the surface might also explain the disappearance of the v_{as} (CH₂) peak above 250 K because the amount left on the surface is beyond the RAIRS detection limit. The additional peak at 1736 cm⁻¹, which appears around 200 K and persists up to 300 K, along with the 1670 cm⁻¹ peak can be tentatively assigned to v(CO) in propanal adsorbed on platinum sites with a different local geometry, such as kink or step sites, or to v(CO) in physisorbed propanal.^{63, 74} The 1806 cm⁻¹

peak present in both the 150 and 200 K spectra disappears at higher temperatures and cannot be readily assigned. Above 300 K, no peak was observed in the RAIR spectra in this region. The adsorbed CO stretch region shown in the right panel of Figure 7.6 shows a broad peak around 2067 cm⁻¹ in the 250 K spectrum, which is slightly redshifted to 2065 cm⁻¹ after annealing the surface to 400 K. This peak can be readily assigned to v(CO) of adsorbed CO based on the experiments of directly adsorbed low coverage CO on Pt/Ru(001) (bottom spectrum of Figure 7.7). The broadness of these peaks suggests a high degree of disorder in the platinum layer of the ~1 ML Pt/Ru(001) surface. Furthermore, the relatively low intensity of these broad peaks compared to the sharper, more intense peaks observed on Ru(001) (top two spectra, Figure 7.7) and Pt(111),⁴³ and the similarly small CO TPR desorption peak observed on this ~1 ML platinum surface suggests that some of the acrolein underwent C-O scission and hydrogenation to propylene as discussed earlier and as seen in Figure 7.3. It is noteworthy that the CO yield from this surface (right panel, Figure 7.6) is less than 0.1 L CO equivalent (bottom spectrum, Figure 7.7). All these observations support our earlier hypothesis of the presence of kink and step sites in the platinum layer of the Pt/Ru(001) NSAs and, importantly, that the ~1 ML platinum system possesses properties that are unique from those observed on Pt(111) or Ru(001).

7.5.3 Comparison with other bimetallic NSAs

The selective hydrogenation of acrolein has been studied on other bimetallic surfaces. Murillo and Chen⁴² have used temperature-programmed desorption (TPD) and high-resolution energy loss spectroscopy (HREELS) to show that the subsurface bimetallic Pt-Ni-Pt(111) system, with the nickel residing below the topmost platinum layer, is active for the partial hydrogenation of acrolein to yield both 2-propenol and propanal with the latter being the main product. The complete hydrogenation product, 1-propanol, was not observed. However, a lower hydrogenation

activity resulting in the desorption of mostly propanal was observed on all the surface Ni/Pt(111) systems they studied. This is different from what was observed on the Pt/Ru(001) bimetallic surfaces reported here with none of the surfaces showing any hydrogenation activity except the \sim 1 ML platinum surface that shows propanal as the only hydrogenation product. This suggests that the morphology of the platinum layer on the Ru(001) substrate, with kinks and steps present along with the terrace sites, enhances the dehydrogenation and decarbonylation pathways of acrolein. The selective hydrogenation activity and other unique properties observed on the \sim 1 ML Pt/Ru(001) can be partly attributed to the optimum balance between the electronic and lateral strain effects within the pseudomorphic platinum layers and the effect induced by the substrate-overlayer interaction.



Figure 7.7 RAIR spectra showing the free CO stretch region only all taken at 90 K. Top two spectra were taken after *1.0 L acrolein* was exposed to a clean Ru(001) surface at 90 K and annealed to the indicated temperatures. Bottom spectrum was taken after *0.1 L CO* was exposed to a 1.6 MLE Pt/Ru(001) NSA at 90 K

7.6 Conclusion

The catalytic properties of Pt/Ru(001) NSAs have been examined via the adsorption and selective hydrogenation of acrolein using TPRS and RAIRS. The TPRS results showed that Pt/Ru(001) NSAs with submonolayer and multilayer platinum coverages show no hydrogenation activity, while propanal desorption was observed on the ~ 1 ML platinum surface. The TPRS results also show that on all the Pt/Ru(001) NSAs, most of the acrolein desorbs molecularly or undergoes decarbonylation to yield CO and lower hydrocarbons, and can also be reduced to yield propylene with the hydrocarbon yield increasing with platinum coverage. Overall, the submonolayer surface and subsurface Pt/Ru(001) systems showed properties similar to Ru(001) but the presence of even low platinum coverages markedly alters the properties of the Ru(001)substrate. Above a platinum coverage of 3 ML, the Pt/Ru(001) NSA effectively acts like a Pt(111) surface. The ~1 ML Pt/Ru(001) NSA was shown to possess properties distinct from those of Pt(111) or Ru(001). Unlike Pt(111), it is active towards acrolein hydrogenation and, unlike Ru(001), it yields propanal as the only hydrogenation product with a peak desorption temperature much higher than that observed on Ru(001). The formation of propanal on the ~1 ML Pt/Ru(001) NSA was also verified with RAIRS.

8. Surface-Enhanced Infrared Response of Isolated Platinum Nanostructures Fabricated on Single Layer Graphene (SLG) on Ru(001)

8.1 Introduction

In this chapter, we present the observation of enhanced infrared intensity on isolated platinum nanoclusters, which were fabricated on a single layer of graphene (SLG) grown epitaxially on Ru(001). Graphene is a well-known, versatile, and ideal two-dimensional material consisting of only one layer of carbon atoms arranged in a honeycomb lattice. It possesses several interesting chemical, mechanical, electronic, optical, and plasmonic properties.¹⁰⁵⁻¹⁰⁸ Graphene was initially synthesized by peeling off graphite using adhesive tapes, however, this method yielded only limited amounts not suitable for industrial use.^{105, 106, 109} Thus, other synthetic methods that enable large scale graphene production have been developed.¹¹⁰ Most of these methods often yield graphene with poor structural ordering and containing defects and impurities. However, fundamental studies into the properties and possible applications of graphene often require the growth of high-quality single-crystalline graphene systems. These have been achieved by growing graphene on different metal surfaces¹⁰⁷ with, for example, the epitaxial growth of graphene on a Ru(001) substrate producing highly crystalline, well-ordered, single layer graphene. The resulting graphene has a periodically corrugated surface due to lattice mismatch between graphene and the Ru(001) surface, and thus provides a good template to guide the adsorption and assembly of functional nanostructures including quantum dots,¹¹¹ preferential adsorption of planar organic molecules,¹¹² and fabrication of well-ordered metal nanoclusters.¹¹³⁻ 116

With the critical role played by carbon materials in many catalytic processes, especially as catalyst supports,^{117, 118} studies of the surface chemistry of metal-graphene systems can

contribute to the fundamental understanding of the role of carbon in many important heterogeneous catalytic reactions. More recently, metal cluster deposition has been studied on the single layer graphene/Ru(001) surface¹¹⁸⁻¹²⁰ with platinum and rhodium found to form dispersed small clusters whereas palladium and cobalt form larger clusters at similar coverages.¹²¹ Previously, strong enhancement in the infrared adsorption of molecules in close proximity to rough metal surfaces has been observed for various metals, especially silver and gold, using ATR spectroscopy^{122, 123} in a technique now referred to as surface-enhanced IR absorption (SEIRA).¹²⁴ Here we have studied the growth of single layer graphene on Ru(001) and the fabrication of isolated platinum nanoclusters on this surface. The graphene layer covers the Ru(001) surface entirely, thereby serving as a chemically inert substrate. Using CO-RAIRS, we also found that the Pt/SLG/Ru(001) system gave up to nine-fold enhanced infrared response compared to the bare Ru(001) surface. To our knowledge, this is the first time such enhancement, which we partly attribute to the presence of isolated platinum nanoclusters, has been reported on platinum in RAIRS experiments in UHV.

The chamber and evaporator setup and experimental details are as described in previous chapters.

8.2 Growth of Single Layer Graphene (SLG) on Ru(001)

Graphene was grown on Ru(001) following the method of Li et al.¹¹³ The clean Ru(001) surface was exposed to ~7.5 x 10^{-8} Torr of C₂H₄ (g) at room temperature and then slowly heated to 1300 K while maintaining the C₂H₄(g) pressure. The sample was kept at that temperature for 18 minutes after which the C₂H₄(g) supply was turned off. The surface is further annealed for 2 minutes before it is slowly cooled to room temperature. The presence of an epitaxial single graphene layer on the Ru(001) substrate is confirmed by a typical LEED image, taken at different regions of the substrate (Figure 8.1), showing sharp, satellite spots surrounding the (1×1) spots of the Ru(001) substrate.¹¹³ Moving the sample across the beam spot of the LEED electron gun shows no appreciable change and/or rotation of the diffraction pattern, which means that the epitaxial graphene layer covers the whole surface and is single crystalline with no multilayer graphene or amorphous carbon, as expected on the Ru(001) surface.^{118, 121}



Figure 8.1 LEED images of epitaxial single layer graphene grown on a Ru(001) substrate. The images were taken at different regions of the Ru(001) surface by moving the sample across the LEED electron gun (with x = 0.510 being the center spot). All images were taken with beam energy of 70 eV at 300 K



Figure 8.2 Left, Auger spectra of the clean Ru(001) surface and single layer graphene grown (SLG) on Ru(001) with the ratio of the positive (+ve) to the negative (-ve) portions of the 273 eV peak included. Right, LEED image taken at 300 K after annealing the surface to 600 K for 1 minute

This was further confirmed by taking the Auger spectra of the graphene/Ru(001) surface and using the ratio of the positive to the negative parts of the 273 eV Auger peak, which is composed of the Ru MNN peak and the C KLL peak. A ratio of 0.46 confirms the presence of a complete, single epitaxial graphene layer.¹⁰¹ Annealing the graphene surface to 600 K for 1 minute and repeating the LEED and AES experiments gave similar results showing that the graphene is stable on the Ru(001) up to, at least, 600 K.

To further verify that the graphene layer completely covers the Ru(001) surface, a TPD experiment of saturation coverage (5.0 L) of CO adsorbed on the SLG/Ru(001) surface at 90 K was carried out and the result shown in Figure 8.3. The absence of any peak in the TPD spectrum corroborates the results from both the LEED and AES measurements.



Figure 8.3 TPD results following a 5.0 L CO exposure (saturation coverage on clean Ru(001)) from (bottom) clean and (top) single layer graphene-covered Ru(001) surface

8.3 Fabrication of Isolated Platinum Nanoclusters on SLG/Ru(001) and Characterization using AES, CO-RAIRS and CO-TPD

As discussed in Chapter 6, Pt/Ru(001) NSAs with different platinum coverages were prepared and characterized with AES, CO-RAIRS, and CO-TPD. Using those platinum coverages as guides, similar amounts of platinum were deposited on the SLG/Ru(001) surfaces for ease of comparison of the resulting CO-RAIRS intensities. Similar to the deposition parameters developed in Chapter 6, platinum was deposited with the evaporator heated to ~1850 K and the Ru(001) substrate around 320 K (and once, at 170 K) followed immediately with taking the Auger spectra of the resulting surface without any post-deposition annealing. This was to ensure that the platinum nanoclusters remain isolated on the surface and do not coalesce into larger islands, which occurs when the surface is heated above 600 K. Afterwards, several RAIR spectra were collected at 90 K by exposing the Pt/SLG/Ru(001) to different amounts of CO up to saturation (5.0 L), followed immediately by a TPD experiment from 100 to 620 K. A post-TPD Auger spectrum was then collected to estimate the amount of platinum left on the surface. The resulting Auger, RAIR, and TPD spectra are presented and discussed below.

Six different platinum coverages were studied – 0.11, 0.17, 0.32, 0.35, 0.85, and 1.0 MLE – with all deposition done at a substrate temperature of 320 K except for the 0.32 MLE surface where the Ru(001) substrate was cooled to 170 K prior to deposition and subsequently allowed to warm to room temperature. None of the surfaces were annealed after deposition except for the 0.85 MLE surface which was annealed to 750 K for 1 minute after deposition. The results obtained on this surface will be presented later.

The morphology and sizes of these platinum nanoclusters can be deduced from the works of Donner and Jakob¹²⁵ and Zhang et al.¹¹⁸ Both groups have shown that platinum nanoclusters preferentially nucleate and grow in the fcc regions within the Moiré unit cells of the graphene/Ru(001) surface. Furthermore they observed that at < 0.5 ML platinum coverage, the platinum clusters are highly dispersed with uniform sizes (~ 3 nm in diameter). However, while Donner and Jakob observed perfectly periodic arrays of platinum islands, Zhang et al. reported randomly distributed platinum clusters. Donner and Jakob suggested this difference could be due to the lower deposition temperature and different deposition rates used by Zhang et al. Since our deposition parameters are similar to those of Donner and Jakob (similar deposition time and substrate temperature) we assume that the platinum nanoclusters studied here will exhibit similar

size distribution and morphology. Thus, from the results of Donner and Jakob, we can deduce that our 0.11 - 0.35 MLE Pt/SLG/Ru(001) systems should display long range order with almost all the Moiré unit cells containing a platinum nanocluster and the fraction of nanoclusters with height exceeding one monolayer increasing steadily with platinum coverage. These monolayer clusters, dominant at low coverages, contain a minimum of 12 platinum atoms (with a presumably hexagonal shape) and with increasing coverage, the number of platinum atoms and the height of the nanoclusters also increases. Further information on the height and shape of these nanoclusters could be obtained from the results obtained by Yi et al.,¹¹⁹ where they also used similar deposition parameters to deposit platinum on the graphene/Ru(001) surface. They showed that, at low coverages, the typical nanocluster heights are 0.5, 0.88, 1.27, and 1.65 nm which corresponds to platinum nancolusters consisting of one, two, three, and four atomic layers, respectively. And with increasing coverage, up to 0.4 ML, the nanoclusters remain separate but increase their height with a concomitant but slow increase in their diameter without coalescence. The diameter of the nanoclusters were also shown to range from 1.7 - 3.7 nm which is similar to what was reported by Donner and Jakob.¹²⁵

From these results, we can safely deduce that our 0.11 - 0.37 MLE Pt/SLG/Ru(001) system consists of highly ordered, monodispersed platinum nanoclusters located in the fcc region of the Moiré unit cells of the single graphene layer. These platinum nanoclusters have heights of up to 4 atomic layers (1.65 nm) and are up to 3 nm in diameter. This tendency of the nanoclusters to increase in height before growing their diameter might be due to a certain confinement effect imposed by the Moiré pattern such that there remains one nanocluster per Moiré unit cell without coalescence, leading to the observed relative uniformity in their sizes.¹¹⁹ At coverages above 0.5

ML, like the 1.0 MLE Pt/SLG/Ru(001) system studied here, neighboring platinum nanoclusters recombine to form larger units extending across borders of a Moiré unit cell.^{119, 125}



Figure 8.4 Auger spectra of different Pt/SLG/Ru(001) surfaces with the platinum monolayer equivalent (MLE) coverage indicated on each spectrum

Here, the platinum monolayer equivalent (MLE) coverages were estimated by taking the ratio of the 64 eV Pt and 273 eV Ru Auger peaks (after normalization, as described in Chapter 6, to remove carbon contribution from the 273 eV peak) collected from different regions of the surface and taking a simple average. The corresponding standard deviation ranged from ± 0.02 at low coverages (up to 0.40 MLE) and \pm 0.18 at higher coverages (up to 1.0 MLE). This shows that, at low coverages, the nanoclusters are relatively uniform in size, in agreement with the results of Yi et al.¹¹⁹ and Donner and Jakob¹²⁵ whereas at higher coverages there is more variation in the size and height of the nanoclusters.



Figure 8.5 RAIR (left) and TPD (right) spectra of saturated (5.0 L) CO on Pt/SLG/Ru(001) with coverages as indicated

From the TPD spectra of saturated (5.0 L) CO on different Pt/SLG/Ru(001) surfaces, shown in Figure 8.5 (right panel), the CO coverages were estimated using the integrated TPD area and comparing with the value of 0.68 ML for the clean Ru(001) surface.^{126, 127} These estimates are listed in Table 8.1 along with similar estimates from some of the Pt/Ru(001) NSAs discussed in Chapter 6.

The peak areas for the 5.0 L CO RAIR spectra taken at 90 K (left panel, Figure 8.5) were also estimated with the positive peak arising from the background CO subtracted out. Similar

estimates were also calculated for the CO-RAIR peaks of some Pt/Ru(001) NSAs shown in Figure 6.8. It is important to note that the integrated RAIR areas were calculated **only** for the peaks arising from CO adsorbed at on-top sites of both platinum and ruthenium, while any peak arising from adsorption at bridge sites was excluded since this area is very small relative to the total area. All these are listed in Table 8.1 along with the RAIR area per CO molecule, which is the ratio of the integrated area of the RAIR peaks to the estimated CO coverage (in ML).

	5.0 L CO Integrated Area			RAIR Area
Surface	TPD (× 10 ⁻⁷)	RAIR	ML equivalent	per CO molecule
bare-Ru	14.0	0.5241	0.680	0.7707
0.12MLE Pt/Ru	10.1	0.4215	0.491	0.8581
0.23MLE Pt/Ru	7.95	0.4937	0.386	1.2789
0.38MLE Pt/Ru	5.70	0.4686	0.277	1.6918
0.87MLE Pt/Ru	5.45	0.4807	0.265	1.8159
0.11MLE Pt/SLG/Ru	0.43	0.0504	0.021	2.3940
0.17MLE Pt/SLG/Ru	0.56	0.1518	0.027	5.5513
0.32MLE Pt/SLG/Ru	0.89	0.3116	0.043	7.2384
0.35MLE Pt/SLG/Ru	1.02	0.2856	0.050	5.7696
~1.0MLE Pt/SLG/Ru	1.81	0.5622	0.088	6.4036

Table 8.1 Integrated TPD Area of saturation coverage of CO on different Pt/Ru(001) and Pt/SLG/Ru(001) surfaces and the ML equivalent

From all these, the RAIR enhancement factor (REF) due to the presence of the graphene layer was estimated for each Pt/SLG/Ru(001) surface by taking the ratio of the RAIR area per CO

molecule for that Pt/SLG/Ru(001) surface to that of the Pt/Ru surface with a similar platinum coverage (as indicated by the Pt/Ru NSA coverages in bracket in the last column of Table 8.2). Similarly, the REF values due to the presence of the graphene layer in the Pt/SLG/Ru(001) surfaces relative to the bare Ru(001) surface were also calculated and included in the table.

	RAIR Enhancement Factor (REF)			
Surface	per Pt/Ru(001) NSA	per bare Ru(001)		
0.11MLE Pt/SLG/Ru	2.79 (0.12 Pt/Ru)	3.11		
0.17MLE Pt/SLG/Ru	4.34 (0.23 Pt/Ru)	7.20		
0.32MLE Pt/SLG/Ru	4.28 (0.38 Pt/Ru)	9.39		
0.35MLE Pt/SLG/Ru	3.41 (0.38 Pt/Ru)	7.49		
~1.0MLE Pt/SLG/Ru	3.53 (0.87 Pt/Ru)	8.31		

Table 8.2 RAIR Enhancement Factors (REF) calculated for different Pt/SLG/Ru(001) surfaces relative to Pt/Ru(001) NSAs of similar coverages (as indicated in brackets) and to bare Ru(001)

From the above, it is clear the the presence of the graphene layer leads to an increase in the infrared response as shown by the enhancement factors in Table 8.2 of up to 4-fold increase (and 9-fold compared to bare Ru(001)). Also, there seems to be no platinum coverage limit (at least up to 1 MLE) for this enhancement effect, though optimum REF values were observed for platinum coverages of ~0.3 MLE where the platinum nanoclusters remain separated with no coalescence or coarsening into big islands.¹¹⁹

It is noteworthy that both the 0.32 and 0.35MLE Pt/SLG/Ru(001) surfaces gave similar enhancement factors even though the former was deposited with the substrate temperature at 170 K and allowed to warm to room temperature compared to 320 K for the latter which suggests

that keeping the substrate temperature at or below room temperature during deposition does not significantly affect the enhancement effect. However, post-deposition annealing does affect the observed REF value as discussed below for the 0.85MLE Pt/SLG/Ru(001) surface, which was grown at similar substrate temperature (320 K) but annealed after deposition to 750 K for 1 minute. The TPD and RAIR spectra of the surface with that of 0.87 MLE Pt/Ru(001) NSA (similar platinum coverage) are shown in Figure 8.6. The calculated REF value using similar procedure as before is 2.74 relative to the 0.87MLE Pt/Ru(001) NSA and 6.47 relative to the bare Ru(001) surface. These values are much smaller than the values obtained for the nonannealed Pt/SLG/Ru(001) surfaces, even those with lower platinum coverages. Thus part of the requirement for better IR enhancement seems to be the presence of isolated platinum nanoclusters rather than platinum islands on the graphene layer. This suggests therefore that the enhancement effect arises, at least in part, from the preference of the platinum nanoclusters to nucleate and grow exclusively within^{118, 119, 125} graphene Moiré unit cells as opposed to their preference for growth along the graphene Moiré boundaries observed in the graphene/Pt(111) system.¹¹⁶ This preference limits the size (height and diameter) of the nanocluster and ensures that the nanoclusters are isolated from one another (at low coverages), both of which are suggested by Osawa¹²⁸ as key requirements in the observation of enhanced IR response. Thus, coalescence of the nanoclusters into larger islands, seen at higher coverages or by annealing above 600 K, leads to a significant reduction in the observed enhancement.



Figure 8.6 Left, RAIR spectra taken at 90 K on 0.85 MLE Pt/SLG/Ru(001) (solid line) and 0.87 Pt/Ru(001) (dashed line) at different CO exposures indicated in the figure. Right, TPD spectra of saturated CO exposure (5.0 L) at 90 K on the same surfaces (spectrum from SLG/Ru(001) surface is included for comparison)
8.4 Pt/SLG/Ru(001) Surface after Temperature-Programmed Desorption Experiment



Figure 8.7 Left, Auger spectra of different SLG/Ru(001) surfaces, as indicated in the figure, showing a reduction in the intensity of the 64 eV Pt peak. All Auger spectra were collected at the same regions on the surface. Right, RAIR spectra of saturated (5.0 L) CO on the Pt/SLG/Ru(001) surfaces shown in the left panel

Auger and RAIR spectra collected on the Pt/SLG/Ru(001) after the TPD experiments show a diminution in the platinum coverage. For the 0.17MLE Pt/SLG/Ru(001) surface, Figure 8.7 (left panel) shows a much reduced intensity for the 64 eV Pt peak in the Auger spectrum collected after the TPD experiments relative to the intensity seen in the spectrum collected immediately after platinum deposition. This diminution in intensity was estimated to be over 70%. The RAIR spectra shown in the right panel of Figure 8.7 corroborate the observation from the Auger experiments with a similar diminution (over 70%) in the intensity of the v(CO) peak around 2070 cm⁻¹ for the post-TPD surface and the absence of the bridge-site CO peak around 1848 cm⁻¹. Since platinum desorption at these temperatures (≤ 650 K) can be easily ruled out (no platinum

desorption, monitored at 194 and 195 amu, was observed by the mass spectrometer), one possible explanation for the diminution might be a reduction in the thickness (or height) of these platinum nanoclusters at elevated temperatures and a coalescing across the graphene Moiré unit cells.¹²¹ This change in the morphology of the platinum nanoclusters on the post-TPD surface can also be seen in the TPD experiments for saturated CO on the 0.30MLE Pt/SLG/Ru(001) surface with the spectra from second and third TPD runs similar but noticeably different from the first TPD spectrum collected immediately after platinum deposition.



Figure 8.8 TPD spectra collected after exposing saturated (5.0 L) CO, at 90 K, to 0.30 MLE Pt/SLG/Ru(001) surface. Run 1 spectrum was collected immediately after deposition while Runs 2 and 3 were collected after Runs 1 and 2, respectively. The integrated TPD area for each spectrum is also included

8.5 Conclusion

Complete single layer graphene was grown on Ru(001) substrate and successfully characterized with AES, LEED, and CO-TPD. Isolated platinum nanoclusters grown on the graphene layer were shown to exhibit enhanced infrared response with REF values of up to 4.0 (or ~ 9.0 relative to the bare Ru(001) surface). This enhancement effect was partly attributed to the preference of the platinum nanoclusters to nucleate and grow exclusively within graphene Moiré unit cells resulting in highly ordered, monodispersed platinum nanoclusters with heights of up to 4 atomic layers (1.65 nm) and up to 3 nm in diameter. Annealing the surface leads to a decrease in the height of the nanoclusters and coalescence into larger islands resulting in a gradual reduction of the observed enhancement. More complete understanding of this enhancement effect observed on isolated metal nanoclusters grown on a graphene layer requires further studies, which might lead to the use of this effect in sensing applications utilizing infrared spectroscopy.

9. Conclusion

In this thesis, studies of selective hydrogenation reactions on single crystal and bimetallic surfaces using several surface techniques, including RAIRS, TPRS, AES, and LEED, have been presented. Ambient pressure hydrogenation of nitrogen atoms on a Pt(111) surface was shown to lead to the formation of NH₃, in contrast to what was observed under UHV conditions where the hydrogenation does not proceed beyond the formation of NH species. Evidence was shown for the formation of NH, NH₂, and NH₃ species under ambient pressure conditions with the relatively high temperature desorption of NH₃ attributed to a delay caused by the desorption of unreacted hydrogen atoms.

The selective hydrogenation of acrolein on Ru(001) was found to lead to the formation of all possible hydrogenation product – propanal, 2-propenol, and 1-propanol – with propanal as the major product. This was confirmed by both TPRS and RAIRS. To further understand the reaction pathways of acrolein on Ru(001), the surface chemistry of the hydrogenation products was studied in detail. It was found that 2-propenol isomerizes on the Ru(001) surface to propanal around 180 K prior to molecular desorption around 200 K, which might explain the low yield of 2-propenol in the acrolein hydrogenation experiments. Furthermore, 2-propenol was also found to self-hydrogenate to 1-propanol around 220 K and reduce to propylene at 130 K. Propanal on the other hand does not undergo any isomerization to 2-propenol, but desorbs molecularly at 175 and 280 K while 1-propanol desorbs molecularly at 227 and 298 K. A reversible hydrogenation-dehydrogenation reaction process was observed between propanal and 1-propanol in the 200 to 320 K temperature range. These findings provided further insights into the hydrogenation pathways of acrolein and lead to a better understanding of the chemistry of acrolein and its hydrogenation products on the Ru(001) surface.

In contribution to the ongoing efforts in the surface science community to bridge the *materials* gap between surface science and catalysis, some studies were carried out on well-characterized bimetallic surfaces. Specifically, a physical vapor deposition setup was designed, built, and optimized for the controlled deposition of platinum on a Ru(001) substrate. The setup can also be used to deposit other materials onto different substrates. In the Pt/Ru(001) bimetallic system, characterized by AES, LEED, CO-TPD, and CO-RAIRS, the platinum atoms were shown to grow pseudomorphically due to the 2.5% lattice mismatch between Pt and Ru. Platinum deposition around room temperature followed by annealing to 750 K for 1 minute was found to lead to the formation of larger platinum islands but annealing to temperatures above 850 K led to the formation of a PtRu surface alloy. To probe the catalytic properties of these wellcharacterized Pt/Ru(001) surfaces, the selective hydrogenation of acrolein was used as a model reaction. The surfaces were found to be completely inactive towards acrolein hydrogenation, except for the 1 ML Pt/Ru(001), which yielded propanal as the only hydrogenation product. The PtRu surface alloy was also found to have no significant effect on acrolein hydrogenation. All the surfaces were found to readily reduce acrolein to propylene at low temperature (around 130 K) whereas high temperature (above 300 K) propylene desorption was observed only with increasing platinum coverages. In general, it was found that the presence of even a small amount of platinum completely alters the catalytic properties of the Ru(001) substrate and at platinum coverages above 3 ML, the Pt/Ru(001) surface effectively behaves like Pt(111). The 1 ML Pt/Ru(001) surface was found to have properties distinct from those of Pt(111) and Ru(001)single crystal surfaces. It is hoped that these studies on well-defined bimetallic surfaces will be continued in the future by utilizing the optimized evaporator setup and deposition procedure to

deposit different metals on varied single crystal surfaces. The catalytic properties of such systems can then be probed using the tools and techniques described above.

In the last chapter, it was shown using AES, LEED, and CO-TPRS that a complete, crystalline, single layer graphene can be grown on Ru(001). Platinum nanoclusters deposited on this graphene layer are known to preferentially nucleate and grow within the Moiré unit cells of the graphene layer resulting in isolated platinum nanoclusters. Using CO-RAIRS, these isolated nanoclusters were found to give enhanced IR response of up to 4-fold increase. It is hoped that this IR enhancement effect arising from the presence of the sandwiched graphene layer which enabled the growth of isolated platinum nanostructures will be further investigated on other metal/graphene/substrate systems apart from the Pt/SLG/Ru(001) system and such studies might lead to the use of these systems in sensing applications with infrared spectroscopy.

In conclusion, some of the results presented in this thesis show examples of novel properties and reactions observed under ambient pressure conditions on single crystal surfaces, and on well-defined bimetallic surfaces in UHV. Hopefully, these have contributed to the understanding of similar processes in industrial catalysis and, with further studies, can aid the design of better heterogeneous catalysts.

Appendix

A1 Deconvolution of TPD/TPRS Data

The first step in the deconvolution procedure is based on the cracking patterns of the molecules – acrolein, propanal, 2-propenol, and 1-propanol. Figure A1 shows these cracking patterns collected in our chamber and also used to determine which mass to monitor for each species during the desorption experiments. From these cracking patterns, m/e = 56, 58, 31, and 57 were selected to follow the desorption of acrolein, propanal, 1-propanol, and 2-propenol, respectively. As these masses are not unique to each compound, the TPRS traces were deconvoluted to remove contributions from other compounds to the selected mass.



Figure A1 Cracking patterns of (clockwise from top left) acrolein, propanal, 1-propanol, and 2-propenol taken after leaking in 5×10^{-8} Torr of each compound into the chamber. Each plot is an average of over 50 scans

The cracking pattern of acrolein shows the following intensity distribution for the masses of interest relative to the intensity of the acrolein parent peak (m/e = 56):

$$I_{M57} = 5.0 \%$$

$$I_{M58} = 0.55 \%$$

$$I_{M31} = 0.37 \%$$

Thus, the contributions from acrolein fragmentation in the desorption traces of each of the hydrogenation products can be removed as follows:

$$\begin{split} I_{M57-M56} &= I_{M57} \, (TPRS) - 0.050 \, I_{M56} \, (TPRS) \\ I_{M58-M56} &= I_{M58} \, (TPRS) - 0.0055 \, \, I_{M56} \, (TPRS) \\ I_{M31-M56} &= I_{M31} \, (TPRS) - 0.0037 \, \, I_{M56} \, (TPRS) \end{split}$$

The next step is to equate the entities on the left hand side to the contributions from pure 2propenol, propanal, and 1-propanol fragmentation respectively based on their fragmentation ratios as listed in Table A1. We assign a value of 1.0 to the mass that is most intense for each molecule.

Table A1 Cracking ratios for propanal, 2-propenol, and 1-propanol

Pure molecule	I _{M31}	I _{M57}	I _{M58}
1-Propanol	1.0	0.0059	0.0042
2-Propenol	0.758	1.0	0.163
Propanal	0.127	0.329	1.0

Thus, for each TPRS data point,

$I_{M57-M56}$	=	$I_{M57}(2\text{-propenol}) + I_{M57}(\text{propanal}) + I_{M57}(1\text{-propanol})$
$I_{M58-M56}$	=	$I_{M58} \left(\text{2-propenol} \right) + I_{M58} \left(\text{propanal} \right) + I_{M58} \left(\text{1-propanol} \right)$
$I_{M31-M56}$	=	I_{M31} (2-propenol) + I_{M31} (propanal) + I_{M31} (1-propanol)

Based on the cracking ratios in Table A1, the above equations have three unknowns across the diagonal which can be solved simultaneously using a 3×3 matrix. These unknowns – I_{M57} (2-propenol), I_{M58} (propanal), and I_{M31} (1-propanol) – gives the *unique* contribution from that mass for that particular species.

The deconvolution of the CO (28 amu), H_2CO (30 amu), ethylene (26 amu), and propylene (39 amu) TPRS traces obtained from each of 2-propenol, propanal and 1-propanol TPRS runs is based on the relative intensity ratios of that particular mass to that of the parent mass of the molecule used in the TPRS experiment.

For this procedure, the sensitivity factors must also be taken into consideration where necessary and the resulting deconvoluted spectra must be inspected for errors and physical meanings because the deconvolution process can sometimes be inexact.

A2 Quantification of TPRS Yields

To quantify the TPRS yields for each hydrogenation product and for the molecularly desorbed acrolein, the mass spectrometer correction factor relative to CO for each compound was determined following the empirical method developed by Ko et al.⁵⁶ In this method, the major mass fragment yields of each species of interest (acrolein, propanal, 2-propenol, and 1-propanol) were determined from its cracking pattern. The correction factor, C, is given by

$$C = \frac{1}{F_m I_x} \sum_{mass \ fragment} \frac{F_m}{G_m \ x \ T_m}$$

where the summation is over all mass fragments for a given species. The mass fragment yield (F_m) is the yield for each m/e relative to that of the most intense peak. The ionization efficiency (I_x) is mostly dependent on the number of electrons and a reasonable correlation relative to CO is:

$$I_x = 0.6 \left(number \ of \frac{electrons}{14}\right) + 0.4$$

The gain of the electron multiplier (G_m) is a function of the molecular weight and approximated relative to CO by:

$$G_m = \sqrt{\frac{28}{MW}}$$

The quadrupole transmission factor (T_m) for each molar mass was obtained from a plot provided by Hiden.¹²⁹ It should be noted that the T_m values obtained from the Hiden plot are similar to those of Ko et al.⁵⁶ given as:

$$T_m = \begin{cases} 10^{(30-MW)/155} & MW > 30\\ 1 & MW < 30 \end{cases}$$

The correction factors obtained using the method described above are listed in Table A2.

Mass fragment	Correction factor
56	7.4
58	9.2
57	5.2
31	1.3
	Mass fragment 56 58 57 31

Table A2. Calculated mass spectrometer correction factors (C)

The TPRS yields were then calculated based on these sensitivity factors and the relative TPRS areas for saturated CO coverage and the TPRS area for a particular molecule (acrolein, propanal, 2-propenol, or 1-propanol) given that CO has an absolute saturation coverage of 0.68 ML on the clean Ru(001) surface.^{127,126} This approach is similar to that used by Murillo and Chen.⁴²

A3 Cleaning Platinum Layers on Ru(001) Substrate

The cleaning of the Pt/Ru(001) NSAs to remove all the platinum involves several cycles of Ar^+ ion sputtering at room temperature (1.0 kV, 7.0 μ A) for several minutes and electron beam annealing to 1500 K (30 seconds) and Ar^+ ion sputtering at room temperature (0.5 kV, 2.5 μ A, 17 minutes) followed by resistively annealing to 850 K until a sharp single peak with no shoulders is observed in a saturated (5.0 L) CO RAIR spectrum at 90 K. As shown in Figure A2, depending on the amount of platinum on the surface, obtaining a clean Ru(001) surface can take more than one week of daily cleaning using the procedure above.



Figure A2 Left, RAIR spectra taken at 90 K after saturated (5.0 L) CO is exposed to the Ru(001) surface after several sputtering cycles as indicated in the figure. The peak/shoulder at 2088 cm⁻¹ is from platinum atoms remaining on the surface. Right, RAIR spectrum of 5.0 L CO on clean Ru(001) with a single, sharp peak at 2056 cm⁻¹ with over 4% intensity and no shoulder due to platinum or any other contaminants on the surface

The surface cleanliness can also be further verified by LEED and AES as shown in Figure A3. The ratio of the positive to the negative portions of the 273 eV peak should be 0.80 for a clean Ru(001) surface.¹⁰¹



Figure A3 Auger spectra (left) and LEED image (right) of a clean Ru(001) surface. Both were collected at room temperature with beam energy of 70 eV for the LEED image

A4 Solution to Mass Drift and Mass Bleed Issues in Pfeiffer-Vacuum QMS 200 on Ambient-Pressure Chamber

The TPRS spectra shown in Figure 3.5 reveal that the intensity ratios for the ammonia fragments (masses 14, 15, 16, and 17) are incorrect with the parent fragment (mass 17) having a lower intensity compared to the mass 16 fragment. This incorrect fragmentation was also observed from the mass spectrometer when pure ammonia gas was introduced into the chamber. Further checks reveal ammonia fragmentation data collected with the same mass spectrometer in 2009 (shown in Figure A4, left panel) having the same incorrect fragmentation ratios. This suggests the problem is from the mass spectrometer itself.



Figure A4 Data collected in 2009, with the Pfeiffer-Vacuum QMS 200, showing the incorrect fragmentation pattern for pure ammonia gas. The correct fragmentation pattern taken from the NIST Chemistry WebBook is shown and is reproduced with permission

Troubleshooting (with remote assistance from a Pfeiffer-Vacuum representative) reveals that the spectrometer was having problems related to mass drift and mass bleed. The former refers to a situation where the monitored m/e value (the peak top) shifts to a different value overtime e.g. m/e 16.02 shifts to 15.56 or 16.41 especially as the operating temperature gets too hot, while the latter refers to a situation where intensities arising from a particular m/e value bleeds (or contributes) to an adjacent m/e value as a result of very narrow peak tops. It was discovered that the operating temperature was over 50 °C compared to the normal temperature of ≤ 35 °C. Over the course of several days, the mass drift and mass bleed issues were resolved as shown by the ammonia fragmentation pattern, collected after fixing the mass spectrometer, in Figure A5. The intensity ratios are now in agreement with those from the NIST WebBook.



Figure A5 Mass fragmentation pattern of pure ammonia gas collected after the mass bleed and mass drift problems in the Pfeiffer-Vacuum QMS 200 were resolved. The intensity ratios are now in agreement with the values from the NIST WebBook shown in Figure A4

A detailed procedure, including daily and monthly checks, to prevent a reoccurrence of these issues while also ensuring the Pfeiffer-Vacuum QMS 200 remain in optimum operating conditions was later developed and handed to the subsequent user(s) of the instrument.

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Publications and Presentations

- Selective hydrogenation of acrolein to propanal on a pseudomorphic Pt/Ru(001) bimetallic surface, <u>D. A. Esan</u> and M. Trenary Topics in Catalysis (Special Issue), 2017, DOI 10.1007/s11244-017-0857-2
- Adsorption and Hydrogenation of Acrolein on Ru(001), <u>D. A. Esan</u>, Y. Ren, X. Feng, M. Trenary J. Phys. Chem. C, **2017**, 121 (8), 4384 4392
- Surface Chemistry of Propanal, 2-Propenol, and 1-Propanol on Ru(001), *D. A. Esan, M. Trenary* Phys. Chem. Chem. Phys., **2017**, 19, 10870 10877
- Spectroscopic Identification of Surface Intermediates in the Decomposition of Methylamine on Ru(001), Y. Ren, <u>D. A. Esan</u>, I. Waluyo, J. D. Krooswyk, M. Trenary J. Phys. Chem. C, 2017 121 (17), 9424 – 9432
- Dynamics of Ion Binding to Graphene Nanostructures, *N. Patra*, *D.A. Esan*, *P. Král* J. Phys. Chem. C, **2013** 117 (20), 10750-10754
- Adsorption and Hydrogenation of acrolein on Ru(001) Oral Presentation at the America Vacuum Society 63rd International Symposium & Exhibition, Nashville, TN, November 10, 2016.

Activities

- **Volunteer Tutor,** African American Academic Network at the University of Illinois at Chicago, 2013 to date
- Member America Vacuum Society (AVS) and America Chemical Society (ACS)
- **Development Knowledge Facilitator** for the **Millennium Development Goals**, 2009 2010

- Student Member, University of Lagos Work-Study Programme Committee, 2007 2008
- Class Representative for Industrial Chemistry students, 2003 2008

Awards

- Best Teaching Assistant, Physical Chemistry Laboratory Course, Spring 2014
- Chicago Consular Corps Scholarship Award, 2012
- Best Graduating Student, Skye Bank Business School, May 2010
- **UNILEVER Award** for **Best Graduating Student in** Chemistry Department, University of Lagos, 2008
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Work Experience

- Research and Teaching Assistant, 2011 2017, University of Illinois at Chicago, U.S.A.
- Risk Management and Information Technology Officer, 2010 2011, Skye Bank PLC, Nigeria
- Teacher, 2009 2010, Community Secondary School, Obrigbene, Bayelsa, Nigeria
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