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The electrocatalytic oxidation of small organic molecules on platinum

Zhao, Qingjun, Ph.D.

Case Western Reserve University, 1993
THE ELECTROCATALYTIC OXIDATION OF SMALL ORGANIC MOLECULES ON PLATINUM

by

QINGJUN ZHAO

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Thesis Advisor: Professor Ernest B. Yeager

Department of Chemistry
CASE WESTERN RESERVE UNIVERSITY

August, 1993.
We hereby approve the thesis of

Qingjun Zhao

candidate for the Ph. D.
degree.*

(signed)  

(Jane Doe) (chair)

(date) June 29, 1993

*We also certify that written approval has been obtained for any proprietary material contained therein.
THE ELECTROCATALYTIC OXIDATION OF SMALL ORGANIC MOLECULES ON PLATINUM

Abstract

by

QINGJUN ZHAO

The major objectives of this thesis research are two folds: 1) to study the mechanisms of the electrocatalytic oxidation of small organic molecules and 2) to understand the factors controlling the kinetics of these processes. Special emphasis has been placed on three small hydrocarbon molecules (methane, ethane and ethylene) which have been considered as possible anodic fuels in direct hydrocarbon-air fuel cells.

An understanding of the mechanisms of the electrocatalytic oxidation of these selected hydrocarbon molecules has been reached by identifying the adsorbed species, intermediates as well as products which are either adsorbed on the electrode surface or dissolved in the electrolyte. Two types of adsorbed species have been identified by means of electrochemical, in situ FTIR and ex situ NMR techniques. Type I species are linearly bonded carbon
monoxide (CO\textsubscript{L}), which can be formed on platinum electrode surfaces from the adsorption of any of the three hydrocarbon molecules investigated in this thesis work. Type II species are alcohol-like (most probably ethylene glycol), which are expected to be formed from the adsorption of C\textsubscript{2} molecules (e.g., ethane and ethylene). Carbon monoxide has been considered as a reaction intermediate rather than just a "blocking agent" for the electrochemical oxidation of small hydrocarbon molecules. The alcohol-like type II species are adsorbed on the platinum surface with higher bonding strength and are not the same as the adsorbed species derived directly from the similar alcohol molecules. These species are expected to be the possible blocking species for the electrocatalytic oxidation of small hydrocarbon molecules with two or more carbon atoms at lower temperatures since they require more positive potentials to be oxidatively desorbed from the electrode surface.

On the basis of the electrochemical and spectroscopic investigations, the possible reaction paths have been proposed by the author. At elevated temperatures, the rate-determining step in the oxidation of these hydrocarbons has been considered to
be the reaction between adsorbed carbon monoxide and water, which is represented as the following:

$$\text{CO}_{ad} + \text{H}_2\text{O}_{ad} \rightarrow \text{COOH}_{ad} + \text{H}^+ + \text{e}^-$$

The temperature effect on the formation and oxidative desorption of the two types of species on platinum has been investigated from room temperature to 180°C. At elevated temperatures (>150°C), the oxidation of these hydrocarbons proceeds through the formation and oxidative desorption of carbon monoxide.

The role played by adsorbed water has been discussed. The involvement of water molecules or OH$_{ad}$ in the oxidation of small organic molecules is expected to depend on the temperature. At lower temperatures (≤ 55°C), the oxidative desorption of the adsorbed organic species cannot take place until OH$_{ad}$ is formed on the surface. The oxidative desorption of adsorbed species, however, can take place at higher temperatures at potentials much more negative than that at which OH$_{ad}$ is formed. At higher temperatures, an adsorbed water has been considered to be the oxidative reagent.

The electrocatalytic oxidation of the three selected small organic molecules has been investigated using low index and high index single crystal platinum electrodes at elevated temperatures. Pronounced sensitivities to the structure have been observed. The
following electrocatalytic activity order for the adsorption and oxidation of all of the molecules studied has been observed:

\[ \text{Pt}(100) > \text{Pt}(111) > \text{Pt}(110) \]

The high activity of \( \text{Pt}(100) \) has been interpreted on the basis of its special atomic structure, which can enhance the C-C bond rupture and oxygenation processes.
DEDICATION

To my wife, Yuyan, and my son, Yang
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# TABLE OF CONTENTS

ABSTRACT ............................................................. ii  
DEDICATION ............................................................. vi  
ACKNOWLEDGEMENTS ..................................................... vii  
TABLE OF CONTENTS .................................................... viii  
LIST OF FIGURES ........................................................ xiii  

## CHAPTER I

REVIEW OF STUDIES OF THE ELECTROCATALYTIC OXIDATION OF METHANE, ETHANE AND ETHYLENE ON PLATINUM

1. 1. Introduction ...................................................... 1  
1. 2. Review of Literature .............................................. 4  
   1. 2. 1. The Electrocatalytic Oxidation of Methane .................. 4  
   1. 2. 2. The Electrocatalytic Oxidation of Ethane .................... 9  
   1. 2. 3. The Electrocatalytic Oxidation of Ethylene ................. 12  

References ............................................................. 22  

## CHAPTER II

THE ELECTROCATALYTIC OXIDATION OF METHANE ON LOW AND HIGH INDEX SINGLE CRYSTAL PLATINUM SURFACES IN HOT PHOSPHORIC ACID

2. 1. Introduction ...................................................... 25  
2. 2. Experimental .................................................... 26  
2. 3. Results and Discussion .......................................... 28  
   2. 3. 1. Hydrogen Adsorption and Desorption at Room Temperature .................................................. 28
2.3.2. Hydrogen Adsorption and Desorption at Elevated Temperatures ......................................................33

2.3.3. The Electrocatalytic Oxidation of Methane .................................................................39

2.3.3.1. On The Three Low Index Single Crystal Platinum Surfaces .................................39

2.3.3.2. On High Index Single Crystal Surfaces ..............50

2.4. Conclusion ..................................................53

References ..................................................54

CHAPTER III

THE ELECTROCATALYTIC OXIDATION OF ETHANE ON PLATINUM

3.1. Introduction .................................................56

3.2. Experimental .............................................58

3.2.1. Potentiodynamic Measurements ..................58

3.2.2. In Situ FTIR Spectroelectrochemical Investigations ......................60

3.3. Results and Discussion ..................................65

3.3.1. Potentiodynamic Investigation ....................65

3.3.1.1. On A Polycrystalline Platinum Electrode Surface ..................................65

3.3.1.2. On The Three Low Index Single Crystal Platinum Electrode Surfaces .................75

3.3.2. In Situ FTIR Investigations .........................83

3.3.2.1. Linear Potential Sweep Studies ..................83

3.3.2.2. Single Potential Step Studies ......................92

3.3.2.3. Mechanism of Formation of Carbon Monoxide from Ethane .........................97

3.4. Conclusion ...............................................101

References ..................................................102
CHAPTER IV

POTENTIODYNAMIC STUDIES OF ADSORPTION AND OXIDATION OF ETHYLENE ON PLATINUM IN ACID MEDIA AT ELEVATED TEMPERATURES

4. 1. Introduction ..............................................104
4. 2. Experimental .............................................105
4. 3. Results and Discussion .................................109

4. 3. 1. Linear Potential Sweep Studies of the Electrocatalytic Oxidation of Ethylene and the Adsorbed Species Generated during the Oxidation ..............................................109

4. 3. 2. The Formation and Oxidative Desorption of Adsorbed Species .............................................115

4. 3. 3. The Electrooxidation of Ethylene on the Three Low Index Single Crystal Platinum Surfaces .............................................121

4. 3. 3. 1. Linear Potential Sweep Studies over a Wide Potential Region .............................................122

4. 3. 3. 2. The Electrocatalytic Oxidation of Ethylene on Pt(100) .............................................124

4. 3. 3. 3. The Electrocatalytic Oxidation of Ethylene on Pt(111) .............................................130

4. 3. 3. 4. The Electrocatalytic Oxidation of Ethylene on Pt(110) .............................................134

4. 3. 4. The Electrocatalytic Oxidation of Ethylene in Hot Phosphoric Acid .............................................137

4. 3. 4. 1. Linear Potential Sweep Studies at Temperatures above 100°C .............................................138

4. 3. 4. 2. The Study of the Electrocatalytic Oxidation of Ethylene Using a Rotating Disk Electrode .............................................141
4. 3. 4. 3. Transient Measurements of the Electrocatalytic Oxidation of Ethylene ..................................................143
4. 3. 4. 4. Stationary Measurements of Electrocatalytic Oxidation of Ethylene Using Gas-fed Electrodes ..............................150

4. 4. Conclusion ..........................................................152
References ........................................................................155

CHAPTER V

IN SITU FTIR AND EX SITU NMR STUDIES OF THE ELECTROCATALYTIC OXIDATION OF ETHYLENE ON PLATINUM

5. 1. Introduction ............................................................157
5. 2. Experimental ..........................................................158
5. 3. Results and Discussion ...............................................164

5. 3. 1. In Situ FTIR Spectroscopic Studies ..............................164
5. 3. 1. 1. The Electrochemical Adsorption and Oxidation of Ethylene at Room Temperature .................................164
5. 3. 1. 2. The Electrochemical Adsorption and Oxidation of Ethylene at 60°C ..........................................................168

5. 3. 2. The Mechanism of the Formation of Carbon Monoxide and Alcohol-like Species ........................................175
5. 3. 3. Unusual Frequency Shift of Carbon Monoxide IR Peaks ..................................................................................187
5. 3. 4. Ex Situ NMR Study of the Soluble Intermediates and Products .................................................................193
5. 3. 5. Possible Mechanism for the Oxidation of Ethylene on Platinum .............................................................199

5. 4. Conclusion ..................................................................201
References ........................................................................203
LIST OF REFERENCES

A. CHAPTER I .............................................. 205
B. CHAPTER II ........................................... 207
C. CHAPTER III ........................................... 209
D. CHAPTER IV ........................................... 210
E. CHAPTER V ........................................... 211
LIST OF FIGURES

Fig. 2-1 ..................................................30
The voltammetry curve of Pt(100) in 85 wt.% H₃PO₄ at room temperature. Sweep rate: 50 mV/s.

Fig. 2-2 ..................................................31
The voltammetry curve of Pt(110) in 85 wt.% H₃PO₄ at room temperature. Sweep rate: 50 mV/s.

Fig. 2-3 ..................................................32
The voltammetry curve of Pt(111) in 85 wt.% H₃PO₄ at room temperature. Sweep rate: 50 mV/s.

Fig. 2-4 ..................................................34
The voltammetry curves of Pt(110), Pt(100) and Pt(111) in 85 wt.% H₃PO₄ at 150°C. Sweep rate: 50 mV/s.

Fig. 2-5 ..................................................37
The voltammetry curves of Pt(111) with different positive potential limits (dashed lines) in 85 wt.% H₃PO₄ at 110°C. The solid line is for the disordered Pt(111) surface after sweeping the potential up to 1.5 V vs. RHE. Sweep rate: 50 mV/s.

Fig. 2-6 ..................................................41
The voltammetry curves of the three low-index single crystal platinum surfaces in 85 wt.% H₃PO₄ saturated with N₂ (dashed line) or 100% CH₄ (solid line) at 1 atm and 150°C. Sweep rate: 50 mV/s.

Fig. 2-7 ..................................................43
The voltammetry curves of low-index single crystal and polycrystalline platinum surfaces in 85 wt.% H₃PO₄ saturated with 100% CH₄ at 1 atm and 150°C after holding the potential at 0.32 V vs. RHE for one minute and sweeping the potential in the positive direction. Sweep rate: 50 mV/s.

Fig. 2-8 ..................................................47
The schematic diagram for the formation of linearly bounded carbon monoxide from adsorbed methane and water on platinum.

Fig. 2-9 ....................................................... 51
The voltammetry curves of Pt(111), Pt(755), Pt(311) and Pt(100) in 85 wt.% H₃PO₄ saturated with 100% CH₄ at 1 atm and 150°C after holding the potential at 0.28 V vs. RHE for one minute and sweeping the potential in the positive direction. Sweep rate: 50 mV/s.

Fig. 3-1 ....................................................... 61
The schematic drawing of the electrochemical cell used for the potentiodynamic studies.

Fig. 3-2 ....................................................... 62
The schematic drawings of optical path (a) and the spectroelectrochemical cell (b) used in the in situ FTIR investigations.

Fig. 3-3 ....................................................... 67
The voltammetry curves of a polycrystalline platinum electrode obtained by sweeping the potential in the positive direction after holding the potential at 0.25 V vs RHE for various length of periods in 0.1 M HClO₄ saturated with ethane at 1 atm and 80°C. Sweep rate: 100 mV/s.

Fig. 3-4 ....................................................... 69
The dependence of the charges corresponding to peak I of each stripping curve in Fig. 3-3 upon holding time (dotted line) and its first derivative with respect to holding time (solid line).

Fig. 3-5 ....................................................... 71
The voltammetry curves of a polycrystalline platinum electrode obtained by sweeping potential in anodic direction after holding the potentials at different values for one min. in 0.1 M HClO₄ saturated with ethane at 1 atm and 80°C. Sweep rate: 100 mV/s.

Fig. 3-6 ....................................................... 72
The dependence of the charge of anodic peak I in Fig. 3-5 with potential (dashed line) and the first derivative of charge with respect to potential (solid line).
Fig. 3-7 ......................................................74
Voltammetry curves obtained by sweeping the potential in the positive direction first (solid line) or cathodic direction first with different negative limits (dashed line) after holding the potential at 0.3 V for 5 min. using a polycrystalline platinum electrode in 0.1 M H$_2$SO$_4$ saturated with ethane at 1 atm and 80°C. The dash-dotted line is the voltammetry curve obtained in an ethane-free electrolyte. Sweep rate: 100 mV/s.

Fig. 3-8a .....................................................76
The voltammetry curve of Pt(110) in 0.1 M H$_2$SO$_4$ at room temperature (dash-dotted line) and 80°C (solid line). Sweep rate: 50 mV/s.

Fig. 3-8b .....................................................77
The voltammetry curve of Pt(100) in 0.1 M H$_2$SO$_4$ at room temperature (dash-dotted line) and 80°C (solid line). Sweep rate: 50 mV/s.

Fig. 3-8c .....................................................78
The voltammetry curve of Pt(111) in 0.1 M H$_2$SO$_4$ at room temperature (dash-dotted line) and 80°C (solid line). Sweep rate: 50 mV/s.

Fig. 3-9 .....................................................80
Voltammetry curves of the polycrystalline and the three low index single crystal platinum surfaces obtained by sweeping the potential in the positive direction after holding the potential at 0.3 V for 1 min. in 0.1 M H$_2$SO$_4$ saturated with ethane at 1 atm and 80°C. Sweep rate: 100 mV/s.

Fig. 3-10 ....................................................85
In situ FTIR spectra obtained during a linear potential sweep (1 mV/s) after holding the potential at 0.3 V for 10 min. in 0.1 M HClO$_4$ saturated with ethane at 1 atm and 60°C. Each spectrum consists of 270 scans with a resolution of 8 cm$^{-1}$ and is subtractively normalized to the reference spectrum at 0.3 V.

Fig. 3-11 ....................................................86
The "absolute" linearly bonded CO spectra obtained by subtractively normalizing all of the spectra to that collected at 0.79 V. All of the experimental conditions are the same as those described in Fig. 3-10.

Fig. 3-12 ................................. 89
Schematic drawing of the splitting of the linearly bonded CO IR peak:
(a) Pt(111) sites
and (b) Pt(100) sites.

Fig. 3-13 ...................................... 91
In situ FTIR spectra in the potential region from 0.79 to 1.3 V vs RHE. Each spectrum was subtractively normalized to that collected at 0.79 V. All of the experimental conditions are the same as those described in Fig. 3-10.

Fig. 3-14 ...................................... 93
In situ FTIR spectra obtained by a single potential modulation from each $E_s$ to 0.8 V after holding the potential at 0.3 V for 10 min. in 0.1 M HClO$_4$ saturated with ethane at 1 atm and 60°C. Each spectrum consists of 500 scans with a resolution of 8 cm$^{-1}$ and was subtractively normalized to that collected at 0.8 V.

Fig. 3-15 ...................................... 96
Plots of CO$_2$ and CO$_x$ IR peak intensities in Fig. 3-14 vs. holding potentials ($E_s$).

Fig. 3-16 ...................................... 99
Schematic drawing of the mechanism of the formation of linearly bonded CO from ethane on a platinum electrode surface.

Fig. 4-1 ...................................... 107
Schematic drawing of the rotating disk electrode used at 150°C.

Fig. 4-2 ...................................... 108
Schematic drawing of a gas-fed electrode holder for stationary measurements at elevated temperatures.

Fig. 4-3 ...................................... 110
Voltammetry curves of a polycrystalline platinum electrode with various positive potential limits in 0.1 M H$_3$PO$_4$ saturated
with ethylene at 1 atm and 80°C. Sweep rate: 100 mV/s. The dash-dotted line is the voltammetry curve of the same electrode in ethylene-free electrolyte.

Fig. 4-4 .................................................................113 Voltammetry curves of a polycrystalline platinum electrode in 0.1 M H₃PO₄ saturated with ethylene or N₂ at 1 atm and 70°C. Sweep rate: 100 mV/s. Dashed line: organic-free; Solid line: the oxidative desorption of adsorbed species formed at 0.3 V vs. RHE by holding the potential for 2 min. and then removing ethylene in the bulk phase; dash-dotted line: with ethylene in the bulk phase.

Fig. 4-5 .................................................................116 Oxidative desorption voltammetry curves for the adsorbed species formed on platinum in 0.1 M H₃PO₄ saturated with ethylene at 0.03 atm and 80°C by holding the potential at 0.22 V for different periods of time: (a) 5 s; (b) 15 s; (c) 30 s; (d) 60 s. Dashed line: anodic part of voltammetry curve of platinum under the same conditions but without ethylene in the electrolyte. Sweep rate: 100 mV/s.

Fig. 4-6 .................................................................118 Oxidative desorption voltammetry curves for the adsorbed species on platinum in 0.1 M H₃PO₄ at different temperatures. Sweep rate: 100 mV/s.

Fig. 4-7 .................................................................119 Oxidative desorption voltammetry curves for the adsorbed species formed on platinum in 0.1 M H₃PO₄ saturated with ethylene at 0.03 atm and 80°C by holding the potential at different values for one minute: (a) 0.12 V; (b) 0.22 V; (c) 0.32 V; (d) 0.4 V; (e) 0.52 V. Dashed line: anodic part of voltammetry curve of platinum under the same conditions but without ethylene in the electrolyte. Sweep rate: 100 mV/s.

Fig. 4-8 .................................................................123 Voltammetry curves (first cycle) of the three low index single crystal platinum surfaces in 0.1 M H₂SO₄ at 80°C. Sweep rate: 50 mV/s.
Fig. 4-9

The voltammetry curve (first cycle) of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-10

The voltammetry curve (first cycle) of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-11

The voltammetry curve (first cycle) of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 0.01 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-12

The voltammetry curve (first cycle) of Pt(111) in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-13

The voltammetry curve (first cycle) of Pt(111) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-14

The voltammetry curve (first cycle) of Pt(110) in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-15

The voltammetry curve (first cycle) of Pt(110) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. Sweep rate: 50 mV/s.

Fig. 4-16

Voltammetry curves of platinum in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm at different temperatures. Solid line: 100°C.
Dash-dotted line: 150°C. Dashed line: 180°C. Sweep rate: 100 mV/s.

Fig. 4-17 ......................................................140
Voltammetry curves of platinum in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 180°C with different positive potential limits. Sweep rate: 100 mV/s.

Fig. 4-18 ......................................................142
Voltammetry curves of a rotating platinum disk electrode in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 150°C with different rotation rates. Sweep rate: 10 mV/s.

Fig. 4-19 ......................................................145
A voltammetry curve of platinum in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 150°C. Sweep rate: 10 mV/s.

Fig. 4-20 ......................................................146
Transient current-time profiles of a platinum electrode in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 150°C. Electrode area: 0.5 cm².

Fig. 4-21 ......................................................148
Deconvolution of a typical transient current-time profile from Fig. 4-20.

Fig. 4-22 ......................................................151
A polarization curve for the electrocatalytic oxidation of ethylene on a gas-fed platinum electrode in 85 wt.% H₃PO₄ at 140°C. Platinum loading: 0.36 mg/cm².

Fig. 5-1 ......................................................161
Schematic drawing of the spectroelectrochemical thin layer cell.

Fig. 5-2 ......................................................162
Schematic drawing of the electrolyte reservoir used for in situ FTIR measurements.

Fig. 5-3 ......................................................165
Subtractively normalized FTIR spectra of the oxidation of adsorbates originating from the adsorption of ethylene on platinum in 0.1 M
HClO₄ saturated with ethylene at 0.01 atm and 25°C. Reference potential: 1.5 V vs. RHE. Sample potentials are shown in the figure. Scan number: 270. Resolution: 4 cm⁻¹. Potential sweep rate: 1 mV/s.

Fig. 5-4
Subtractively normalized FTIR spectra of the oxidation of adsorbates originating from the adsorption of ethylene on platinum in 0.1 M HClO₄ saturated with ethylene at 0.01 atm and 60°C. Reference potential: 1.5 V vs. RHE. Sample potentials are shown in the figure. Other conditions are the same as in Fig. 5-3.

Fig. 5-5
Subtractively normalized FTIR spectra of linearly bonded carbon monoxide on platinum at different potentials and temperatures. Reference potentials: 0.94 V at 25°C and 0.8 V at 60°C. Other conditions are the same as in Fig. 5-3.

Fig. 5-6
The variation of CO₂ IR band intensity vs. potentials at two temperatures: (a) 60°C. (b) 25°C.

Fig. 5-7
Subtractively normalized FTIR spectra for the formation and oxidation of CO₂ on platinum at different holding potentials in 0.1 M HClO₄ saturated with ethylene at 0.01 atm and 60°C. Reference potential: 0.8 V vs. RHE. Resolution: 4 cm⁻¹. Scan number: 500.

Fig. 5-8
Voltammetry curves of oxidative desorption of CO (long dashed line), adsorbates originating from ethylene (solid line) and adsorbates originating from ethylene modified laterally by CO (dash-dotted line). The short dashed line is the voltammetry curve of platinum in organic-free electrolyte at 25°C. Sweep rate: 100 mV/s.

Fig. 5-9
Voltammetry curves of oxidative desorption of CO (solid line), adsorbates originating from
ethylene (long dashed line) and CO modified laterally by adsorbates originating from ethylene (dash-dotted line). The short dashed line is the voltammetry curve of platinum in organic-free electrolyte at 25°C. Sweep rate: 100 mV/s.

Fig. 5-10 .........................................................182
The variation of CO IR peak intensity vs. holding potential and temperature: (a) 25°C, (b) 60°C, and (c) 80°C. Resolution: 4 cm⁻¹. Scan number: 500.

Fig. 5-11 ..........................................................188
The dependence of frequency of the IR peak for CO_L with potential at two temperatures: (a) 60°C. (b) 25°C. The data are from Fig. 5-5.

Fig. 5-12 ..........................................................190
The intensity change of CO_L IR peaks with time at 0 V vs. SCE on platinum in 0.1 M HClO₄ saturated with carbon monoxide at 0.1 atm and 25°C. Flow rate of electrolyte: 1.35 ml/min. Resolution: 4 cm⁻¹. Scan number: 16.

Fig. 5-13 ..........................................................191
The frequency shift of CO_L with coverage at 0 V vs. SCE on platinum in 0.1 M HClO₄ saturated with carbon monoxide at 0.01 atm and 25°C. Flow rate of electrolyte: 1.35 ml/min. Resolution: 4 cm⁻¹. Scan number: 16.

Fig. 5-14 ..........................................................195
A voltammetry curve of platinum at 80°C in 0.1 M H₃PO₄ (dashed line) and 0.1 M H₃PO₄ used for the oxidation of ethylene at the same temperature for 4 hours under potentiodynamic conditions (solid line). Sweep rate: 100 mV/s.

Fig. 5-15 ..........................................................196
H⁺ NMR spectra: (a) blank electrolyte (0.1 M D₃PO₄ in D₂O), (b) 0.1 M D₃PO₄ in D₂O used for the oxidation of ethylene at 80°C for 28 hours under potentiodynamic conditions.

Fig. 5-16 ..........................................................198
Voltammetry curves of platinum at 80°C in 0.1 M H₃PO₄ (dashed line), 0.1 M H₃PO₄ with 10⁻⁴ M C₂H₄(OH)₂ (dash-dotted line) and 0.1 M H₃PO₄ used for the oxidation of ethylene at the same temperature for 4 hours under potentiodynamic conditions (solid line). Sweep rate: 100 mV/s.
CHAPTER I

REVIEW OF STUDIES OF THE ELECTROCATALYTIC OXIDATION OF METHANE, ETHANE AND ETHYLENE ON PLATINUM

1.1. Introduction

The investigation of the electrocatalytic oxidation of small hydrocarbons has considerable importance in terms of both applied and fundamental research. The detailed understanding of the mechanisms of these reactions will help the selection of more active electrocatalysts, which will impact the development of direct hydrocarbon fuel cells. This understanding will also aid in the elucidation of electrochemical reaction mechanisms of more complex organic compounds.

Using hydrocarbons as anodic fuels for hydrocarbon-oxygen fuel cells has been a research topic for more than one century. A fuel cell using ethylene as the anodic fuel was studied by William Grove[1] in 1874. Using hot concentrated phosphoric acid as the electrolyte, Heath and Worsham[2] discovered that saturated hydrocarbon molecules, which are notoriously inert, could also be electrocatalytically oxidized on platinum. Unfortunately, the kinetics of the electrocatalytic oxidation of saturated and unsaturated
hydrocarbon molecules are very slow even on platinum and its alloys, which so far are considered to be the most active electrocatalysts for the oxidation of small organic molecules. The slow kinetics has seriously inhibited the development of direct hydrocarbon fuel cells.

During the last several decades, a major effort has been directed toward the elucidation of the mechanisms for the electrooxidation of small aliphatic hydrocarbons and comprehensive progress has been made. A detailed understanding of the mechanisms, however, has not been achieved yet. Different, even controversial, results have been obtained in some research groups, which have led to different conclusions. This situation might have resulted from differences in the experimental techniques and conditions. Another possible reason for the incomplete understanding of the mechanisms of the electrocatalytic oxidation of hydrocarbons is the lack of molecular level information about the nature of adsorbed species and intermediates in these reactions. Considering the complexity of these electrochemical reactions (for example, even for methane, eight electrons are involved in the complete oxidation), it is very difficult to identify the reaction paths and to attain a micro-level
understanding of the reaction mechanisms without molecular information. A more complete understanding of the mechanisms of electrooxidation of hydrocarbons would strengthen the predictive base with which to identify the most active electrocatalysts for these reactions.

Molecular level information on the nature of adsorbed species and possible intermediates can be provided by examining their vibrational features using in situ spectroelectrochemical techniques. One of the most powerful techniques is in situ Fourier transform infrared (FTIR) spectroscopy, which has been successfully used in investigating the adsorption and oxidation of small oxygenated organic molecules\( ^3 \) (e.g., CH\(_3\)OH, etc.) in recent years. By taking advantage of this technique, the adsorption and oxidation of selected small hydrocarbons on platinum has been further examined in this dissertation research.

The kinetics of many electrochemical reactions are sensitive to the surface morphology of the electrodes, particularly the crystallographic orientation\(^4\). Using only polycrystalline electrodes, the kinetics cannot be completely understood, because the electrocatalytic activity depends on special sites,
which vary from one crystal plane to another. By using well-defined surfaces of platinum, including low index and high index single crystal surfaces, the electrochemistry of small hydrocarbons has been extensively investigated in this work at different temperatures.

1.2. Review of Literature

The adsorption and catalytic oxidation of hydrocarbon molecules at gas-solid interfaces at much higher temperatures have been extensively studied because of the relevance to organic synthesis. Such studies of the gas-solid interface may be of some help in understanding reactions of the same species at solid-liquid electrolyte interfaces. This review will, however, focus on the literature related to the electrochemical adsorption and oxidation of selected small aliphatic hydrocarbon molecules, including methane, ethane and ethylene.

1.2.1. The Electrocatalytic Oxidation of Methane

Methane is a major constituent in natural gas. It has been used as an energy source via low-efficiency combustion since pre-historic times. The possibility of achieving higher efficiency usage of this fuel via
electrochemical oxidation in fuel cells has given rise to active research efforts in both industry and academia. It is well known that methane is inactive in terms of the electrochemical adsorption and oxidation at ambient temperature even on platinum, which is generally considered to be one of the most active electrocatalysts for adsorption and oxidation of organic molecules. When the temperature is elevated to above 60 °C, however, it becomes electrochemically active, although the reaction rates are relatively slow[5-10]. The investigation of the electrocatalytic adsorption and oxidation of methane involve mainly two aspects: the identification of the adsorbed species based on the potentiodynamic studies[8, 10-12] and the acquisition of kinetic parameters by means of stationary (point by point) measurements[7, 9].

The studies of adsorption of methane on platinum[7-8, 10-12] showed that methane is dissociatively adsorbed on platinum and simultaneously interacts with adsorbed water to form a partially oxygenated species. The kinetics of these processes have been suggested[8] to be controlled by the diffusion of methane molecules to the electrode surface, especially at elevated temperatures, which was evidenced by a positive effect of pressure of
methane. These partially oxygenated species adsorbed on platinum have been classified as type I or 0-type species in the field of electrocatalytic oxidation of small hydrocarbons[13]. The same type of adsorbed species has also been observed during the electrosorption of ethane and ethylene at elevated temperatures, which will be reviewed later.

The type I or 0-type species has some specific electrochemical features: it is non-desorbable at a cathodic potential once it is formed on the electrode surface and can be more easily oxidized than another type of species (type-II species) discussed later. The type II species can only be formed from the electro-adsorption of hydrocarbon molecules with more than one carbon such as ethane and ethylene. A detailed comparison between type I and type II species is shown in Table 1-1.
Table 1-1. Comparison between two types of adsorbed species originating from the electro-adsorption of small hydrocarbon molecules.

<table>
<thead>
<tr>
<th>Type I species (O-type species)</th>
<th>Type II species (CH-type species)</th>
</tr>
</thead>
<tbody>
<tr>
<td>originating from the electro-adsorption of hydrocarbons with one or more than one carbon atom ($C_X \geq 1$).</td>
<td>originating from the electro-adsorption of hydrocarbons with more than one carbon atom ($C_X &gt; 1$).</td>
</tr>
<tr>
<td>partially oxygenated</td>
<td>partially dehydrogenated</td>
</tr>
<tr>
<td>non-desorbable when $E &lt; 0.1$ V vs. RHE.</td>
<td>desorbable when $E &lt; 0.1$ V vs. RHE.</td>
</tr>
<tr>
<td>require less positive potential to be oxidized (in double layer region).</td>
<td>require more positive potential to be oxidized (in oxide region).</td>
</tr>
</tbody>
</table>
Using the linear potential sweep technique, Niedrach\textsuperscript{[11-12]} observed a single oxidation peak in the double layer region of platinum in 80 wt.% H\textsubscript{3}PO\textsubscript{4} at 130 °C, which is located at the same potential as the oxidation of CO, HCOOH and reduced CO\textsubscript{2}. By controlling the adsorption potential and time, Sustersic\textsuperscript{[10]} found this peak can be split up into two adjacent peaks, which were considered as the oxidation of two types of species with similar forms of molecular structures.

Taking into account the electrons per platinum site required for the adsorbate or the ratio of adsorption and desorption charges, Taylor\textsuperscript{[8]} and Sustersic\textsuperscript{[10]} suggested that the possible molecular structures of these O-type adsorbates of methane are = COH, -CHO, =CO or their mixtures. Their relative contribution in the adsorbed layer depends strongly on the adsorbate coverage and adsorption potential. The major form of the adsorbed species during the initial electrosorption of methane, however, was suggested always to be linearly bonded carbon monoxide\textsuperscript{[10]}, which plays an important role in the kinetics of the over-all reaction of methane to yield carbon dioxide.

By performing stationary measurements using platinized platinum electrodes, both Hsieh et al.\textsuperscript{[9]} and Sustersic et al.\textsuperscript{[10]} have obtained a 2.3 (RT/F)
Tafel slope in the less positive potential region. Hsieh et al. interpreted mechanistically the overall reaction in terms of the following successive steps:

\[ \text{CH}_4 \rightarrow (\text{CH}_3)_{\text{ad}} + \text{H}^+ + e^- \quad (1) \]

\[ (\text{CH}_3)_{\text{ad}} \rightarrow \text{intermediates} \quad (2) \]

where step (2) was assumed to be the rate determining step. This interpretation has been criticized by Sustersic[10] based on consideration of the complexity of the reaction and the involvement of O-type species at less positive potentials under stationary conditions. With the same Tafel slope, Sustersic[10] proposed a different sequence of consecutive reactions:

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow (\text{CO})_{\text{ad}} + 6\text{H}^+ + 6e^- \quad (3) \]

\[ (\text{CO})_{\text{ad}} + \text{H}_2\text{O} \rightarrow (\text{COOH})_{\text{ad}} + \text{H}^+ + e^- \quad (4) \]

\[ (\text{COOH})_{\text{ad}} \rightarrow \text{CO}_2 + \text{H}^+ + e^- \quad (5) \]

where step (4) is rate-determining.

No compromise conclusion about the kinetic mechanisms of the electrooxidation of methane on platinum has been made so far. The investigation directed to this aspect is still in an early stage.

1. 2. 2. The Electrocatalytic Oxidation of Ethane

When one of the hydrogens of a methane molecule is replaced by another methyl group (\(-\text{CH}_3\)), the resulting ethane molecule shows a dramatically different
electrochemical behavior. The electrosorption rate of ethane on platinum is almost ten times larger than that of methane\cite{11}, which may be partially due to the higher solubility of ethane in aqueous solution and the lower energy required to break the first C-H bond\cite{14}. Secondly, the adsorbates formed through the adsorption of ethane on platinum are more complex than that obtained from methane.

Agreement has been reached among many research groups, which is that there are at least two types of adsorbed species that can be formed on a platinum electrode surface in acid media as a result of the electrochemical adsorption of ethane. The type I species has the identical molecular structure and electrochemical behavior to the species formed through the electrochemical adsorption of methane\cite{15}. These results indicate that some of the ethane molecules diffusing to the platinum electrode surface undergo C-C bond rupture and are simultaneously oxygenated by the adjacent adsorbed water molecules. These species can be anodically oxidized at the same potential as those formed from methane, giving rise to a well-defined anodic peak within the double layer region of platinum in the cyclic voltammetry curves. The type II species has been considered to be a CH type species that is
partially deprotonated without breaking the C-C bond\textsuperscript{[13]}. The same type of adsorbate has also been suggested for the adsorption of ethylene and acetylene\textsuperscript{[16]}. The oxidative desorption of this type of species from the electrode surface requires a more positive potential and gives a broad anodic peak in the oxide region of platinum\textsuperscript{[13]}. Unlike the type I species, the type II species can be electrochemically desorbed (hydrogenation) to yield ethane and a few percent of methane\textsuperscript{[6, 15]}. The type II species has been suggested as the parent species of type I \textsuperscript{[16-17]}. In other words, a type II species can be transformed into a type I species.

By changing the temperature under the constant saturation pressure of ethane, Niedrach\textsuperscript{[15]} and Solis\textsuperscript{[18]} found that the ratio of type I and type II species formed from ethane depends strongly on the temperature. Much more type I species is formed on the surface at elevated temperatures. Type II species, on another hand, predominate at lower temperatures (< 45° C).

The point by point potentiostatic measurements\textsuperscript{[15]} of the electrooxidation of ethane on platinum show a linear Tafel region at less positive potentials, from 0.3 V to 0.45 V vs. RHE, with a Tafel slope of 2.3
(RT/F), which was the same as that for methane\[9-10\]. This E-logI linear relationship has been found to be broken at more positive potentials, which may be due to mass transport control or a change in the state of the surface\[17\]. A mechanism for the oxidation of ethane has been proposed by Tyurin\[17\]:

\[
\begin{align*}
\text{C}_2\text{H}_6\text{sol} & \rightarrow \text{Type II species} + \text{H}_\text{ad} & (6) \\
\text{H}_\text{ad} & \rightarrow \text{H}^+ + \text{e}^- & (7) \\
\text{Type II species} & \rightarrow \text{Type I species} & (8) \\
\text{H}_2\text{O} & \rightarrow \text{OH}_\text{ad} + \text{H}^+ + \text{e}^- & (9) \\
\text{Type I species} + \text{OH}_\text{ad} & \rightarrow \text{CO}_2 + \text{e}^- & (10) \\
\text{Type II species} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{e}^- & (11)
\end{align*}
\]

where steps (8) and (9) are considered as rate-determining at less positive potentials, which means that the conversion of type II species to type I is the rate determining step in the overall reaction of ethane to produce CO\(_2\). At more positive potentials the reaction will take place mostly through step (11).

The influence of pressure of ethane on the oxidation rate has been examined by Tyurin\[17\], who showed a positive effect of the pressure of ethane on the kinetics of the overall reaction.

1. 2. 3. The Electrocatalytic Oxidation of Ethylene
Compared with other small hydrocarbon molecules, ethylene has been more extensively studied with respect to heterogeneous adsorption, hydrogenation and oxidation. The adsorption of ethylene has been investigated at both gas-solid interfaces and liquid-solid interfaces. The gas phase adsorption has been investigated due to interest in chemical catalysis. In this case, the nature of the adsorbed species originated from ethylene and the dependence on the structure of the substrate surface can be examined by taking advantage of modern surface science techniques such as LEED, AES, UPS and EELS. Ethylidyne (≡CCH₃) has been detected as the major adsorbed species formed from the adsorption of ethylene followed by rearrangement[19-27]. Regarding the initial stages of the adsorption of ethylene, two alternative models have been suggested, e.g., associative and dissociative adsorption models. For associative adsorption, the π-bonding-component of the C≡C double bond of ethylene is broken, and the orbitals are released to form two σ-bonds with the metal surface, which is represented as follows:

\[ \text{H}_2\text{C}=\text{CH}_2 + \text{M-M} \rightarrow \text{H}_2\text{C(M)-C(M)H}_2 \] (12)
For the dissociative adsorption of ethylene, hydrogen atoms are split off without rupture of the double bond. This process is as follows:

$$H_2C=CH_2 + 4M \rightarrow HC(M)=C(M)H + 2MH$$  \hspace{1cm} (13)

Based on the consideration of adsorption energies, the associative adsorption model (12) is favored by a number of investigators. On the gas-solid interface, the adsorbed ethylene, which is initially parallel to the surface, will be rearranged to form ethylidyne. A possible scheme for the rearrangement of adsorbed ethylene to yield the ethylidyne species has been proposed by Kang and Anderson[28] based on a semiempirical molecular orbital calculation using the atom superposition and electron delocalization molecular orbital (ASED-MO) method. No literature reports have appeared concerning such processes occurring on liquid-solid interfaces.

Unlike the gas-solid interface, the adsorption of ethylene on the solid electrode-liquid electrolyte interface (i.e., electroosorption) has been thought to be more complex. Comparing the oxidative desorption of adsorbed species originating from ethylene and acetylene, Gilman[16] suggested that identical species are involved, which would indicate that the adsorption of ethylene is dissociative and that the species
remaining on the surface is an adsorbed acetylene molecule. Johnson\(^{29}\), however, found that the kinetic behavior of ethylene is different from that of acetylene and suggested that the electrosorption of ethylene is associative. The associative adsorption model has also been suggested by Wieckowski\(^{30}\) based on the results of lateral modification experiments, in which other types of molecules such as carbon monoxide were co-adsorbed. If the associative model is true, the initial resulting adsorbed species should have a similar molecular structure to that originating from the adsorption of ethane. The experimental results obtained in this laboratory using the in situ FTIR technique shows that the adsorbed species originating from ethane and ethylene do have similar structures, which indicates that the adsorption of ethylene is associative. Thus, the species formed from the adsorption of ethylene at the electrode-electrolyte interface is not too dissimilar from those formed at the gas-solid interface, where the associative adsorption of ethylene takes place\(^{28}\).

Compared with the adsorption of ethylene on the gas-solid interface, the electrosorption of ethylene (e. g., at the platinum-electrolyte interface) is actually a replacement process involving adsorbed
solvent (mainly water), and the lateral interaction of adsorbed ethylene with such adsorbed solvent cannot be overlooked. As mentioned earlier, the adsorption process at the gas-solid interface involves rearrangements of fragments of the initially adsorbed ethylene. By contrast, the adsorption process at the electrode-electrolyte interface can involve interaction between various types of adsorbed species, including solvent and electrolyte ions. The various follow-up steps, rearrangement at the gas-solid interface and interaction with adsorbed solvent at the electrode-electrolyte, will give rise to totally different adsorbed species remaining on the surfaces. An example from the literature of such a difference is provided by Wieckowski et al.[31]. By transferring a platinum electrode pre-covered with adsorbed species originating from the electrosorption of ethylene in the hydrogen region (i.e., the potential region corresponding to hydrogen adsorption) back to the UHV chamber, they found no ethylidyne species on the surface but some unknown "alcohol-like" species. The formation of "alcohol-like" species indicates that the interaction between initial adsorbed ethylene and water is so strong that an oxygenation process has taken place. As will be shown later, water can play an important role
in both the adsorption and oxidative desorption processes of hydrocarbon molecules, even at relatively less positive potentials compared to those required to form adsorbed OH species.

The linear potential sweep voltammetry (LPSV) technique has been used to diagnose the electrochemical nature of adsorbed species formed from ethylene by several research groups. Due to variations in experimental conditions, however, the results do not always coincide with each other. Using the LPSV technique, Gilman [32] observed only a single broad anodic peak in the oxide region at a platinum electrode in 0.1 M HClO₄ at 30°C and assigned that to the electrooxidation of Type II species. In contrast to this result, Stickney et al.[33] observed two well-separated peaks in a positive potential sweep also in 0.1 M HClO₄ at 23°C but using the thin layer technique and a lower potential sweep rate (2 mV/s). While conducting the LPSV experiments at elevated temperatures (≥ 80°C), even using different concentrations and types of electrolytes, Griffith[34], Michri[35] and Gilman[16] all reported that two well-defined peaks were observed for platinum in solutions saturated with ethylene. In 1979, Triaca et al.[36] further examined the temperature effect on the
electrooxidation of adsorbed species arising from ethylene on platinized platinum in 0.5 M H₂SO₄. They observed only a single, broad oxidation peak centered at 1.2 V vs. RHE at 40°C but observed two distinct oxidation peaks as the temperature was elevated to 80°C. They also pointed out that the adsorbates formed at low temperature (e.g., 40°C) cannot be completely oxidized even at quite positive potentials (1.5 V vs. RHE), but all of the adsorbates can be electrochemically removed from the platinum surface at 80°C at the same anodic potential sweep limit as that at 40°C.

According to those results, the electrochemical desorption of ethylene-derived adsorbates on platinum is strongly dependent on the experimental conditions, especially the temperature. A possible explanation for the wide variety of oxidative desorption behavior may be that the types of adsorbed species vary with certain experimental conditions. The presence of two oxidation peaks has been considered to be related to the oxidative desorption of type I and type II adsorbed species [16, 34-35]. Nevertheless, this explanation has been a point in question. The appearance of more than one anodic peak indicates the existence of more than one species on the electrode surface during the
anodic potential sweep but does not sufficiently prove existence of these same species before the potential sweep starts. For example, the presence of a second peak at a more positive potential may be due to the oxidation of a product formed during the potential sweep up to the potential for the second peak. This question cannot be clearly answered just by the common electrochemical techniques. Molecular level information about the adsorbed species and products at different potentials should be obtained to elucidate these peaks on a cyclic voltammetry curve by means of modern in situ spectroscopic techniques.

By means of chemical[37], mass spectroscopic[38] and gas chromatographic[39] analyses, the overall reaction for the electrocatalytic oxidation of ethylene on platinum electrodes in acid solution has been established to be as follows:

\[ \text{C}_2\text{H}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \]  

(14) with 100% efficiency. Based on the determination of the Tafel slope, and the pH and pressure dependencies by stationary electrochemical measurements, Wroblowa et al.[37] and Bockris et al.[40] suggested the following mechanistic steps for the electrocatalytic oxidation of ethylene:

\[ \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{ad} \]  

(15)
\[ \text{H}_2\text{O} \rightarrow \text{OH}_\text{ad} + \text{H}^+ + \text{e}^- \quad (16) \]

\[ \text{C}_2\text{H}_4\text{ad} + \text{OH}_\text{ad} \rightarrow \text{C}_2\text{H}_3\text{ad} + \text{H}_2\text{O} \text{ (or C}_2\text{H}_4\text{OH}_\text{ad}) \quad (17) \]

\[ \text{C}_2\text{H}_3\text{ad} \text{ (or C}_2\text{H}_4\text{OH}_\text{ad}) + \text{......} \rightarrow \text{......} \]

\[ \rightarrow 2\text{CO}_2 + 11\text{H}^+ + 11\text{e}^- \quad (18) \]

The formation of Pt-OH\text{ad} on the platinum surface (16) was considered to be the rate-determining step. A kinetic equation has been derived from this consideration:

\[ i = k \ a_{\text{H}_2\text{O}} \ (1-\theta_E) \ \exp(\betaE/RT) \quad (19) \]

where \( \theta_E \) is the coverage of adsorbed ethylene. The enhancement of the reaction rate by increasing pH was thought to be due to a decrease of the potential of zero charge (pzc) on platinum, which results in an increase of the surface coverage of water molecules which could react with adsorbed ethylene at preferred orientations. The negative pressure effect was interpreted to be due to a decrease of the coverage of water (1-\( \theta_E \)).

The pressure effect on the electrocatalytic oxidation of ethylene has also been examined by Triaca et al.[41] using a potentiodynamic technique with low potential sweep rate (2-10 mV/s). In contrast to the results obtained by Bockris, he obtained a positive effect of pressure on the oxidation of ethylene over
the pressure range from $10^{-3}$ to 1 atm in 1 N H$_2$SO$_4$ and suggested a different mechanism:

$$C_2H_4 \rightarrow C_2H_4\text{ad}$$ (20)

$$C_2H_4\text{ad} \rightarrow C_2H_2\text{ad} + 2H^+ + 2e^-$$ (21)

$$C_2H_2\text{ad} \rightarrow R_\text{ad} + H^+ + e^-$$ (22)

$$C_2H_2\text{ad} + H_2O \text{ (or H}_2O\text{ad)} \rightarrow R_\text{HOH}_\text{ad} + H^+ + e^-$$ (23)

$$R_\text{ad} \text{ (or R}_\text{HOH}_\text{ad) + H}_2O \text{ (or H}_2O\text{ad) } \rightarrow CO_2 + H^+ + e^-$$ (24)

The electron transfer step (22) or (23) followed the electrosorption of ethylene has been considered as the rate-determining step, from which the following kinetic equation has been derived:

$$i = k \theta E \exp(\alpha FE/RT)$$ (25)

Although ethylene has been more extensively studied than other hydrocarbon molecules, the electrochemical reaction mechanism is still in question. Without information about the adsorbed species formed on platinum electrodes at different potentials and temperatures, the overall reaction mechanism derived just from the Tafel slope and the pressure dependence may be misleading, especially in the case of the electrocatalytic oxidation of complex molecules, which involves a number of reaction steps.
References


CHAPTER II
THE ELECTROCATALYTIC OXIDATION OF METHANE ON LOW AND
HIGH INDEX SINGLE CRYSTAL PLATINUM SURFACES
IN HOT PHOSPHORIC ACID

2.1 Introduction

The electrocatalytic oxidation of methane has been investigated by several research groups during the last several decades, with the research being motivated primarily by interest in fuel cells[1-5]. Platinum has been indicated to be the most active electrocatalyst for the oxidation of methane. On platinum surfaces in acid media at elevated temperatures, methane can be electrochemically converted to carbon dioxide based on the following equation[6, 7]:

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \]  

(1)

One of the important steps in this overall reaction has been proposed to involve the formation of an oxygen-containing species, e.g., CHO, CO or COH[1,2,5].

All of these previous investigations, however, have been conducted on polycrystalline platinum surfaces, either smooth bulk platinum or Teflon-bonded platinum black. The lack of surface structural control
has limited the more detailed understanding of the electrooxidation mechanism of methane.

In this chapter, the electrocatalytic oxidation of methane has been further examined using well-defined surfaces which include low-index and selected high-index surfaces. The objective has been to correlate the kinetics and mechanisms of reaction (1), and the formation of oxygenated species, with the surface structures in the form of terraces and steps.

Since methane electrooxidation requires elevated temperatures in order to yield significant currents, phosphoric acid was used in this work as the working electrolyte due to its stability and high conductivity at temperatures above 150°C. The main disadvantage of this acid, however, is anion adsorption on platinum surfaces. This effect will also be examined on the single crystal platinum surfaces both at room temperature and at elevated temperatures.

2.2. Experimental

The single crystal platinum electrodes (6.35 mm diameter, 6.35 mm thick and 99.999% pure) were purchased from Metal Crystal and Oxide Ltd. (Cambridge, England). The crystals were oriented by Laue back-scattering to better than 1° and then polished down to
0.1 μm using standard metallurgical techniques (increasingly finer grades of emery paper, diamond paste, and finally alumina). Before each experiment, the single crystals were annealed at 1000 ± 50°C[8] for 10-20 min. in the reducing region of a hydrogen flame and then cooled down in a hydrogen gas trap. The electrode surface was protected with a drop of ultra-pure water when transferring the electrode into an electrochemical cell. This drop of water on the platinum surface plays three important roles in transferring the electrode from the cooling trap to the electrochemical cell: (1) protecting the electrode surface from contamination by laboratory air and possible impurities floating on the electrolyte surface; (2) making the formation of a meniscus much easier without wetting the sides of the electrode by bulk electrolyte. The electrode was introduced into the electrolyte under potential control (typically 0.8 V vs. RHE). A hanging meniscus of about 3 mm height was formed between the single crystal surface and the bulk electrolyte. For platinum the height of the hanging meniscus should not be smaller than 2.5 mm to prevent wetting of the sides of the electrode[9]. A piece of platinum foil (2 cm², 99.999% purity) was used as the counter electrode. The reference electrode used
was a reversible hydrogen electrode (RHE) in the same electrolyte but at room temperature and in the absence of methane. All of the potentials reported here are referred to the potential of this reference electrode.

Phosphoric acid (85 wt.%) was purchased from Mallinckrodt and further purified by treatment with 50% \( \text{H}_2\text{O}_2 \) and platinum black/\( \text{H}_2 \), as described elsewhere\cite{10}. Ultrahigh purity (UHP) \( \text{N}_2 \) from Matheson was used to deaerate the electrolyte. The reactant gas, methane, was also purchased from Matheson with 99.99% purity and used without further purification.

The temperature was controlled in an air oven within \( \pm 2^\circ\text{C} \). Two thermocouples, one inside the electrolyte and another outside the electrochemical cell, were used to control and check the temperature.

An EG \& G PARC Model 175 Universal Programmer, an EG \& G PARC Model 173P Potentiostat and a Yokogawa Model 3033 X-YY' recorder were used as the main instruments.

2.3. Results and Discussion
2.3.1. Hydrogen Adsorption and Desorption in 85 wt.% \( \text{H}_3\text{PO}_4 \) at Room Temperature

The state of the platinum surfaces was examined initially at room temperature in 85 wt.% phosphoric
acid solution using the linear sweep cyclic voltammetry technique. The hydrogen adsorption/desorption features were compared with those reported earlier which are indicative of high quality single crystal surfaces at room temperature.

On the Pt(100) surface (Fig. 2-1), a pair of complementary sharp, symmetric peaks located at 0.31 V in both the positive and negative sweeps directions was observed. These peaks have been assigned to strongly adsorbed hydrogen\[^{11}\]. Compared with similar peaks obtained using other types of electrolytes (e.g., HClO\(_4\) and H\(_2\)SO\(_4\)), the peaks obtained in concentrated phosphoric acid are much sharper. The same situation holds for the sharp peak located at 0.08 V on the Pt(110) surface (Fig. 2-2). These features have been interpreted in the light of the strong adsorption of the molecular H\(_3\)PO\(_4\) and the ionic form H\(_2\)PO\(_4^-\) in the concentrated aqueous phosphoric acid solution\[^{12}\].

On the Pt(111) surface (Fig. 3-3), the cyclic voltammogram is quite different from those obtained in perchloric and sulfuric acids. A pair of very sharp complementary peaks, which are characteristic of the Pt(111) surface, were almost totally absent. Instead, a pair of narrow peaks at a potential of 0.27 V was observed, which have been assigned by Tanaka et al.\[^{11}\]
Fig. 2-1. The voltammetry curve of Pt(100) in 85 wt.% H₃PO₄ at room temperature. Sweep rate: 50 mV/s.
Fig. 2-2. The voltammetry curve of Pt(110) in 85 wt.% H₃PO₄ at room temperature. Sweep rate: 50 mV/s.
Fig. 2-3. The voltammetry curve of Pt(111) in 85 wt.% H₃PO₄ at room temperature. Sweep rate: 50 mV/s.
to the adsorption/desorption of phosphate. The basic experimental evidence leading to this assignment was that these two complementary narrow peaks became larger and sharper with increasing concentration of phosphoric acid[12]. At that time, however, it was not well understood why the total hydrogen coverage on the Pt(111) surface increased with increasing concentration of phosphoric acid. Is it possible that these two peaks correspond to the adsorption/desorption of a special type of hydrogen bound at specific types of sites? The answer is positive, as will be shown later.

2.3.2. Hydrogen Adsorption and Desorption in 85 wt.% $\text{H}_3\text{PO}_4$ at Elevated Temperatures.

As the temperature is elevated to higher values, the cyclic voltammograms of Pt(110), Pt(100) and Pt(111) change dramatically. Figure 2-4. shows three cyclic voltammograms obtained in 85% phosphoric acid at 150°C. There are several special features which are different from those obtained at room temperature. First, the hydrogen adsorption/desorption features on all of the single crystal surfaces were affected by the phosphate anions but to different extents for the different crystallographic orientations. The hydrogen adsorption/desorption peaks on Pt(110) have been pushed
Fig. 2-4. The voltammetry curves of Pt(110), Pt(100) and Pt(111) in 85 wt.% H₃PO₄ at 150°C. Sweep rate: 50 mV/s.
to more negative potentials, which may indicate stronger adsorption of phosphate-related anions on Pt(110) than on the other two surfaces. The sharp hydrogen adsorption/desorption peaks that are characteristic of the (111) and (100) surfaces at room temperature either become broader or disappear. They became two broader unsymmetric peaks (0.245 V and 0.28 V) on the Pt(100) surface and two very small symmetric peaks (0.2 V) on the Pt(111) surface. Secondly, anodic current peaks were observed in the double layer region on all three surfaces at 150°C. There are two peaks on the Pt(110) (0.58 V and 0.71 V) and Pt(111) surfaces (0.53 V and 0.68 V) but only one dominant peak (0.63 V) on Pt(100). Measurements on a polycrystalline platinum surface show that the appearance/disappearance of these peaks takes place reversibly with increasing/decreasing temperature[13]. Various techniques for the purification of phosphoric acid have been used by Clouser[14] but were not successful in eliminating these peaks. The nature of the species giving rise to these peaks and the formation mechanisms for these species have been studied in several research groups[13-15]. These species have usually been thought of as being acid-derived. In 1978, Vogel and Baris[15] found evidence which suggested that, at higher
temperatures and concentrations of phosphoric acid, adsorbed phosphide formed by reductive adsorption of phosphoric acid is responsible for these peaks. The reaction to form phosphide is written as follows:

$$H_3PO_4 + 5H^+ + 5e^- + Pt \rightarrow Pt-P + 4H_2O \quad (2)$$

Returning to the subject of the special types of hydrogen adsorption/desorption that give rise to a pair of complementary narrow peaks on the Pt(111) surface, this result (Fig. 2-4) indicates that, at elevated temperatures, the special adsorption sites for hydrogen adsorption are occupied by phosphoric acid-derived anions and the complementary peaks become much suppressed. Furthermore, it should be mentioned that the characteristics of this pair of complementary peaks on the Pt(111) surface also depend on the positive potential limit. The appearance and disappearance of this pair of complementary peaks have been observed by increasing the positive potential limit from 0.9 V to 1.5 V at an increment of 100 mV each time. To avoid the adsorption of acid-derived species at 150°C, the cyclic voltammogram of the Pt(111) surface was measured at 110°C and the results are shown in Fig. 2-5. In Fig. 2-5, three dotted lines correspond to three different positive potential limits: 0.9 V, 1.0 V and 1.1 V. If the potential limit is 0.9 V or more
Fig. 2-5. The voltammetry curves of Pt(111) with different positive potential limits (dashed lines) in 85 wt.% H$_3$PO$_4$ at 110°C. The solid line is for the disordered Pt(111) surface after sweeping the potential up to 1.5 V vs. RHE. Sweep rate: 50 mV/s.
negative to this value, the complementary peaks at 0.3 V will not appear (dotted line in Fig. 2-5), which shows that the specific sites corresponding to the complementary peaks on the Pt(111) surface have been blocked by either impurities or acid-derived species. As the potential limit was increased to more positive values than 0.9 V, the surface sites for the hydrogen adsorption/desorption, which cause the complementary peaks at 0.3 V, were recovered (two dashed lines). While the positive potential window was opened to more and more positive values up to 1.45 V, the voltammetry curves in the hydrogen region remained unchanged. This unusual stability of Pt(111) has also been found at room temperature\(^{[12]}\). However, once the positive potential limit is set at 1.5 V, where substantial oxygen generation occurs, the peaks at 0.3 V will disappear (not shown in this Figure). In this case, the surface can be considered as disordered. Moving the potential window back to 1.0 V, the voltammetry curve of this disordered surface is obtained and shown in Fig. 2-5 (solid line). Comparing the voltammetry curves of Pt(111) before and after the surface is disordered (one of the dashed lines and the solid line in Fig. 2-5), it may be concluded that these two complementary peaks at 0.3 V on Pt(111) could
correspond to hydrogen adsorption/desorption on some active and well-defined (111) terraces. These terraces are very stable over a wide potential range unless the potential is positive enough that oxygen generation takes place.

2.3.3 The Electrocatalytic Oxidation of Methane.

The electrocatalytic oxidation of methane has been investigated on the three low index single crystal platinum surfaces. In order to gain more detailed understanding of the dependence of the kinetics of the oxidation reaction on the density and orientation of steps, several selected high index single crystal platinum surfaces have also been used.

2.3.3.1 On The Three Low Index Single Crystal Platinum Surfaces

Figure 2-6 shows the cyclic voltammograms of the three low index single crystal surfaces with and without methane in 85% phosphoric acid at 150°C. On the basis of the anodic current in both the positive and negative potential sweeps on the three low-index single crystal surfaces, the Pt(100) surface has the highest electrocatalytic activity for both complete or partial oxidation of methane (Fig. 2-6(a)). In the
Fig. 2-6. The voltammetry curves of the three low-index single crystal platinum surfaces in 85 wt.% H$_3$PO$_4$ saturated with N$_2$ (dashed line) or 100% CH$_4$ (solid line) at 1 atm and 150°C. (a). Pt(100). (b). Pt(111). (c). Pt(110). Sweep rate: 50 mV/s.
positive potential sweep, a sizable anodic current peak centered at 0.66 V was observed. As the potential was swept back in the reverse direction, a broad anodic current peak was observed covering almost the whole double layer region. Compared with this anodic peak, the lack of current in the less positive potential region in the anodic sweep implies that the surface has been blocked by the accumulation of adsorbates derived from the partial oxidation of methane. This voltammogram (Fig. 2-6(a)) was very stable, i.e., did not change with the number of cycles, which shows that the adsorbates of methane can be completely desorbed at this positive potential limit. Surprisingly, both the Pt(111) (Fig. 2-6(b)) and Pt(110) (Fig. 2-6(c)) surfaces lack electrocatalytic activity for the oxidation of methane on this sweep time scale.

Figure 2-7 shows the voltammetry curves of the three low index single crystal surfaces obtained by sweeping the potential in the positive direction after holding the potential at 0.32 V for 1 min. For comparison, the voltammetry curve on a polycrystalline platinum surface which had been pretreated in the same way as single crystal surfaces (e.g., H₂-air annealing and cooling in H₂) is also shown in Fig. 2-7 (dotted line).
Fig. 2-7. The voltammetry curves of low-index single crystal and polycrystalline platinum surfaces in 85 wt.% H$_3$PO$_4$ saturated with CH$_4$ at 1 atm and 150°C obtained by sweeping the potential in the positive direction after holding the potential at 0.32 V vs. RHE for one min. Sweep rate: 50 mV/s.
In this experiment the adsorption of methane is permitted for a longer time than it the potential is swept continuously. An anodic peak was observed for the Pt(111) surface at a more negative potential (0.58 V) than that on the Pt(100) surface (0.68 V). This result implies that the adsorption of methane on the Pt(111) surface is a slow process and the adsorbates formed on this surface are weakly bound to the surface and therefore require a less positive potential to be desorbed. Stronger adsorption of methane on the Pt(100) surface would explain the much larger and sharper anodic current peak (0.68 V). The sharpness of this peak is related to the change of coverage of the adsorbates with potential. The same phenomenon has been observed for the oxidative desorption of carbon monoxide to yield solution phase carbon dioxide[16]. This has been interpreted as being due to the coupling of two different surface processes. These are, in particular, the desorption of the adsorbate and the discharge of water on the surface. On the Pt(110) surface, one broad, low intensity anodic current peak was observed. The peak potential is the same as the first peak (shoulder) in the voltammogram for the polycrystalline surface. In this adsorption experiment, the Pt(110) surface shows once again the
poorest electrocatalytic activity for the adsorption and oxidation of methane.

In summary, the adsorption and oxidation of methane on platinum are strongly surface structure-dependent. The Pt(100) surface has the highest electrocatalytic activity and the Pt(110) surface has the lowest activity for these surface processes. The same results have also been obtained for the oxidation of ethane, discussed in chapter III.

In order to interpret the different electrocatalytic activities of different crystallographic orientations for the adsorption and oxidation of methane, the nature of the adsorbates formed on the surfaces and the possible mechanisms of these processes should be first discussed. It is well accepted that the adsorbed species formed on platinum in the hydrogen region in acid media from the adsorption of methane include oxygenated species which have been defined as type I or O-type species\[17\]. The molecular structures which have been suggested are CHO, COH or CO-like\[^{1,4}\]. These oxygenated species are thought to be formed by the interaction of adsorbed methane with the adsorbed water. Linearly bonded carbon monoxide has been detected in this laboratory during the adsorption of ethane on a polycrystalline
platinum surface in acid media using an in situ FTIR spectroscopic technique. Considering that identical adsorbates may be involved during the adsorption of both methane and ethane$^{17}$, a very likely adsorbate derived from methane on platinum is linearly bonded carbon monoxide. The possible stepwise formation of linearly bonded carbon monoxide from methane is shown in Figure 2-8. Forming incipient bonds to both C and H is suggested as the first step, which is followed by the breaking of C-H bond and formation of adsorbed CH$_3$ad. Adsorbed water molecules on the neighboring sites are required to form a reaction transient complex ([(CH$_3$)$_{ad}$-OH$_2$)$_{ad}$]). This complex will be further dehydrogenated, as low molecular weight alcohol molecules do, to form linearly bonded carbon monoxide. The carbon monoxide formed at less positive potentials will accumulate on the surface until the potential is changed to more positive potentials where carbon monoxide is oxidatively desorbed from the surface to yield carbon dioxide. The whole reaction mechanism can be represented as follows:

\[
\text{CH}_4 \to (\text{CH}_3)_{\text{ad}} + \text{H}^+ + \text{e}^- \quad (3)
\]

\[
2 \text{[H}_2\text{O + Pt} \to (\text{H}_2\text{O})_{\text{ad}} \quad (4)
\]

\[
(\text{CH}_3)_{\text{ad}} + (\text{H}_2\text{O})_{\text{ad}} \to [(\text{CH}_3)_{\text{ad}}-(\text{OH}_2)_{\text{ad}}] \quad (5)
\]

\[
[(\text{CH}_3)_{\text{ad}}-(\text{OH}_2)_{\text{ad}}] \to (\text{CO})_{\text{ad}} + 5\text{H}^+ + 5\text{e}^- \quad (6)
\]
Fig. 2-8. The schematic diagram for the formation of linearly bounded carbon monoxide from adsorbed methane and water on platinum.
\[(\text{CO})_{\text{ad}} + (\text{H}_2\text{O})_{\text{ad}} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (7)\]

where step (3) may be rate-determining\(^3\). This mechanism also shows that the water molecules adjacent to the adsorbed organic species play a very important role in the partial oxidation of methane to carbon monoxide at relatively negative potentials and the subsequent oxidative desorption of the carbon monoxide thus formed.

Based on this general mechanism of the adsorption and oxidation of methane on platinum, the surface structure sensitivity of these processes may be interpreted. The fact that the Pt(100) surface has the highest electrocatalytic activity for the adsorption and oxidation of methane is very possibly due to the following effects:

1. The Pt(100) surface is more lightly poisoned by the phosphoric acid-derived anions, evidenced by the current peaks for the adsorption/desorption of hydrogen, which leave more free sites for the adsorption of both methane and water molecules;

2. The specific arrangement of atoms on this surface may promote the formation of the \([(\text{CH}_3)_{\text{ad}}-(\text{OH}_2)_{\text{ad}}]\) reactant complex with a favorable steric configuration; and
3. The strong adsorption of hydrogen on this surface may favor the further decomposition of the reactant complex to form linearly bound carbon monoxide.

The possible reason corresponding to this low electrocatalytic activity of the Pt(110) surface may be that electrolyte anions or impurities adsorb in the "trough" of the "washboard" surface of Pt(110) and can not be replaced either by methane or water molecules. The possible surface sites available for the adsorption of methane or water may be just the top rows of surface atoms. The effective surface coverage of active sites would be greatly decreased and, therefore, the coverage of adsorbates derived from the partial oxidation of methane would be quite small.

For the Pt(111) surface, it is very probable that the adsorbed intermediates are not completely dehydrogenated. In other words, adsorbates consisting of C, H and O are formed instead of linearly bonded carbon monoxide. The C-H-O adsorbates require less positive potentials than linearly bounded carbon monoxide to be oxidatively desorbed from the surface. Future work is needed to identify the possible molecular structure of these kinds of adsorbates formed specifically on the Pt(111) surface.
2. 3. 3. 2. On The High Index Single Crystal Platinum Surfaces

The significant difference for the adsorption and oxidation of methane on Pt(100) and Pt(111) intrigued the author and prompted him to study some high index single crystal surfaces in the [011] zone of the unit stereographic triangle. Figure 2-9 shows the voltammetry curves for the oxidation of methane on selected single crystal surfaces in [011] zone. As the ratio of atoms with the (100) orientation to those with the (111) orientation increases, the anodic peak potential shifts to more positive values and approaches that on Pt(100). Secondly, the anodic charges corresponding to the current peaks increase as the step sites are introduced into the (111) terraces. This result supplies further evidence that the atomic arrangement with the orientation of (100) will favor the partial oxidation of methane but the species formed on these sites seems to be more strongly adsorbed, requiring more positive potentials to be further oxidized. The same kind of effect has also been observed for the oxidation of formic acid on single crystal platinum surfaces[18]. The definition of electrocatalytic activity of a particular orientation of platinum electrode surfaces for the oxidation of the
Fig. 2-9. The voltammetry curves of Pt(111), Pt(755), Pt(311) and Pt(100) in 85 wt.% H₃PO₄ saturated with CH₄ at 1 atm and 150°C obtained by sweeping the potential in the positive direction after holding the potential at 0.28 V vs. RHE for one min. Sweep rate: 50 mV/s.
hydrocarbons studied here, however, is different from that for the oxidation of small oxygenated organic molecules such as formic acid. For the oxidation of small oxygenated organic molecules, the electrocatalytic activity is defined by the extent of formation of carbon monoxide on a particular surface, which has been considered as a poison species, and the potential required for the oxidative desorption of carbon monoxide. The smaller the coverage of carbon monoxide formed on the surface and the more negative the potential required to remove it, the higher the electrocatalytic activity of this surface for the oxidation of these oxygenated organic molecules. It was observed, however, that a surface does not have electrocatalytic activity for the oxidation of methane if it cannot promote the formation of carbon monoxide on the surface by partial oxidation of methane. The same phenomena have been also observed for the oxidation of ethylene, which will be discussed in Chapter IV. The key difference between the oxidation of hydrocarbon molecules and that of small oxygenated organic molecules is that carbon monoxide originating from the partial oxidation of hydrocarbon molecules is an intermediate rather than a poison species for the complete oxidation of the hydrocarbon.
2.4. Conclusion

This work shows that the electrocatalytic oxidation of methane on platinum has a strong surface structural sensitivity. The Pt(100) surface has the highest electrocatalytic activity considering the magnitude of the anodic current in both the anodic and cathodic sweep directions. The major factors that contribute to the higher electrocatalytic activity of Pt(100) are 1) that it appears to be less poisoned by the phosphoric acid-derived anions at elevated temperatures; and 2) a favorable atomic arrangement exists on the surface which is suitable for the formation of the \([(\text{CH}_3)\text{ad}^-\text{(OH}_2\text{)ad}]\) transient complex. Introducing Pt(100) steps into the Pt(111) surface enhances the formation of the active reactant complex and thus the kinetics of the oxidation of methane. The Pt(110) surface is more seriously poisoned by the acid or acid-derived anions at elevated temperatures, which results in the poorest electrocatalytic activity for the Pt(110) surface for the adsorption and oxidation of methane. Different types of adsorbates may form on the Pt(111) surface. Future work is necessary to identify the possible structure of these types of adsorbates.
References


CHAPTER III
THE ELECTROCATALYTIC OXIDATION OF ETHANE ON PLATINUM

3.1. Introduction

The electrocatalytic oxidation of ethane as well as the electro-adsorption of this molecule has been investigated on platinum surfaces by several research groups\(^1\)\(^-\)\(^5\) with the main interest related to the development of hydrocarbon-air fuel cells. Although ethane molecules are much more active with respect to adsorption and oxidation on platinum at more moderate temperatures than methane, the reaction kinetics are still too slow to obtain reasonable current densities in practical applications such as fuel cells. The blocking of active sites on the platinum surface by formation of strongly adsorbed intermediates is the major factor responsible for the rapid decay of the electrocatalytic activity of the platinum electrode. Based on studies of the oxidative desorption of these strongly adsorbed species on a platinum electrode surface, two types of species were suggested by Breiter\(^6\): partially oxygenated single carbon (C\(_1\)) species and dehydrogenated species, in which the C-C
bond has not been broken. The distribution of these two types of species and their possible interconversion have also been examined[1, 4]. Molecular level information, however, is generally lacking with respect to these adsorbed species, particularly on well-defined electrode surfaces at an atomic level.

In the present work, the electrocatalytic oxidation of ethane has been further studied and the emphasis has been placed on the following:

- the time and potential dependence of the formation of strongly adsorbed species;
- the molecular structures of these species;
- the effect of electrode surface structure and
- the comparison of ethane and methane electrocatalysis.

Platinum, the most active catalyst so far available for the electrocatalytic oxidation of ethane, has been used as the working electrode. Information about the adsorption and oxidation of ethane was first collected using conventional potentiodynamic techniques. These helped in the understanding of the electrochemical behavior of ethane, the nature of the adsorbed species and also the influence of external
factors on these electrochemical processes. The molecular structures of adsorbed species and the products of their further oxidation were obtained by studying their vibrational spectra using the in situ FTIR spectroelectrochemical technique. Single crystal platinum surfaces were also examined under potentiodynamic conditions, which greatly help in the molecular level understanding of the mechanisms of these surface processes.

3. 2. Experimental

3. 2. 1. Potentiodynamic Measurements

The working electrode was either a piece of polycrystalline platinum foil (Johnson Matthey, 99.999% purity, 1 cm², 0.1 mm thickness) or single crystal platinum rod (Metal Crystals and Oxides Ltd., Cambridge, England. 99.999% pure). The preparation of single crystal platinum surfaces has been described in Chapter II. The stationary hanging meniscus electrode (HME) technique was employed in these single crystal studies. A piece of platinum wire mesh (5 cm², 99.999% purity) was used as the counter electrode. A reversible hydrogen electrode (RHE) involving platinized platinum at the same temperature as the
working electrode was used as the reference electrode and all the potentials reported in this chapter are referred to this RHE electrode.

The electrolytes used here were either 0.1 M HClO₄ or 0.1 M H₂SO₄, which were prepared by dilution from concentrated Ultrex reagents (J. T. Baker, inc.) with ultra-pure CO₂-free water (18 MΩ cm). Both the UHP nitrogen gas used for deaerating the electrolytes and the CP grade ethane (Johnson Matthey) were first bubbled through the same electrolyte trap before feeding to the electrochemical cell.

The electrochemical cell (Fig. 3-1) was made of Pyrex glass and had three conventional chambers which were separated from each other by glass frits. A Luggin capillary extended from the reference chamber was also situated at the center of the main, working electrode chamber. This cell was positioned in a water bath where the temperature was well-controlled (±0.1° C).

An EG & G PARC Model 175 Universal Programmer, an EG & G PARC Model 173 Potentiostat and a Yokogawa Recorder were used as the main instruments in this part of experiments.
3.2.2. In Situ FTIR Spectroelectrochemical Investigations

Since elevated temperatures (e.g., 60°C) are needed to obtain a reasonable rate of oxidation of ethane, a new spectro-electrochemical cell has been designed and machined for these higher temperature measurements. The schematic drawing of this cell is shown in Fig.3-2a. This cell can be used at elevated temperatures up to 130°C without leakage of liquid. Each connection part is specifically sealed by using a Viton O-ring or taking advantage of differing thermal expansion coefficients of different materials. The working platinum electrode, which had a nearly elliptical shape with an area of 1.7 cm², was thermally molded in Kel-F at 330°C and polished using standard metallurgical polishing methods. Any Kel-F or alumina that remained on the platinum electrode surface during the polishing was removed with ultrasonic cavitation produced with an ultrasonic generator at ca. 50 KHz. The electrode was then washed with ultrapure water and the acid electrolyte. After the electrode was mounted on a Kel-F rod, a CaF₂ dove prism was seated on the top of the electrode and fixed to the cell body by a window holder with three small screws. The electrode can be
Fig. 3-1. The schematic drawing of the electrochemical cell used for potentiodynamic studies.
Fig. 3-2. The schematic drawings of optical path (a) and the spectroelectrochemical cell (b) used for the in situ FTIR investigations.
moved back and forth to the dove prism using a micrometer. This micrometer can move forward or backward without rotation, which ensured that the electrode can always be pushed against the optical window each time at the same position. Since the parallelism of the electrode and optical window base cannot be perfect without using optical alignment, the same "azimuthal" position is required to compare different sets of data. A platinum wire (0.5 mm diameter) loop served as the counter electrode. A thin Teflon tube (1 mm ID) was used as the Luggin capillary and extended out of the spectroscopic sample chamber to an electrolyte reservoir, where a reference RHE was connected. The hydrophobicity of the Teflon tube, however, can result in the formation of a gas bubble at elevated temperatures, which may lead to a very high resistance in the Luggin capillary. Therefore, a very thin platinum wire (0.1 mm diameter) was put into this thin Teflon tube to make ionic connection in case of formation of a gas bubble.

FTIR measurements were conducted using an IBM Instruments IR-98A (Bruker 113) Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled HgCdTe (MCT) detector. The optical source and the detector chamber were kept under vacuum and
separated from the sample chamber with KBr windows. The sample chamber was purged with dry nitrogen. The sample optical table consists of the spectroelectrochemical cell and several spherical and plane mirrors. The optical path is illustrated in Fig. 3-2b.

The mirror-finished platinum electrode was further electrochemically cleaned inside the FTIR cell by cycling the electrode between 0.05 V to 1.5 V (vs. RHE) while the temperature was being raised. The electrolyte was replaced several times before the measurements began. The cleanliness of the electrode surface and the electrolyte finally were electrochemically and spectroscopically examined at a working temperature (60°C), which will be described in detail in Chapter V. The electrode was then held at 0.3 V (vs. RHE) for ten min. as the ethane gas was feeding into the cell. In order to reduce the strong absorption of infrared light by the solvent, the electrode was pushed against the optical window and an electrolyte thin layer was formed between the electrode and the optical window.

Two potential programs, linear potential sweep and single potential step, which are adaptable to irreversible surface reactions, were adopted in these
investigations. For the linear potential sweep program, the first spectrum (270 scans) was first collected at the holding potential (E₁) and then the potential was swept in the positive direction at a sweep rate of 1 mV/s. While sweeping the potential the IR spectra were continuously collected. Each spectrum involved 270 scans which consumed about 100 s and therefore covers a potential increment of about 100 mV. The potential reported for each spectrum, however, corresponds to the potential in the middle of these scans. Instead of sweeping the potential to more positive values, the single potential step program permits the potential to be stepped directly to a positive value at which particular adsorbates can be oxidatively desorbed. In both cases, the spectra were calculated as 
\[-(1-R_s/R_T),\]
where \(R_s\) and \(R_T\) are the reflectance of the electrode surface at the sample and reference potentials, respectively.

3.3. Results and Discussion

3.3.1. Potentiodynamic Investigations

3.3.1.1. On A Polycrystalline Platinum Electrode Surface
The adsorption and oxidation of ethane were first examined on a polycrystalline platinum electrode surface in 0.1 M HClO₄ solution saturated with ethane at 1 atm and 80°C. Figure 3-3. shows the voltammetry curves of oxidative desorption of adsorbed species formed at a potential of 0.25 V vs. RHE by holding for different times. Two adjacent peaks were observed in the double layer region of platinum at low coverage. While increasing the adsorption time, the distribution of these two adjacent peaks is changed and the total charge increased until the second anodic peak began to develop in the oxide region of platinum. For clarity, the peaks in the double layer region and the anodic peak in the oxide region of platinum are defined here as the peaks Ia, Ib and II. Peak I has been observed for adsorption and oxidation of a number of small organic molecules which include oxygenated[7-10] (such as CH₃OH, COOH and reduced CO₂) and hydrocarbons[11-12] (such as CH₄ and C₂H₄). The splitting of this peak into two adjacent peaks under some conditions has also been reported. The charge under peak I and its dependence upon adsorption time are plotted in Fig. 3-4. The first point in the Q-t curve is a theoretical point, which arises from the assumption that the coverage of adsorbed species is zero at zero time.
Fig. 3-3. The voltammetry curves of a polycrystalline platinum electrode obtained by sweeping potential in anodic direction after holding the potential at 0.25 V vs RHE for various length of periods in 0.1 M HClO₄ saturated with ethane at 1 atm and 80°C. Sweep rate: 100 mV/s.
Within the very beginning 30 s, the adsorption process proceeds relatively rapidly and greater than two thirds of the saturation coverage is reached. After this point more adsorbates were built up on the surface but at a much slower rate until the surface was saturated. The saturation charge is about 420 $\mu$C/cm$^2$ and was obtained within ca. 4 min. This saturation charge, however, did not stay constant in the following adsorption period but instead decreased with time to compensate the growing anodic band in the oxide region of platinum. This coverage "decrease" may be interpreted as follows: while more adsorbed species corresponding to peak II were formed in the longer adsorption time on the surface sites adjacent to the adsorbed species corresponding to peak I, the free sites required for the further oxidation of adsorbate I were partially occupied by organic molecules instead of water molecules, which resulted in the incomplete oxidation of adsorbate I in the potential region for calculating the anodic charge.

From these time dependent measurements it can be concluded that the formation of adsorbate I plays a very important role in the adsorption and oxidation of ethane at least on platinum. The formation rate is so high that this causes an almost immediate loss of
Fig. 3-4. The dependence of the charge corresponding to peak I of each stripping curve in Fig. 3-3 upon holding time (dotted line) and its first derivative with respect to the holding time (solid line).
electrocatalytic activity of the platinum electrode until the adsorbate can be oxidatively removed from the surface by polarizing the electrode to more positive potentials. The formation of this type of adsorbed species on the electrode surface is also potential dependent. Figure 3-5 shows the voltammetry curves of the oxidative desorption of adsorbed species formed at different holding potentials. The electrode was held at different potentials for the same time (1 min.) in 0.1 M HClO₄ saturated with ethane at 1 atm and 80°C. The total oxidative desorption charge depends strongly on the holding potential. The charge contributed by peak Ia was observed to be potential and coverage dependent. It was increasing as the total charge increased.

Integrating peak I in all of the voltammetry curves in Fig. 3-5 produces the Q-E relationship (Fig. 3-6), which shows a bell shaped curve. Differentiating these points vs. potential shows that the potential sensitive region with respect to the formation of adsorbate I is between 0.15-0.4 V vs. RHE, and the maximum formation potential is 0.26 V, which is close to the open circuit potential of the Pt/ethane electrode. This means in a practical sense that the
Fig. 3-5. The voltammetry curves of a polycrystalline platinum electrode obtained by sweeping potential in anodic direction after holding the potentials at different values for one minute in 0.1 M HClO$_4$ saturated with ethane at 1 atm and 80°C. Sweep rate: 100 mV/s.
Fig. 3-6. The dependence of the charge of anodic peak I in Fig. 3-5 with potential (dashed line) and the first derivative of the charge with respect to potential (solid line).
electrode has already been poisoned by the formation of adsorbate I before operation of the fuel cell.

The same types of measurements have been done using 0.1 M H₂SO₄ solution and the same results have been obtained as in 0.1 M HClO₄ except that peak I became little bit broader in the sulfuric acid solution.

With regard to the interest of concerning the bonding strength of the adsorbates responsible for peak Ia and Ib to the electrode surface, the adsorbates formed at 0.3 V vs. RHE were perturbed by coupling adsorption/desorption of hydrogen at more negative potentials. The electrode was first held at 0.3 V vs. RHE for 5 min. and then the potential was swept in either positive-going (stripping) direction directly or in negative-going direction (perturbing) first to different negative potential limits. The results are shown in Fig. 3-7 where the dash-dotted line corresponds to the voltammetry curve obtained in ethane-free electrolyte, the solid line represents the anodic stripping voltammetry without the perturbation and the dashed lines are negative-going first curves with different potential limits. This figure shows that the species corresponding to the peak Ia can be partially removed from the surface by applying a more
Fig. 3-7. Voltammetry curves obtained by sweeping the potential in the anodic direction first (solid line) or cathodic direction first with different negative limits (dashed line) after holding the potential at 0.3 V for 5 min. using a polycrystalline platinum electrode in 0.1 M H₂SO₄ saturated with ethane at 1 atm and 80°C. The dash-dotted line is the voltammetry curve obtained in an ethane-free electrolyte. Sweep rate: 100 mV/s.
negative potential. In situ FTIR results shown later tell that the molecular structures of adsorbed species corresponding to both peak Ia and peak Ib are identical. One reasonable possibility, therefore, is that the species giving peak Ia was formed on the different surface sites from those for species giving peak Ib and they can be more mobile and be easily oxidized. The picture focusing on this point will be more clear after the following studies using well defined single crystal electrode surfaces.

3. 3. 1. 2. On The Three Low Index Single Crystal Platinum Electrode Surfaces.

The three low index single crystal platinum surfaces were first characterized by the adsorption/desorption of hydrogen in 0.1 M H₂SO₄ in the absence of ethane at both room temperature and 80°C. The voltammetry curves of Pt(110), Pt(100) and Pt(111) are shown in Fig. 3-8a, 3-8b and 3-8c, respectively. The hydrogen adsorption/desorption characteristics on all three surfaces at room temperature are close to those reported in the literature except the current spike on Pt(111) surface which is not as sharp as that reported. As the temperature was elevated to 80°C, the voltammetry curves of Pt(110) and Pt(100) surfaces took
Fig. 3-8a. The voltammetry curve of Pt(110) in 0.1 M H$_2$SO$_4$ at room temperature (dash-dotted line) and 80°C (solid line): Sweep rate: 50 mV/s.
Fig. 3-8b. The voltammetry curve of Pt(100) in 0.1 M H$_2$SO$_4$ at room temperature (dash-dotted line) and 80°C (solid line): Sweep rate: 50 mV/s.
Fig. 3-8c. The voltammetry curve of Pt(III) in 0.1 M H₂SO₄ at room temperature (dash-dotted line) and 80°C (solid line): Sweep rate: 50 mV/s.
more changes than that of Pt(111). The hydrogen adsorption and desorption peaks on Pt(110) were suppressed and the peak potentials shifted to more negative values. Although the hydrogen adsorption and desorption charges on Pt(100) did not change very much, the current peaks became distorted and unsymmetric. The main factor responsible for these suppressing and distorting may be the anion adsorption and desorption which was possibly enhanced by elevating the temperature. The voltammetry curve of Pt(111) at 80°C, having sharp contrast with Pt(110) and Pt(100), did not change very much compared with that at room temperature. This indicated, to some extent, insensitivity to the anion effect. No voltammetry curves of three low index platinum surfaces at elevated temperatures are available so far in the literature for comparison.

The formation of adsorbed species I on these three single crystal surfaces have been examined at 80°C by linearly potential sweep after the electrode potential was held at 0.3 V vs. RHE for one minute. Figure 3-9 shows the anodic stripping spectra obtained on these single crystal surfaces and also, for comparison, it includes the spectrum obtained using a polycrystalline platinum rod electrode that has been pretreated as
Fig. 3-9. Voltammetry curves of a polycrystalline and three low index single crystal platinum surfaces obtained by sweeping potential in anodic direction after holding the potential at 0.3 V for 1 min. in 0.1 M H₂SO₄ saturated with ethane at 1 atm and 80°C. Sweep rate: 100 mV/s.
single crystal surfaces (i.e., H₂-annealing and cooling). This result suggests that the formation and oxidation of adsorbed species I are strongly surface structure dependent. If the charges of those peaks are considered as the criteria for activity, Pt(100) surface has the highest activity toward the formation and oxidation of adsorbed species I but Pt(110) surface is totally inert for these processes. Although the oxidative desorption potential of adsorbates formed on Pt(111) is more negative to that on Pt(100), the charge is more than three times smaller than that on Pt(100). If only the anodic desorption charges or the current intensities are considered, then the electrocatalytic activity of three low index single crystal platinum surfaces goes in the following order:

Pt(100) > Pt(111) > Pt(100)

It should be recalled that the same electrocatalytic activity order and even the same anodic current shapes have been observed during the adsorption and oxidation of methane molecules (CH₄) on the same surfaces (chapter II). Similar characteristics have been reported in the study of the anodic behavior of adsorbates formed from methanol on single crystal platinum surfaces[13]. This kind of similarity of surface structure sensitivity produces some positive
clues for interpreting the adsorption and oxidation of small and even larger saturated hydrocarbon molecules.

These dramatic differences in the electrocatalytic activity for the adsorption and oxidation of small hydrocarbons on three surfaces may partially result from differences in the sensitivity to anion action. The surface atomic configuration, however, plays an even more important role in the adsorption and oxidation of these molecules. This will be discussed later after the molecular structure of adsorbed species has been identified by the in situ FTIR measurements.

Comparing the voltammetry curves of the three low index single crystal surfaces with that of the polycrystalline surface (Fig. 3-9), peaks Ia and Ib might be assigned to the oxidation of adsorbed species formed on the Pt(111) and Pt(100) domains on the polycrystalline surface. This suggests that the splitting of the anodic current peak in the double layer region of a polycrystalline surface is due more to the oxidation of species adsorbed on different surface sites than to the oxidation of species with different molecular structures[5]. The further information supplied by this comparison is that the polycrystalline surface pretreated by annealing consists more of Pt(111) domains than Pt(100) domains,
which causes the polycrystalline surface to have lower
electrocatalytic activity than Pt(100) surface.

3.3.2. In Situ FTIR Investigations

The in situ FTIR spectroelectrochemical technique
has been successfully used in studying the adsorption
and oxidation of small organic molecules. It is a
powerful tool to identify the adsorbed species on the
electrode surface and provide spectroscopic information
about the on-going electrochemical reactions on the
surface. It was, therefore, expected that the adsorbed
species from ethane and their electrochemical behavior
can be well understood by using this technique.

3.3.2.1. Linear Potential Sweep Studies

The linear potential sweep covers the potential
region from 0.3 V to 1.3 V (vs. RHE), in which the
adsorbed species formed at 0.3 V can be oxidatively
desorbed form the surface as discussed above. The
spectra collected in the whole potential region has
been divided and treated in two parts. Fig. 3-10 shows
the spectra in the wavenumber region from 1700 cm⁻¹ to
2500 cm⁻¹ at different potentials. No IR band in other
frequency regions except for the migration of
perchlorate ion (1100 cm\(^{-1}\)) induced by the charge transfer has been observed in the potential region of 0.3 V to 0.79 V. Each sample spectrum shown in Fig. 3-10 was obtained by subtractively normalized to the so-called reference spectrum collected at 0.3 V. The number above each spectrum is a averaged potential in the potential region where the spectrum covered. By this plotting way, the peak point-up and peak point-down IR bands indicate formation and disappearance of species, respectively. If the species existed at both potentials and its vibration frequency shifted with potential, it will give a bipolar peak in the spectrum due to the subtraction of these two spectra at two different potentials.

The bands at about 2040 cm\(^{-1}\) can be assigned to linearly bonded CO and those at 2345 cm\(^{-1}\) to carbon dioxide. The first information obtained here is that linearly bonded CO was formed at the holding potential (0.3 V vs. RHE). As the potential became more positive than 0.3 V, the adsorbed carbon monoxide started to be oxidized to yield carbon dioxide, which was evidenced by the decrease of the CO peak and the increase of the solution phase CO\(_2\) peak. This process took place starting at 0.47 V (appearance of CO\(_2\) peak) and ended at 0.68 V (no further increase of CO\(_2\) peak intensity).
Fig. 3-10. In situ FTIR spectra obtained by a linear potential sweep modulation (1 mV/s) after holding potential at 0.3 V for 10 min. in 0.1 M HClO₄ saturated with ethane at 1 atm and 60°C. Each spectrum contains 270 scans with a resolution of 8 cm⁻¹ and subtractively normalized to the reference spectrum at 0.3 V.
Fig. 3-11. The "absolute" linearly bonded CO spectra obtained by subtractively normalizing all the spectra to that collected at 0.79 V. All the experimental conditions are as same as those described in Fig. 3-10.
The anodic current peak in the double layer region of platinum (peak I) on the voltammetry curve, accordingly, can be well interpreted as the oxidative desorption of linearly bonded carbon monoxide which was formed in the hydrogen region of platinum.

In order to follow the oxidative desorption of linearly bonded CO on the surface, the spectrum collected at 0.79 V where CO was totally removed from the surface was chosen as a new reference, to which all the spectra collected were subtractively normalized. This type of treatment will give the absolute peak intensity at each potential\[14\]. The results obtained by this treatment are shown in Fig. 3-11. First, the strong CO peak starts to decrease at potential 0.47 V and totally disappeared at 0.68 V due to the oxidative desorption. Secondly, it is very interesting to notice that the CO peaks are not symmetric. The splitting of linearly bonded CO IR peak has been reported but without interpretation in the investigation of the adsorption and oxidation of carbon monoxide in 0.1 M NaClO4 absolute methanol solution\[15\]. One possible interpretation for this unsymmetric feature is that these CO bands may have resulted from superposition of two peaks, where the higher frequency side has a higher intensity. Recalling the anodic current Peaks Ia and
Ib developed in the double layer region of a polycrystalline platinum electrode and the separation of those peaks on Pt(111) and Pt(100) in the potentiodynamic studies, these two superpositioned IR peaks may be assigned to the linearly bonded CO adsorbed on Pt(111) and Pt(100) sites (Fig. 3-12), respectively. The higher frequency side peak belongs to the linearly bonded CO on Pt(111) surface sites and the lower frequency side to the same type of CO but adsorbed on Pt(100) surface sites. Due to the different quantities of CO formed on the two different types of sites, the IR peak intensities are different, which leads to an unsymmetric IR peak after superposition.

The differences of vibration frequencies of linearly bonded CO on Pt(111) and Pt(100) may be understood by taking into account the differences in bonding strength of carbon monoxide on different surface sites. The stronger the bonding of carbon monoxide to the surface, the lower the vibrational frequency. The carbon monoxide formed on Pt(111) sites involves weaker bonding to the surface than that on Pt(100) sites, which is evidenced by the requirement of less positive potentials to remove oxidatively the carbon monoxide adsorbed on Pt(111) (Fig.3-9).
Fig. 3-12. The schematic drawing of the splitting of linearly bonded CO IR peak: (a). Pt(111) sites and (b). Pt(100) sites.
Therefore, the vibration frequency of carbon monoxide linearly bonded on the Pt(111) sites is higher than that of carbon monoxide bonded on Pt(100) sites.

Further work using single crystal platinum surfaces to examine the vibration frequency shifts with surface orientations at the same coverage is needed to verify the interpretation.

The second part of spectra in the potential region from 0.79 V to 1.3 V is shown in Fig. 3-13. The spectra shown in this figure were subtractively normalized to the spectrum collected at 0.79 V where linearly bonded carbon monoxide has been oxidative desorbed from the surface. Fig. 3-13a shows that the carbon dioxide signal grew again in this potential region, which suggests that some types of adsorbed species were oxidized to yield at least partially carbon dioxide. Fig. 3-13b shows the corresponding spectra in the low frequency region. The negative peaks at ca. 1057 cm\(^{-1}\) may be assigned to the C-O stretching vibration of \(-\text{enol}\) organic groups and may be responsible for the appearance of carbon dioxide peaks in this potential region. These results indicate that the species responsible for the peak II in the voltammetry curves (Fig. 3-3) have an "alcohol-like" structure with C-C bond remained. The word "alcohol
Fig. 3-13. In situ FTIR spectra in the potential region from 0.79 to 1.3 V vs RHE. Each spectrum was subtracively normalized to that collected at 0.79 V. All the experimental conditions are as same as those described in Fig. 3-10.
like" is used here to distinguish the adsorbed species detected now from those formed directly from alcohol (like ethanol). In the later case, the species are not adsorbed as strongly as those derived from the adsorption and partial oxygenation of ethane. The species formed from ethane may have two carbon atoms bonded to the platinum surface. This possibility is good since the C–C bond will break easily and, simultaneously, the adsorbates will be oxidized to carbon dioxide. The vibration frequency of the \(-\text{enol}\) group is close to the cut-off region of CaF\(_2\) optical window, which makes the spectra so noisy. A proper window materials with less adsorption such as ZnSe should be selected to satisfy the measurements in this frequency region in the future work.

3.3.2.2. Single Potential Step Studies

The dependence of the formation of linearly bonded carbon monoxide on adsorption potential has also been examined with in situ FTIR spectroscopy together with potential step techniques. The measurements were conducted for each adsorption potential separately. The positive potential limit was 0.8 V vs. RHE for all of the measurements. At this potential the adsorbed carbon monoxide can be totally removed from the
Fig. 3-14. In situ FTIR spectra obtained with a potential step from each Es to 0.8 V after holding potential at Es for 10 min. in 0.1 M HClO₄ saturated with ethane at 1 atm and 60°C. Each spectrum involves 500 scans with a resolution of 8 cm⁻¹ and was subtractively normalized to that collected at 0.8 V.
surface. The CO IR band in this type of subtractively normalized spectrum will reflect directly the total amount of carbon monoxide formed at the adsorption potential as mentioned above. Fig. 3-14 shows the spectra obtained from these measurements. As it shows, dramatic potential dependence of the formation of linearly bonded carbon monoxide has been observed. Two interesting characteristics, in addition to the unsymmetric CO\(_L\) peak at higher coverage, have also been observed by this type of measurements: The CO\(_L\) peak at 0.2 V was more symmetric and new bands appeared at 1720 cm\(^{-1}\) if the potentials was held at more negative potentials (0.1 V to 0.2 V).

Recall that the predominant anodic current peak is peak Ib (Fig. 3-5) at a potential between 0.1 V to 0.2, V and that this peak has been considered to correspond to the oxidation of linearly bonded CO on the Pt(100) sites. The more symmetric peak shape may be understood by thinking that this type of carbon monoxide contributed most of this IR peak. Furthermore, this figure shows a 38 cm\(^{-1}\) wavenumber shift of CO\(_L\) band from 0.2 V to 0.3 V. This shift is too large to be explained just on the basis of Stark effect arising from the electric field at the interface. This
frequency shift should include the effect of change in surface adsorption sites.

If at 0.1 V and 0.2 V the adsorbed CO\textsubscript{L} is formed mostly on the Pt (100) sites, the question is: what species are on the Pt(111) sites at those potentials? The IR peaks at 1708 cm\textsuperscript{-1} and 1720 cm\textsuperscript{-1} may lead to the answer. These negative peaks are usually assigned to the production of carbonyl group species which are like COOH or HCO. Looking for the COOH peak in the "fingerprint" region has failed. The IR band at ca 1700 cm\textsuperscript{-1}, therefore, can be assigned to HCO species. Before the potential was stepped to 0.8 V, the oxygenated species may already have been formed on the surface sites at 0.1 V or 0.2 V but they were not completely dehydrogenated and may be some sort of alcohol. The HCO species produced at 0.8 V may not be stable and can be further oxidized to carbon dioxide. Fig. 3-15 shows the changes of intensity of both carbon dioxide and carbon monoxide IR peaks vs. adsorption (holding) potentials. The same bell shape curve as that obtained by potentiodynamic studies (Fig. 3-6) has been observed. It is especially important to point out here, however, that the ratio of intensity of carbon dioxide to that of carbon monoxide is higher at 0.1 V and significant higher at 0.2 V than at more positive
Fig. 3-15. Plots of CO$_2$ and CO$_L$ IR peak intensities in Fig. 3-14 vs holding potentials (Es).
potentials. The extra carbon dioxide produced at these more negative potentials may be contributed by the further oxidation of HCO species.

3. 3. 2. 3. Mechanism of Formation of Carbon Monoxide from Ethane

Carbon monoxide has been detected as one of the intermediates during the oxidation of small oxygenated organic molecules, like methanol, which can be easily understood by the dehydrogenation of this types of molecules. The formation of carbon monoxide from ethane at hydrogen region of platinum, however, is not so straightforwardly understandable. Since this process involves two major steps: C-C bond breaking and oxygenation, one of the challenging question is if and how these processes can take place at these not so positive potentials.

The over-all reaction can be represented by the following equation:

\[
C_2H_6 + 2H_2O \rightarrow 2COad + 10H^+ + 10e^- \quad (1)
\]

where water molecules serve as the oxygen source. The value of standard free energy of adsorbed CO is not available so far. If using the gas phase value of free energy of CO, the standard reduction potential \( E^0 \) was
calculated to be 0.24 V vs. SHE at room temperature. This process is thermodynamically feasible.

The breaking of C-C bond in the adsorption process on platinum-gas interface has been established\(^{[18]}\). On the platinum-liquid interface, this process may be further enhanced by the interaction with adsorbed water molecules on neighboring surface sites according to the reaction-pair mechanism\(^{[19]}\). This interaction finally leads to the formation of C-O bond in the molecular form of alcohol, which is the precursor species of formation of carbon monoxide. If this interpretation is acceptable, the following steps driving to the formation of carbon monoxide from these precursors will be easily understood by considering their further dehydrogenation. The whole process is shown schematically in Fig. 3-16. It can be also represented by the following stepwise reactions:

\[
\begin{align*}
2\text{H}_2\text{O} &\rightarrow 2\text{H}_2\text{O(ad)} \quad (2) \\
\text{C}_2\text{H}_6(\text{g}) &\rightarrow \text{C}_2\text{H}_4(\text{ad}) + 2\text{H}^+ + 2\text{e}^- \quad (3) \\
\text{C}_2\text{H}_4(\text{ad}) + 2\text{H}_2\text{O(ad)} &\rightarrow \\
&\rightarrow 2\text{H}_2\text{COH(ad)} + 2\text{H}^+ + 2\text{e}^- \quad (4) \\
2 \quad [\text{H}_2\text{O} &\rightarrow 2\text{H}_2\text{O(ad)}] \quad (5) \\
2 \quad [\text{H}_2\text{COH(ad)} + \text{H}_2\text{O(ad)} &\rightarrow \\
&\rightarrow \text{CO(ad)} + \text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^-] \quad (6)
\end{align*}
\]
Fig. 3-16. The schematic drawing of mechanism of formation of linearly bonded CO from ethane on a platinum electrode surface.

\[ \text{C}_2\text{H}_6\text{ad} + 2\text{H}_2\text{O}_{\text{ad}} \rightarrow 2\text{CO}_{\text{ad}} + 10\text{H}^+ + 10\text{e}^- \]
where step (6) is thought to take place by means of water involvement\textsuperscript{[16-17]}. According to this mechanism, free sites around each adsorbed ethane molecule are required to adsorb water or discharge protons. The slow adsorption rate of ethane on platinum surface can satisfy this requirement.

The sensitivity of formation of carbon monoxide to the surface structure of platinum electrodes may be fairly well understood based on this mechanism. The first role played by the surface structure is the different extent of weakening the C-C bond. It has been pointed out by Somorjai and Yeates\textsuperscript{[18]} that the four-fold adsorption sites on Pt(100) are more active toward the C-C bond breaking than the three fold sites on Pt(111). Secondly, the strong interaction of hydrogen in a water molecule with Pt (100) surface\textsuperscript{[20]} will enhance both the oxygenation (4) and dehydrogenation (6) by weakening the H-O bond of a water molecule. Both of these two factors give rise to the higher formation rate of carbon monoxide on Pt(100) surface than that on Pt(111). Due to the weak interaction between carbon and platinum atom on Pt(111), furthermore, the carbon monoxide formed later will have a higher vibration frequency and be easily oxidized. The loss of electrocatalytic activity on
Pt(110) can be simply interpreted as that the anion adsorbed in the "though" cannot be removed at not very positive potentials, which reduces the adsorption sites for both ethane and required water molecules to form carbon monoxide.

3. 4. Conclusion

The adsorption of ethane on platinum in acid media is potential and surface structure dependent. The adsorbates formed on a polycrystalline surface have been identified as linearly bonded carbon monoxide (ca. 2040 cm⁻¹) and alcohol-like species (1057 cm⁻¹) by means of in situ FTIR spectroscopic technique. The single crystal studies show the following electrocatalytic activity order for the formation of linearly bonded carbon monoxide:

Pt(100) > Pt(111) > Pt(110)

The intrinsic roles played by the electrode surface structure are the catalytic activity toward weakening the C-C bond, capturing the oxygen from adsorbed water and balancing the competition of ethane, water and anions. It has been suggested that water molecules not only play a role in the oxidation of carbon monoxide but also in the formation of carbon monoxide.
References


11. Q. Zhao, This thesis, Chapter II.


CHAPTER IV

POTENTIODYNAMIC STUDIES OF THE ADSORPTION AND OXIDATION
OF ETHYLENE ON PLATINUM IN ACID MEDIA AT ELEVATED
TEMPERATURES

4.1. Introduction

The major interest of studying the
electrocatalytic adsorption and oxidation of ethylene
stems from two important aspects: it will provide a
predictive base for identification of more active
electrocatalysts needed to develop direct hydrocarbon
fuel cells and sensors and highlight the understanding
of the mechanisms of electrooxidation of more complex
organic molecules.

The possibility of using ethylene as anodic fuel
to develop a hydrocarbon-air fuel cell has been
explored back to nineteen century. While a relatively
large amount of research in the 1960's was focused on
fuel cells with hydrocarbons or alcohols as the fuel in
industrial and government laboratories, the research
was gradually decreased and phased out in most
industrial electrochemical laboratories in the 1970's.
The principal problem with cells operating on such
fuels at low and moderate temperatures (< 200°C) was
the lack of sufficiently active catalysts for the
oxidation of hydrocarbon and alcohol fuels. The present research effort are aimed at identifying and understanding the factors controlling the mechanisms and kinetics of these electrooxidation reactions. The research approach is a fundamental one with emphasis on molecular level understanding of the oxidation processes.

The electro-adsorption and electrocatalytic oxidation of ethylene on platinum have been further examined in this thesis work using both electrochemical and spectroelectrochemical techniques. The results will be reported in the following two chapters. In this chapter, the influence of temperature, electrolyte, pressure of ethylene and the surface structure on the kinetics of adsorption and oxidation will be reported.

4.2. Experimental

The electrochemical measurement set-up and the preparation of single crystal platinum surfaces were the same as described in Chapter III. The working electrodes with polycrystalline structure were either platinum foil or a rotating disk. The rotating disk electrode used at higher temperatures (e.g., 180°C) was made in the similar way described by Clouser[1].
The schematic drawing of this electrode is shown in the Fig. 4-1. Briefly, this electrode consists of two parts: a piece of common shaft fitting the Pine rotator and an exchangeable electrode head. The platinum disk electrode head was thermally modelled in Kel-F material and restrained by a platinum O-ring with a rectangle section. This electrode has been shown to have no leaking for hours of measurement at 150°C.

The phosphoric acid has been purified by the procedure described in Chapter II of this dissertation and a reference therein. The 0.1 M \( \text{H}_2\text{SO}_4 \) was prepared by dilution of concentrated Ultrex reagents (J. T. Baker, inc.) with ultra-pure and \( \text{CO}_2 \)-free water (18 M\( \Omega \) cm). CP grade ethylene and its mixture with UHP \( \text{N}_2 \) was purchased from Johnson Matthey.

The galvanostatic stationary measurements of the electrocatalytic oxidation of ethylene were conducted using CWRU-fabricated Pt/C gas-fed electrodes. This kind of electrode consists of two layers: backing layer and electrocatalyst layer. The electrocatalyst layer was fabricated using Prototech material which contained 10 wt.% platinum on active carbon. The final platinum loading on electrode is about 0.36 mg/cm\(^2\). This working electrode was held in a special electrode holder, which is shown in Fig. 4-2. The electrode
Fig. 4-1. The schematic drawing of the rotating disk electrode used at 150°C.
Fig. 4-2. The schematic drawing of a gas-fed electrode holder for the stationary measurements at elevated temperatures.
holder is made of Kel-F material which is chemically stable at a temperature up to 150°C. The current collector is a piece of platinum sheet O-ring connected to a platinum lead wire that comes out the electrode holder through the gas outlet channel. A (Pt)Hg/Hg2HPO4(s)/85% H3PO4 electrode has been made by the author in the way described in the literature[2] and used as the reference electrode. The potentials have been converted to RHE and reported with IR correction. A piece of platinum gauze (5 cm²) was used as the counter electrode.

All of the measurement instruments used here were the same as described in Chapter II.

4.3. Results and Discussion

4.3.1. Linear Potential Sweep Studies of The Electrocatalytic Oxidation of Ethylene and The Adsorbed Species Generated During The Oxidation

The electrooxidation of ethylene on a polycrystalline platinum electrode in 0.1 M H3PO4 at 80 °C was first studied using a linear potential cyclic sweep method. Fig. 4-3 shows the voltammetry curves of platinum with different positive potential limits.
Fig. 4-3. Voltammetry curves of a polycrystalline platinum with various positive potential windows in 0.1 M H$_3$PO$_4$ saturated with ethylene at 1 atm and 80°C. Sweep rate: 100 mV/s. The dash-dotted line is the voltammetry curve of the same electrode in ethylene-free electrolyte.
(solid lines). The dash-dotted line corresponds to the voltammetry curve obtained before ethylene was introduced into the system. In the anodic sweep direction the reaction begins at 0.5 V (vs. RHE), which is evidenced by the onset of anodic current. The anodic current increases with potential polarization and finally reaches the maximum at ca. 0.95 V. The current decreases at more positive potentials where the surface of electrode has been gradually oxidized. As the potential is swept back in the cathodic direction from the positive potential limits, the whole reaction is totally blocked by the surface oxide. The reaction, however, restarts once the free sites are available by reducing the surface oxide. The onset potential of this anodic current is dependent on the positive potential sweep limits and the sweep rate, in other words, on the coverage of surface oxide and time involved in this measurement technique. The more positive the potential limit and the faster the sweep rate, the more negative the onset potential of this hysteric current.

There is a shoulder at ca. 0.85 V on the voltammetry curves obtained in the positive-going sweep direction. It indicates that the whole anodic peak is resulted from at least two superposition peaks. In
order to examine the origination of these peaks and see if they originate from the oxidative desorption of adsorbed species, ethylene in the electrolyte was removed by purging the electrolyte with \( \text{N}_2 \) after the potential was held in hydrogen region, which permitted the adsorption of ethylene on the electrode surface. Fig. 4-4 shows a typical curve of this type of measurements (solid line), which was conducted in 0.1 M \( \text{H}_3\text{PO}_4 \) at 70°C by holding the potential at 0.3 V for 2 min. For comparison, the voltammetry curve of the same electrode in the presence of bulk ethylene (dash-dotted line) and that obtained in the organic-free electrolyte (dashed line) are also shown in this figure. Three interesting features are observed in Fig. 4-4:

1. For the measurement of the oxidative desorption of the adsorbed species, the current profile in the cathodic direction from 1.5 V was identical to that of platinum in organic-free electrolyte, which indicates that the adsorbed species formed at 0.3 V can be totally removed from the electrode surface under this potential limit. The anodic current profile (solid line), therefore, originated from the oxidation of all possible adsorbed species.
Fig. 4-4. Voltammetry curves of a polycrystalline platinum electrode in 0.1 M H₃PO₄ saturated with ethylene or N₂ at 1 atm and 70°C. Sweep rate: 100 mV/s. Dashed line: organic-free; Solid line: the oxidative desorption of adsorbed species formed at 0.3 V vs RHE by holding potential for 2 minutes and then removing ethylene in the bulk phase; Dash-dotted line: with ethylene in the bulk phase.
2. Two anodic peaks (peak I and peak II) are observed for the oxidative desorption of the adsorbed species. It has been suggested\(^3\)-\(^4\) that these two peaks originate from the oxidation of at least two types of species with different molecular constituents, i.e., the O-type species and CH-type species.

3. The current profiles in the presence (dash-dotted line) and absence (solid line) of ethylene in the bulk electrolyte overlapped at the initial part. This overlapping suggests that the swollen part mentioned above on the voltammetry curve in the presence of bulk ethylene is due to the oxidative desorption of adsorbed species. It also indicates that the oxidation of bulk ethylene takes place after removing these adsorbed species. The kinetics of oxidation of ethylene, therefore, has been shown to be controlled by the kinetics of formation and desorption of these adsorbed species.

To examine the anion effects on the electrooxidation of ethylene, the same measurements have been conducted in different types of acid electrolytes (i.e., \(\text{H}_3\text{PO}_4\), \(\text{H}_2\text{SO}_4\), \(\text{HClO}_4\), TFMSA). The anions derived from these acids have been observed to influence the adsorption/desorption of hydrogen at different extents. No variation of the voltammetry
curves, however, has been observed, which indicates that the selected anions has no effect on the adsorption and oxidation of ethylene. This behavior may be due to the relatively higher adsorption ability of ethylene on platinum surface than those of selected anions.

4.3.2. The Formation and Oxidative Desorption of Adsorbed Species

As mentioned above the adsorbed species play a very important role in the electrooxidation of ethylene. Their formation and oxidative desorption have been further examined. In order to decrease the readsoption of ethylene from the bulk solution, the examination was conducted in electrolyte saturated with ethylene at lower partial pressures of ethylene. Fig. 4-5 shows the current profiles (solid line) for the oxidative desorption of adsorbed species with different coverage, obtained by linearly sweeping the potential in positive-going direction after holding potential at 0.22 V for different periods of time in 0.1 M H₃PO₄ saturated with 0.03 atm ethylene at 80°C. As the coverage increases with longer holding time the intensity of peak I grows much faster than that of peak II. Peak I was also split into two adjacent peaks at
Fig. 4-5. Oxidative desorption voltammetry curves for the adsorbed species formed on platinum in 0.1 M H$_3$PO$_4$ saturated with ethylene at 0.03 atm and 80°C by holding the potential at 0.22 V for different period of time: (a) 5 s.; (b) 15 s.; (c) 30 s.; (d) 60 s. Dashed line: anodic part of voltammetry curve of platinum under the same condition but without ethylene in the electrolyte. Sweep rate: 100 mV/s.
low coverage (short time adsorption), which is similar to that observed for the adsorption of ethane. The in situ FTIR measurements for the adsorption and oxidation of ethylene which will be reported in Chapter V gives similar results. This provides good evidence that for the adsorption and oxidation of ethane, which shows that the species responsible for peak I are linearly bonded carbon monoxide and those for peak II are alcohol-like species, most probably ethylene glycol.

The oxidative desorption of linearly bonded carbon monoxide taking place far before the formation of Pt-OH suggested that water molecules have been involved in this desorption process rather than Pt-OH at least at this temperature (80°C). The oxidative desorption potential does vary with temperature. Fig. 4-6 shows the oxidative desorption profiles for the adsorbed species at various temperatures from 25°-70°C. The first feature in this figure is that the peak I moves dramatically to more negative potential as the temperature was elevated. This moving is expected and also important in the view of operating a fuel cell. Another feature in this figure is that the ratio of carbon monoxide to alcohol-like species has been increased by elevating temperature, which indicates
Fig. 4-6. Oxidative desorption voltammetry curves for the adsorbed species on platinum in 0.1 M H₃PO₄ at different temperatures. Sweep rate: 100 mV/s.
Fig. 4-7. Oxidative desorption voltammetry curves for the adsorbed species formed on platinum in 0.1 M H$_3$PO$_4$ saturated with ethylene at 0.03 atm and 80°C by holding the potential at different values for one minute: (a). 0.12 V; (b). 0.22 V; (c). 0.32 V; (d). 0.4 V; (e). 0.52 V. Dashed line: anodic part of voltammetry curve of platinum under the same condition but without ethylene in the electrolyte. Sweep rate: 100 mV/s.
that the C-C bond rupture and oxygenation process can be greatly enhanced by elevating temperature.

As in the case of adsorption of ethane on platinum, the formation of two types of species through adsorption of ethylene is also potential dependent. Fig. 4-7 shows the oxidative desorption current profiles for adsorbed species formed at different potentials (one min.) in 0.1 M H₃PO₄ saturated with ethylene at 0.03 atm and 80°C. The adsorption is strongly potential dependent and the maximum adsorption potential is in the potential range from 0.2–0.3 V which is around the pzc of platinum[5] and also the open circuit potential of platinum/ethylene electrode. The contribution of two adjacent peaks to peak I is also potential dependent, which shows to some extent the similarity to the adsorption of ethane which suggested to the linearly bonded CO adsorbed on different surface sites.

The formation and desorption of adsorbed species through the adsorption of ethylene on platinum, the formation of carbon monoxide is the critical process and depends dramatically on the temperature and potential.

The possible mechanism for formation of these oxygenated species in hydrogen region will be discussed
in detail in the next chapter. The oxidative desorption potential for carbon monoxide at elevated temperatures falls in the potential region far before that of formation of the surface Pt-OH, which has been usually considered the most active oxidative agent[6]. The very possible oxidative agent working here is the adsorbed water molecules rather than Pt-OH. The interaction between adsorbed CO and water has been elucidated based on a so-called "reaction pair" mechanism[7], which will be discussed later.

4. 3. 3. The Electrooxidation of Ethylene on The Three Low Index Single Crystal Platinum Surfaces

As mentioned above the formation of carbon monoxide plays very important role in the electrooxidation of ethylene. The overall reaction can be represented in the following equation:

$$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_{\text{ad}} + 8\text{H}^+ + 8\text{e}^-$$  \hspace{1cm} (1)

On the basis of operating potential region of a fuel cell, this reaction takes place giving rise to a dead-end product (CO$_{\text{ad}}$), which has been called "poison species" in the literature. From equation (1) it can be literally seen that there should be two important single steps which are involved in the overall reaction: rupture of C-C bond and oxygenation of
adsorbed hydrocarbon. The question, accordingly, comes out whether these processes are sensitive to the atomic structures of platinum surface. The electrooxidation of ethylene, therefore, was further investigated using the single crystal platinum surfaces.

4.3.3.1. Linear Potential Sweep Studies in a Wide Potential Region

Since more positive potential is required to oxidize the type II species, the positive potential window was opened to almost 1.5 V vs. RHE in the following measurements. This extension of the positive potential limit, however, will unavoidably result in the reconstruction of the surface structure[8]. Only the first potential cycle, therefore, is meaningful to the understanding of the sensitivity to the surface structure. Fig. 4-8 shows the voltammetry curves (first cycle) of three low index platinum surfaces in 0.1 M H₂SO₄ at 80°C. These voltammetry curves are close to those obtained at ambient temperature[8-9]. Both hydrogen adsorption/desorption and Pt-OH formation are sensitive to the surface structure. The peak potential for the formation of Pt-OH on Pt(111) surface is almost 200 mV more positive to that on both Pt(100) and Pt(110). Pt(111) surface, therefore, shows a
Fig. 4-8. Voltammetry curves (first cycle) of three low index single crystal platinum surfaces in 0.1 M \( \text{H}_2\text{SO}_4 \) at 80°C. Sweep rate: 50 mV/s.
relatively higher stability toward the potential changes.

4.3.3.2. The Electrocatalytic Oxidation of Ethylene on Pt(100).

The well prepared single crystal electrode was introduced into the electrolyte under potential control (0.8 V). The height of the electrolyte meniscus (ca. 3 mm) was set to the same value for each measurement. The potential was swept in the negative-going direction first and then back in the positive-going direction. The voltammetry curve of Pt(100) obtained in this way in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C is shown in Fig. 4-9. When the potential is linearly swept to 0.17 V vs. RHE in the negative-going direction, the cathodic current begins increasing. This cathodic current has been assigned to the electrochemical reduction of ethylene[10] to yield ethane. As the potential is swept back to more positive values, two well separated anodic peaks at 0.82 V and 1.0 V were observed. The first peak (at 0.82 V) is originated from the oxidative desorption of type I adsorbed species, i.e., carbon monoxide which has been considered to be responsible for the swollen part (shoulder) in the voltammetry
Fig. 4-9. The voltammetry curve (first cycle) of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C. Sweep rate: 50 mV/s.
Fig. 4-10. The voltammetry curve (first cycle) of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. Sweep rate: 50 mV/s.
**Fig. 4-11.** The voltammetry curve (first cycle) of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 0.01 atm and 80°C. Sweep rate: 50 mV/s.
curve of a polycrystalline surface (Fig. 4-3). The second peak (at 1.0 V) corresponds to the oxidative desorption of type II species and the oxidation of bulk ethylene.

These assignments will be seen more clearly through the measurements using low partial pressures of ethylene. Fig. 4-10 shows the voltammetry curve of Pt(100) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. The cathodic current for the reduction of ethylene decreases dramatically compared to that in Fig. 4-9 due to the decrease of saturated concentration of ethylene. Two anodic peaks are still there but the ratio of their intensities has been greatly changed. The peak at 0.97 V, which has been assigned to the oxidation of ethylene from bulk phase and the oxidative desorption of type II adsorbed species, is almost four times smaller than that obtained in the solution saturated with ethylene at 1 atm pressure. Under this condition, the oxidative desorption of type II adsorbed species contributes most of this peak. The anodic peak at 0.75 V, assigned to the oxidative desorption of adsorbed carbon monoxide, has a higher intensity than that in Fig. 4-9 and becomes much sharper. The formation of CO layer is a very fast process on Pt (100) surface. The maximum coverage of adsorbed CO can
be obtained as the potential was swept in the less positive potentials.

As the saturation partial pressure of ethylene decreases down to 0.01 atm, shown in Fig. 4-11, the second peak is totally lost and the only peak for oxidation of adsorbed carbon monoxide is observed in the positive-going direction. This result indicates that the formation of carbon monoxide is a preliminary step for the adsorption of ethylene, especially at low coverage of adsorbed species.

Concerning the electrocatalytic activity to the C-C bond rupture and oxygenation processes, Pt(100) surface is much better than the polycrystalline platinum and also, will be shown later, better than Pt(111) and Pt(110) surfaces. Although carbon monoxide is formed as the result of C-C bond rupture and oxygenation on the surface, it is better than the formation of other adsorbed species with C-C bond retaining (e.g., type II species). Taking into account the formation of carbon dioxide as the final product for the electrocatalytic oxidation of ethylene or other hydrocarbon molecules on platinum, the C-C bond has to be ruptured and the oxygen atoms have to be supplied. Since the dehydrogenation process goes so fast and so many water molecules are required (four
water molecules for each ethylene molecule) for each adsorbed hydrocarbon molecule, the formation of carbon monoxide is unavoidable due to the starving of oxygen. Carbon monoxide can be, therefore, considered as one of the intermediates for the oxidation of ethylene or other hydrocarbon molecules rather than a "poison species". In this sense, the electrocatalytic activity of a special surface can be compared by easiness of formation of carbon monoxide. Pt(100) is, accordingly, a better surface than a polycrystalline surface toward the oxidation of ethylene.

4.3.3.3. The Electrocatalytic Oxidation of Ethylene on Pt(111).

Fig. 4-12 shows the voltammetry curve of Pt(111) obtained under the same conditions in Fig. 4-11. Three anodic peaks are observed in the positive-going direction. The peak located at 1.17 V is most probably related to the surface oxidation and oxidation of bulk phase ethylene. The predominant peak at 0.97 V can be originated from the oxidation of type II adsorbed species. The intensity of this peak is more than four times smaller than that obtained using Pt(100). It shows that Pt(111) surface has a much worse electrocatalytic activity than Pt(100) toward the
Fig. 4-12. The voltammetry curve (first cycle) of Pt(111) in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C. Sweep rate: 50 mV/s.
oxidation of ethylene. As discussed above, the lower electrocatalytic activity for the oxidation of ethylene on Pt(111) surface may reflect the low electrocatalytic activity for breaking C-C bond during ethylene adsorption. This interpretation is also evidenced by the smaller intensity of the peak at 0.71 V, which can be assigned to the oxidative desorption of carbon monoxide. Based on the study of a gas-solid interface[11], it has been proposed that C-C bond can be more easily broken on a rectangle atomic surface structure (Pt(100)) than on a triangle structure (Pt(111)). The adsorption of ethylene on the liquid-solid interface studied here may copy the same structure sensitivity as on a gas-solid interface, at least for several initial steps.

The electrocatalytic oxidation of ethylene on Pt(111) has also been examined using low saturation partial pressures, Fig. 4-13 shows the voltammetry curve of Pt(111) in 0.1 M H₃PO₄ saturated with ethylene at 0.1 atm and 80°C. The intensities of peak I (0.72 V) and II (0.91 V) and the ratio of their intensities did not change too much compared with that in Fig. 4-12. This low sensitivity of peak I and II to the concentration of ethylene in both Fig. 4-12 and 4-13 shows that these peaks are related to the oxidative
Fig. 4-13. The voltammetry curve (first cycle) of Pt(111) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. Sweep rate: 50 mV/s.
desorption of adsorbed species. Since the formation of carbon monoxide is not enhanced by reducing the concentration of ethylene in the electrolyte as on Pt(100), the free sites are not available for the oxidation of bulk ethylene at less positive potentials where CO can be desorbed.

Based on these measurements, the major adsorbed species on Pt(111) surface is type II species. Since more positive potentials are required to desorb oxidatively this type of species, they are really the poison species rather than carbon monoxide. Once type II species are oxidatively removed from the surface, the potential is already in the region of surface oxidation. Surface oxidation gives platinum oxide that is not active toward the oxidation of ethylene. The lower electrocatalytic activity of Pt(111) than Pt(100) is, therefore, due to the preferred formation of type II species.

4.3.3.4. The Electrocatalytic Oxidation of Ethylene on Pt(110)

Fig. 4-14 shows the voltammetry curve of Pt(110) under the same condition in Fig. 4-12. One broad anodic peak with a shoulder at 1.03 V is observed. This shoulder is mostly due to the surface oxidation of
Fig. 4-14. The voltammetry curve (first cycle) of Pt(110) in 0.1 M H₂SO₄ saturated with ethylene at 1 atm and 80°C. Sweep rate: 50 mV/s.
**Fig. 4-15.** The voltammetry curve (first cycle) of Pt(110) in 0.1 M H₂SO₄ saturated with ethylene at 0.1 atm and 80°C. Sweep rate: 50 mV/s.
Pt(110), which is clearly shown in Fig. 4-8. Pt(110) surface has been found to be worst surface toward the oxidation of methane and ethane. The same behavior is also observed for the oxidation of ethylene studied in this chapter. The same broad anodic peak but with low intensity is also observed as decreasing the partial pressure of ethylene from 1 atm to 0.1 atm (Fig. 4-15). It is hard to tell whether this peak is due to the oxidative desorption of adsorbed species or not. The in situ spectroscopic measurements are needed to understand the oxidation behavior of ethylene on this surface.

4.3.4. The Electrocatalytic Oxidation of Ethylene in Hot Phosphoric Acid

The formation and oxidative desorption of the adsorbed species have been proved to be temperature dependent in the temperature region from 25-70°C (Fig. 4-6). More carbon monoxide can be formed at elevated temperature and it is more predominant than the formation of type II species. One of the strategies to eliminate the formation of type II species is, therefore, to elevate the temperature to much higher values. The investigation conducted at higher temperatures will also help to find out what is the
most negative potential sufficient to oxidize the adsorbed carbon monoxide and restore the electrode surface.

4.3. 4. 1. Linear Potential Sweep Studies at Temperatures above 100°C

The linear potential sweep studies were conducted in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and the temperature was varied from 100 to 180°C. The voltammetry curves are shown in Fig. 4-16. The first important feature that should be point out here is that the first anodic peak in the anodic direction moves to more negative potential (0.47 V) as the temperature was elevated to 180°C. The second feature is the anodic current in the cathodic direction increases greatly with temperature increase. When the potential reaches the value negative to 0.4 V the surface begins to be poisoned by the accumulation of carbon monoxide.

In order to examine the formation of type II species at 180°C, the potential window opening technique was used. Fig. 4-17 shows the voltammetry curves of a polycrystalline platinum at 180°C with different potential windows. When the potential was changed back in the negative-going direction from different windows, the anodic currents did not change
Fig. 4-16. Voltammetry curves of platinum in 85 wt.% $\text{H}_3\text{PO}_4$ saturated with ethylene at 1 atm but different temperatures. Solid line: 100°C. Dash-dotted line: 150°C. Dashed line: 180°C. Sweep rate: 100 mV/s.
Fig. 4-17. Voltammetry curves of platinum in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 180°C with different positive potential windows. Sweep rate: 100 mV/s.
much for each different window, which indicates that very small amount of type II species has been formed at 180°C. The major paths for the electrocatalytic oxidation of ethylene at this higher temperature (180°C), accordingly, should be the formation and oxidation of carbon monoxide.

4.3.4.2. The Study of The Electrocatalytic Oxidation of Ethylene Using A Rotating Disk Electrode.

The electrocatalytic oxidation of ethylene is controlled by the kinetic process rather than mass transfer at lower temperature (below 100°C). At higher temperatures, however, mass transfer of ethylene may gradually control this reaction due to decreasing of the solubility of ethylene in the electrolyte and increasing the kinetic rate. The electrocatalytic oxidation of ethylene has been investigated at 150°C using a rotating disk electrode. Fig. 4-18 shows the voltammetry curves of this rotating disk electrode in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 150°C. The anodic current of electrocatalytic oxidation of ethylene increases with increasing of rotating speed, which shows the kinetics to be at least partially controlled by the mass transfer process. Plotting 1/i
Fig. 4-18. Voltammetry curves of a rotating platinum disk electrode in 85 wt.% H₃PO₄ saturated with ethylene at 1 atm and 150°C with different rotating speeds. Sweep rate: 10 mV/s.
vs. $1/\omega^{1/2}$ at several potentials does give straight line but with negative intercepts. This distortion may be resulted from the over convection of electrolyte at higher rotating speeds. The current peak on the initial part of a voltammetry curve in this figure may be related to the oxidative desorption of carbon monoxide, which will be analyzed in the next part.

4.3.4.3. Transient Measurements of the Electro-catalytic Oxidation of Ethylene

The linearly potential sweep technique is a quicker method to examine the electrochemical behavior of ethylene. Since both potential and time are changing during the sweep, however, the electrochemical features resulted are not so easily understood. Transient measurements will be helpful to interpret the results obtained by the linearly potential sweep technique.

Fig. 4-19 shows a typical voltammetry curve of platinum in 85 wt.% $\text{H}_3\text{PO}_4$ saturated with ethylene at 1 atm, 150°C and a sweep rate of 10 mV/s. The information obtained from this figure is that the electrocatalytic oxidation of ethylene will not take place until those adsorbed species are going to be removed oxidatively from the surface at 0.5 V. How
long it will take to remove those adsorbed species at this potential and then how this time depends on the polarization potential, however, are not known. The following transient measurements can give a more satisfied answer to these questions.

Fig. 4-20 shows both the potential program to clean and stabilize the electrode surface and the current-time profiles obtained by stepping the potential from 0.3 V to different positive values are shown in Fig. 4-19 (the small circles on the curve). All the profiles have a U-shape. The current first increases sharply and then drops to a very low value followed by increasing again. The similar type of profiles have been reported for the electrocatalytic oxidation of formaldehyde[12] and methanol[7]. When the potential was stepped to the potentials that are negative to 0.5 V, the current drops to zero immediately, which indicates that the surface is still covered by the adsorbed species and the small current signal is only for the double layer charging. If the potential is stepped to 0.5 V or positive to that, however, the reaction begins to take place at a very low rate after a time delay of about 12 s. The time delay for the onset of reaction becomes shorter and shorter as the potential is stepped to more and more
Fig. 4-19. A voltammetry curve of platinum in 85 wt.% $\text{H}_2\text{PO}_4$ saturated with ethylene at 1 atm and 150°C. Sweep rate: 10 mV/s.
Fig. 4-20. Transient current-time profiles of a platinum electrode in 85 wt.% $\text{H}_3\text{PO}_4$ saturated with ethylene at 1 atm and 150°C. Electrode area: 0.5 cm$^2$. 
positive potentials. When the potential is stepped to potential above 0.67 V (not shown in this figure), no time delay has been observed.

To understand the composites of this type of transient current profiles, the schematic drawing is shown in Fig. 4-21. The typical anodic current profile has been divided into three components: the double layer charging current, the CO oxidation current and the current for the oxidation of ethylene from the bulk solution. The time required to remove the adsorbed carbon monoxide and restore the free site for oxidation of ethylene from bulk solution is potential dependent. The more positive the potential, the higher the rate of oxidation of carbon monoxide and the shorter the time required. This potential dependence of reaction time is mostly related to the activity change of adsorbed water molecules which are adjacent to the adsorbed carbon monoxide. The activity of water reaches the maximum at the potentials where Pt-OH can be formed on the surface.

Based on this transient study, the best anodic working potential in a ethylene-air fuel cell is close to 0.55 V at 150°C. This potential (0.55 V) does not look good from the point of view of the application. A
Fig. 4-21. Deconvolution of a typical transient current-time profile in Fig. 4-20.
possible way to change the potential in a more favorable direction will be studied in the future work.

Concerning the mechanism of the electrocatalytic oxidation of ethylene on platinum, both the linearly potential sweep and transient measurements have supplied the positive clues to understand the major steps in the macro-level. At the potentials around 0.3 V which is also the open circuit potential of a hydrocarbon anode, the intermolecular interaction between hydrocarbon and water both adsorbed on platinum surface at a elevated temperature leads to the formation of carbon monoxide, which blocks the active sites for the further reaction of ethylene. This process takes place too fast to be avoided in the present platinum-organic anodic system. During a potential step or sweep to more positive potentials, the early stages of the reaction taking place on the surface should be removal of the adsorbed layer oxidatively.

The oxidative desorption of adsorbed carbon monoxide may start at some special surface sites or so-called island edge[13] where the discharge of water becomes possible. The oxygen-supplier which triggers the reaction may not necessarily be OHad, but its precursor state[14]. The potentials of anodic current
showing up are below 0.65 V, which is much more negative to the potential of formation of OH$_{ad}$ species$^{[15]}$. The precursor state of OH$_{ad}$ may be an adsorbed water molecule with extremely intra-bond-stretching as a consequence of bonding to the platinum and polarization of potential. The reactivity of precursor of OH$_{ad}$ increases as increasing potential polarization$^{[14]}$. The kinetic rate of oxidative desorption of adsorbed species will, therefore, depend on the reactivity of precursor of OH$_{ad}$ and in turn on the potential.

A "reaction-pair" mechanism for the oxidation of carbon monoxide on platinum has been suggested by Gilman$^{[7]}$, in which the adsorbed carbon monoxide is first attacked by the adjacent adsorbed water molecule and forms a [CO-H$_2$O]$_{ad}$ complex. This reaction model has also been verified by Shiller and Anderson$^{[16]}$ with the atom superposition and electron delocalization molecular orbital (ASED-MO) theory.

4.3.4.4. Stationary Measurements of Electro-catalytic Oxidation of Ethylene Using Gas-fed Electrodes

A result obtained by a galvanostatic measurement using a CWRU-fabricated Pt/C gas-fed electrode (0.36
Fig. 4-22. A polarization curve for the electrocatalytic oxidation of ethylene on a gas-fed platinum electrode in 85 wt.% $\text{H}_3\text{PO}_4$ at 140°C. Platinum loading: 0.36 mg/cm$^2$. 

CWRU - fabricated Pt/C gas-fed electrode  
(Prototech 10 wt.% Pt on C)  
85 wt.% $\text{H}_3\text{PO}_4$  
$T = 140^\circ\text{C}$  

slope=160 mV/decade
mg/cm$^2$) in 85 wt.% H$_3$PO$_4$ at 140°C is shown in Fig. 4-22. The open circuit potential is ca. 0.3 V vs. RHE. The Tafel slope measured is 160 mV/decade, which is very close to the theoretical value for one electron transfer step at this temperature ($2.303\times(2RT/F)$). Using gas-fed electrode the stable potential value can be obtained within five minutes which is contrast to the measurements using a smooth or platinized platinum electrode, where the stable value cannot be obtained within 30 minutes[17]. The major reason related to this difference in the speed to reach the stationary state may be that the mass transfer can be better if a gas-fed electrode is used. Based on this Tafel slope, and the information supplied by the linear potential sweep and transient measurements, the rate-determining step for the electrocatalytic oxidation of ethylene at elevated temperatures is very possibly as the following

$$\text{CO}_{\text{ad}} + \text{H}_2\text{O}_{\text{ad}} \rightarrow \text{COOH}_{\text{ad}} + \text{H}^+ + e^- \quad (2)$$

COOH$_{\text{ad}}$ formed from this reaction will be further oxidized to carbon dioxide with a much higher kinetic rate.

4.4. Conclusion

Through the potentiodynamic studies of the electrocatalytic oxidation of ethylene in the acid
media at various temperatures, the following preliminary understanding has been reached:

1. The adsorption of ethylene is a fast process most probably due to the presence of $\pi$-bond in these molecules. The $\pi$ electron donation to the platinum and back-donation from platinum d-orbital electron to the $\pi^*$ orbital of ethylene make ethylene strongly adsorbed on the surface[18].

2. The adsorbed ethylene will interact literally with adsorbed water molecules to yield carbon monoxide and type II species, mostly, alcohol-like species. The kinetic rate of this partial oxidation of ethylene depends on the temperature, the potential and surface structure but less on the electrolyte anions.

The higher the temperature, the higher the ratio of coverage of adsorbed carbon monoxide to type II species.

The favored potential region for the formation of carbon monoxide is between 0.25–0.35 V vs. RHE, the potential region which the pzc of platinum and OCP of platinum/ethylene electrode belong to.

Pt(100) surface has the highest electrocatalytic activity toward both the formation of carbon monoxide and the oxidation of ethylene. On Pt(111) surface the major adsorbed species are type II species. This
surface showed much less activity for the oxidation of ethylene than Pt(100) surface. Pt(110) surface is the worst one for the oxidation of ethylene.

3. The potential of oxidative desorption of carbon monoxide strongly depends on the temperature. The higher the temperature, the more negative this potential. The oxidative agent that triggered the desorption of carbon monoxide is suggested to be the precursors of OH$_{ad}$, a highly stretched water molecule, rather than OH$_{ad}$.

4. A Tafel slope of 160 mV/decade is obtained at 140°C using a gas-fed electrode. The oxidation of carbon monoxide by the adsorbed water to yield COOH is considered as the rate-determining step for the electrocatalytic oxidation of ethylene in an acid media at elevated temperatures.
References


CHAPTER V
IN SITU FTIR AND EX SITU NMR STUDIES OF
ELECTROCATALYTIC OXIDATION OF ETHYLENE ON PLATINUM

5.1. Introduction

The formation and oxidation of adsorbed species on platinum have been demonstrated in the last chapter to play very important roles in the electrocatalytic oxidation of ethylene. At least two types of adsorbed species have been formed during the electrocatalytic adsorption of ethylene. The identification of the molecular structures of these adsorbed species and other possible intermediates is necessary to understand the mechanism of formation of these species, and, in turn, to gain insight into the mechanism of the electrocatalytic oxidation of ethylene.

In situ FTIR spectroscopic techniques have been successfully used in the studies of adsorption and oxidation of small oxygenated organic molecules (e.g., methanol\(^1\), formic acid\(^2\), ethanol\(^3\), ethylene glycol\(^4\)). Molecular level information about the adsorbates and the products of a reaction has been obtained and used to promote the understanding of the kinetic mechanism of electrocatalytic adsorption and oxidation of these molecules. This technique has also
been shown in this laboratory to be suitable for the studies of electrochemical adsorption and oxidation of hydrocarbon molecules by coupling a specific spectroelectrochemical cell which can be operated at elevated temperatures. The results obtained by in situ FTIR studies for the adsorption and oxidation of ethylene on platinum at both room temperature and elevated temperatures will be reported in this chapter.

The electrochemical adsorption and oxidation of ethylene includes a number of steps to yield carbon dioxide as the final products. In addition to the adsorbed species on platinum surface, some sort of intermediates may come into the solution phase. The detection of these intermediates shares the equal importance to supply the reaction information with identification of adsorbed species. The ex situ $^1$H NMR technique has been used in this work to pick up the possible intermediates or products produced by the oxidation of ethylene.

Based on these measurements, the possible mechanisms of formation of adsorbed species and oxidation of ethylene on platinum will be discussed.

5.2. Experimental
The spectroelectrochemical cell used for in situ FTIR measurements of adsorption and oxidation of ethylene and the sample optical table has been shown in chapter III (Fig. 3-1). The preparation of electrode and the electrolytes are the same as described in chapter III.

There are two major procedures for the in situ FTIR measurements:

1. Checking the cleanliness of electrochemical system electrochemically and spectroscopically.

The ethylene-free electrolyte was first deaerated by UHP N₂ and then fed into the spectroelectrochemical cell. Several potential cycles between 0.05 V and 1.45 V at a sweep rate of 100 mV/s were done to clean and stabilize the electrode. Then the electrolyte was withdrawn from the cell and a fresh electrolyte was fed in again. If the first potential sweep in the positive-going direction after holding potential at 0.3 V for 5 min. shows no anodic peak except for the surface oxidation, the electrochemical system is thought to be electrochemically clean. For the spectroscopic check of cleanliness of the system, the subtractively normalized spectra were taken at different potentials after the electrode was held at 0.3 V for 10 min. and pushed against the optical
window. No appearance of any IR bands in the interested frequency and potential regions except for solvent provides the evidence that the electrochemical system is spectroscopically clean.

2. Establishing the adsorption of reactants and conducting FTIR measurements.

After the cell was proved to be clean of any impurity, the electrode was held at different potentials followed by introducing the reactant (C<sub>2</sub>H<sub>4</sub> or CO) into the cell. After 10 min. adsorption of reactant, the electrode was pushed against the optical window and the first spectrum was collected at these holding potentials. As the potential was sweeping (1 mV/s) or stepped to more positive potentials, the sample spectra were collected. These sample spectra will be subtractively normalized to a selected reference spectrum, which gives the spectra reported.

A new spectroelectrochemical cell (Fig. 5-1) has also been used for the studies of IR frequency shift of carbon monoxide, which are caused only by change of the coverage. The main features of this new cell are the following:

1. The electrolyte can flow into the thin layer between the optical window and working electrode through the center hole at working electrode. The flow
Fig. 5-1. A schematic drawing of the spectroelectrochemical thin layer cell.
Fig. 5-2. The schematical drawing of the electrolyte reservoir used for in situ FTIR measurements.
rate of electrolyte can be well controlled by the pressure in a special electrolyte reservoir (Fig. 5-2).

2. These cell arrangements permit the variation of electrolytes without change of the thin layer thickness, and make it possible for the measurements of frequency shift caused by coverage change of adsorbed carbon monoxide without perturbing electrode potential.

3. All the glass-to-glass and Teflon-to-glass joints are F & P type, which ensured no leaking of solution. The feeding tube (0.5 mm ID) is enclosed in a thicker flexible Teflon tube and N₂ keeps flowing between these two tubes to inhibit the air penetration into the thinner tube.

The H¹ NMR measurements were conducted using a Varian Associate XL-200 NMR spectrometer. 1% tetramethylsilane in Chloroform-d₁ filled in a coaxial capillary was used as an external standard.

CP grade ethylene or its mixture in UHP N₂, UHP carbon monoxide or its mixture in UHP N₂ and UHP N₂ were purchased from Johnson Matthey. 85 wt.% D₃PO₄ in D₂O (Aldrich Chemical Company, Inc.) was used as received without further purification. D₂O (minimum 99.9% atom % D, Isotec, Inc.) was double distilled with platinum black (0.5 g/100 ml D₂O) under vacuum. Ethylene glycol (Fisher) was used as purchased.
Other instruments and chemicals are the same as in chapter III.

5. 3. Results and Discussion

5. 3. 1. In Situ FTIR Spectroscopic Studies.

5. 3. 1. 1. The Electrochemical Adsorption and Oxidation of Ethylene at Room Temperature.

The electrochemical adsorption and oxidation of ethylene were first studied at room temperature using in situ FTIR coupled with a linear potential sweep program. The holding potential was 0.2 V vs. RHE (holding for 10 min.). The potential was then swept in the anodic direction at a sweep rate of 1 mV/s, the spectra were continuously collected and each spectrum contains 270 interferometric scans which consumed ca. 110 s.. In order to obtain the surface concentration of the adsorbed species, the spectrum collected at 1.5 V, where the adsorbed species can be completely oxidatively desorbed, is selected as the reference spectrum. The spectra resulted from subtractively normalizing all the sample spectra to this reference spectrum are shown in Fig. 5-3.

The positive peaks represent the species remained on the electrode surface at each potential indicated in
Fig. 5-3. Subtractively normalized FTIR spectra of oxidation of adsorbates originated from the adsorption of ethylene on platinum in 0.1 M HClO₄ saturated with ethylene at 0.01 atm and 25°C. Reference potential: 1.5 V vs RHE. Sample potentials are showing inside the figure. Scan number: 270. Resolution: 4 cm⁻¹. Potential sweep rate: 1 mV/s.
the figure. The intensity of each band is directly related to the quantity of corresponding species. In contrast, the negative peaks mean that more species corresponding to these peaks have been produced at 1.5 V than at the potentials indicated in the figure. The intensity of each pointing down band, however, just reflects the difference of the quantity of these species at the potential indicated and reference potential (1.5 V). In other words, the lower the peak height, the small the difference of the quantity of corresponding species at both sample potential and the reference potential.

There are two sets of positive peaks in the frequency region from 900 cm\(^{-1}\) to 3000 cm\(^{-1}\). The first set of positive peaks is located at ca. 2000 cm\(^{-1}\) with frequency shifts at different potentials. The species corresponding to these peaks has been assigned to the linearly bonded carbon monoxide (CO\(_L\))[5]. The potential induced frequency shift of these peaks is about 81 cm\(^{-1}/V\), which is much higher than that obtained for the adsorption of carbon monoxide itself (30 cm\(^{-1}/V\))[6]. The possible reason corresponding to this unusual frequency shift will be discussed later. These peaks at ca. 2000 cm\(^{-1}\) totally disappeared at 0.82 V vs. RHE, which indicates carbon monoxide
adsorbed on the electrode surface has been completely oxidized at this potential. The oxidation of carbon monoxide produces carbon dioxide, which is evidenced by the negative IR peaks at 2345 cm\(^{-1}\). The carbon dioxide peaks will not change too much after carbon monoxide has been oxidized, which tells that all the carbon dioxide produced is from the oxidation of carbon monoxide.

The second set of positive peaks is located at 1038 cm\(^{-1}\) that can be assigned to the adsorbed species with -enol function group\(^7\) (-C-OH) or, simply speaking, alcohol-like species. The intensities of these bands did not change with the potential in the region 0.2 to 0.71 V, where carbon monoxide is oxidized. The alcohol-like species start oxidatively desorbing from the surface at 0.82 V and finish at 1.38 V. This process covers a wide potential region and produces mainly the species giving rise the negative IR peaks at 1778 cm\(^{-1}\), which may be assigned to the carbonyl group species, and small amount of carbon dioxide evidenced by small change of peak heights of the peaks at 2345 cm\(^{-1}\).

A set of negative peaks located at 1107 cm\(^{-1}\) was originated from the migration of perchlorate anion
(ClO₄⁻) into the thin layer induced by the passage of charge between the working and counter electrodes[8].

In summary of the measurements done at room temperature, the following information has been obtained:

1. Two types of adsorbed species formed at hydrogen region (0–0.35 V) on platinum are linearly bonded carbon monoxide and alcohol-like species. Linearly bonded carbon monoxide can be completely oxidized at potentials negative to 0.82 V. The oxidation of alcohol-like species takes place after carbon monoxide has been removed from the surface and covers a wide potential region (0.82 V – 1.38 V).

2. The oxidation of carbon monoxide and alcohol-like species produces carbon dioxide and carbonyl group species, respectively.

5. 3. 1. 2. The Electrochemical Adsorption and Oxidation of Ethylene at 60°C.

To examine the temperature effect on the formation of carbon monoxide and alcohol-like species and their oxidative desorption, similar measurements have been conducted at 60°C. The results are shown in the Fig. 5-4 which have been plotted in the same way as done in Fig. 5-3. The same types of peaks have been observed
Fig. 5-4. Subtractively normalized FTIR spectra of oxidation of adsorbates originated from the adsorption of ethylene on platinum in 0.1 M HClO₄ saturated with ethylene at 0.01 atm 60°C. Reference potential: 1.5 V vs RHE. Sample potential are showing inside the figure. Other conditions are the same as Fig. 5-3.
as at room temperature but with the following different characteristics:

1. The peak positions of both linearly bonded carbon monoxide and alcohol-like species shift to relatively higher frequency region than those obtained at room temperature.

2. The potential (0.69 V) where oxidative desorption of carbon monoxide finishes and the oxidative desorption of alcohol-like species starts is 130 mV negative to that at room temperature (0.82 V).

3. The peak intensity of linearly bonded carbon monoxide is much higher than that obtained at room temperature. The potential induced frequency shift of linearly carbon monoxide with potential decreased to 55 cm\(^{-1}/V\), which is still higher than the common value (30 cm\(^{-1}/V\)).

In order to focus on the temperature effect on the formation of linearly bonded carbon monoxide, Fig. 5-5 is plotted using two new reference potentials (0.94 V at 25°C and 0.8 V at 60°C) where the carbon monoxide can be totally removed from the surface. This figure clearly shows that the IR peaks of carbon monoxide varies significantly with the temperature change. The peak areas in this figure at both room temperature and 60°C have been integrated and the results are shown in
Fig. 5-5. Subtractively normalized FTIR spectra of linearly bonded carbon monoxide on platinum at different potentials and temperatures. Reference potentials: 0.94 at 25°C and 0.8 V at 60°C. Other conditions are the same as in Fig. 5-3.
Fig. 5-6. The variation of CO\textsubscript{L} IR peak intensity vs potentials at two temperatures: (a). 60°C. (b). 25°C.
Fig. 5-6. The dramatic change of CO\textsubscript{L} peak intensity with temperature indicates the significant change of partial coverage of CO\textsubscript{L} on the electrode surface. More carbon monoxide has been formed at elevated temperature, which is in agreement with the potentiodynamic studies (Fig. 4-6 in Chapter IV).

The potential dependence of formation of carbon monoxide has also been examined at 60°C by this in situ FTIR technique coupled with a single potential step program. The adsorption process at various potentials was conducted as described above. After the electrode was pushed against the optical window, the first spectrum was collected with 500 interferometric scans. The potential was then stepped to 0.8 V vs. RHE where carbon monoxide can be oxidatively desorbed at 60°C. The second spectrum was collected at this potential (0.8 V) after one min. delay. The first spectrum is then subtractively normalized to the second spectrum. The resulted spectra are shown in Fig. 5-7. The potential dependence of the formation of carbon monoxide has been observed from this figure. In addition to the formation of linearly bonded carbon monoxide at 0.1 V and 0.2 V, a small amount of bridge bonded carbon monoxide (1801 cm\textsuperscript{-1} and 1832 cm\textsuperscript{-1}) has
Fig. 5-7. Subtractively normalized FTIR spectra for the formation and oxidation of CO₂ on platinum at different holding potentials in 0.1 M HClO₄ saturated with ethylene at 0.01 atm and 60°C. Reference potential: 0.8 V vs RHE. Resolution: 4 cm⁻¹. Scan number: 500 cm⁻¹.
been detected. The favored potential region for the formation of linearly bonded carbon monoxide is between 0.2 V to 0.3 V, which is once again in agreement with the results obtained by the potentiodynamic studies (Fig. 4-7 in Chapter IV).

By recalling the results obtained with potentiodynamic studies and relating these to the information obtained here, it is possible to make assignments for the peaks on the voltammetry curves:

- Peak I:
  Type I species: linearly bonded carbon monoxide (CO_L).

- Peak II:
  Type II species: Alcohol-like species (-C-OH).

5.3.2. The Mechanism of the Formation of Carbon Monoxide and Alcohol-like Species.

To the author's knowledge, it is the first time that carbon monoxide has been spectroscopically detected as one type of the adsorbed species formed during the electrochemical adsorption of ethylene on platinum. Whether carbon monoxide does come or does not come from the partial oxidation of ethylene has been a subject of the author's consideration. The
possible sources of formation of carbon monoxide have been carefully analyzed. In general, there are mainly three possible sources which can cause the formation of carbon monoxide on platinum: the reduction of carbon dioxide, carbon monoxide as an impurity in the ethylene gas tank and the partial oxidation of ethylene. The possibility of each of these sources will be discussed in the following part.

The reduction of carbon dioxide: It has been demonstrated\textsuperscript{9-10} that carbon dioxide can be electrochemically reduced to carbon monoxide on a platinum electrode in acid media. This source, however, has been ruled out here based on the following considerations:

1. The platinum electrode was held at 0.2 V vs. RHE when ethylene was introduced into the electrolyte and the infrared spectra were all collected during the first anodic sweep. No products, including carbon dioxide from ethylene oxidation, were accumulated in the solution during the time the adsorption was completed.

2. Carbon dioxide is very weakly adsorbed on platinum comparing to ethylene. The adsorption of carbon dioxide, therefore, is not possible in the
presence of ethylene even if there is trace of carbon
dioxide in the electrolyte.

3. Carbon monoxide has been detected after the
adsorption of ethylene at 0.3 V to 0.5 V, where carbon
dioxide cannot be electrochemically reduced.

In summary, the carbon monoxide detected here is
not from the electrochemical reduction of carbon
dioxide.

**Carbon monoxide impurity**: Carbon monoxide gas can
strongly interact with platinum. This possible source
should be carefully verified.

1. The relative adsorption ability of carbon
monoxide and ethylene has been compared by the lateral
modification technique. In order to avoid deep partial
oxidation of ethylene at elevated temperature, the
measurements were conducted at room temperature.
Ethylene was first allowed to adsorbed on a platinum
electrode for 10 min. and then carbon monoxide was
introduced into the system for 15 minutes without
changing of potential. The oxidative desorption of
this adsorbed layer was conducted by the linear
potential sweep in the anodic direction. Fig 5-8 shows
the results of these measurements. The dashed line and
solid line correspond to the oxidative desorption of
Fig. 5-8. Voltammetry curves for oxidative desorption of (a). CO (long dashed line), (b). adsorbates originated from ethylene (solid line) and (c) the adsorbates originated from ethylene modified laterally by CO (dash-dotted line). The short dashed line is the voltammetry curve of platinum in organic-free electrolyte at 25°C. Sweep rate: 100 mV/s.
adsorbed species formed directly from carbon monoxide and ethylene alone, respectively. The dash-dotted line is for the oxidative desorption of adsorbed species of ethylene modified by carbon monoxide. These results show that carbon monoxide does have a higher adsorption ability than ethylene, which is evidenced by appearance of the anodic peak at 0.85 V on the dash-dotted line. The potential of oxidative desorption of carbon monoxide has been dragged to more positive value in the case of presence of adsorbed ethylene. If the modification procedure was reversed, in other words, carbon monoxide was allowed to adsorb on the surface first, the later coming ethylene cannot replace the adsorbed carbon monoxide too much as shown by the dash-dotted line in Fig. 5-9. Only the carbon monoxide corresponding to the pre-peak of the solid line was replaced by the coming ethylene.

This kind of modification measurement show that carbon monoxide has a higher adsorption ability than ethylene, which is in agreement with the conclusion reported in the literature[11]. If there were some carbon monoxide impurity in the ethylene gas tank, therefore, it would result in the observation of carbon monoxide IR bands in the in situ FTIR measurements.
Fig. 5-9. Voltammetry curves for the oxidative desorption of (a). CO (solid line), (b). adsorbates originated from ethylene (long dashed line) and (c). CO attacked by the adsorbates originated from ethylene (dash-dotted line). The short dashed line is the voltammetry curve of platinum in organic-free electrolyte at 25°C. Sweep rate: 100 mV/s.
The following two analysis, however, will show that this source is not applicable here.

2. The ethylene reactant gas has been analyzed by Matheson Gas Company. The level of carbon monoxide impurity in the CP grade ethylene is 25 ppm. Based on the low partial pressure (1% ethylene balanced with UHP N₂) used here, the solubility of carbon monoxide at 60°C (ca. 10⁻⁴ M/l[¹²]) and the electrolyte volume (5 ml), the total quantity of carbon monoxide in the solution is just 10⁻¹³ mole, which is totally out of the sensitivity of IR instrument even considering that all of it adsorbed on the electrode surface.

3. A dramatic temperature effect on the formation of carbon monoxide by the adsorption of ethylene has been observed (Fig. 5-6). Another way to verify the possibility of involving carbon monoxide impurity is, therefore, to see the temperature effect on the adsorption of carbon monoxide itself. In situ FTIR measurements of adsorption of carbon monoxide at different potential and temperatures have been done in this thesis work. The variation of IR peak intensities with potential and temperature is plotted in Fig 5-10. From this figure, it can be seen that the intensity or quantity of carbon monoxide adsorbed at 0.2 V decreases with increasing temperature, which is contrast to
Fig. 5-10. The variation of CO IR peak intensity vs holding potentials and temperatures: (a). 25°C, (b). 60 °C, and (c). 80°C. Scan number: 500. Resolution: 4 cm⁻¹.
the results in Fig. 5-6. If there was a carbon monoxide impurity in the ethylene gas tank, therefore, the quantity of adsorbed carbon monoxide at room temperature in Fig. 5-6 would have been at least close to the coverage of carbon monoxide detected at 60°C, since carbon monoxide has a higher adsorption ability than ethylene.

All of the analysis done above suggests that the carbon monoxide detected in the in situ FTIR measurement of the adsorption of ethylene is not from the impurities but the partial oxidation of ethylene.

**Partial oxidation of ethylene in hydrogen region of platinum:** The main product of complete oxidation of ethylene on platinum in acid media has been detected as carbon dioxide\(^{[13-14]}\). The whole process, obviously, should involve two important steps: rupture of C-C bond and oxygenation. The kinetics of these two processes are certainly dependent on the potential and temperature. Concerned with the formation of carbon monoxide and alcohol-like species in the hydrogen region of platinum, these two processes (C-C rupture and Oxygenation) are also required. The question having been asked, therefore, are whether the C-C bond rupture and oxygenation processes can take place in
hydrogen region and how the temperature influences these processes in this region.

1. C-C bond rupture and oxygenation.

Ethylene can be strongly adsorbed on platinum by a bonding interaction of \( \pi \)-orbital of ethylene with the empty \( dz_2 \) orbital of platinum atoms on the electrode surface and the back bonding from partially filled \( dxz \) orbital of platinum to the \( \pi^* \)-orbital of ethylene\[^{15}\]. The strong platinum-ethylene bonding interaction results in the weakening of the C-C bond and increment in the length of this bond\[^{15}\]. When this type of interaction is sufficiently strong the C-C bond may be ruptured. This can be supported by the formation of methane in the electrocatalytic reduction process\[^{16}\]. On the other hand, the water molecules adsorbed on the electrode surface can serve as not only an oxygen supplier for the oxygenation of adsorbed organic molecules but also a promoter for the C-C bond rupture and formation of carbon monoxide. It has been reported that the adsorption of both methanol and ethanol on platinum in an aqueous acid solution can lead to the formation of carbon monoxide\[^{3, 17}\]. No carbon monoxide, however, was detected in a nonaqueous solution\[^{18}\]. But once a small amount of water was
added into the nonaqueous solution the same results as in the aqueous solution can be obtained[18]. It clearly shows that the presence of water will not only enhance the dehydrogenation of \(-\text{enol}\) group but also, importantly, promote the C-C bond rupture of ethanol. In the case of adsorption of ethylene, from the hydration of the adsorbed species to the C-C bond rupture and finally to the formation of carbon monoxide, water molecules on the electrode surface plays a very important role. The adsorption of ethylene on gas-solid and liquid-solid interfaces has been compared based on the studies conducted by the combination of electrochemical and UHV techniques[19]. and it has been concluded that the adsorbates of ethylene on two types of interfaces are totally different. Oxygenated species has been detected in the hydrogen region on a liquid-solid interface, which may serve another evidence for the possibility of oxygenation process taking place in the hydrogen region.

In conclusion, carbon monoxide and alcohol-like species can be formed in the hydrogen region of platinum by C-C bond rupture and oxygenation during the adsorption of ethylene.
2. Temperature effect.

The C-C bond rupture and oxygenation processes can be dramatically influenced by the temperature. As the temperature is elevated, the kinetic rates of both C-C bond rupture and oxygenation processes increase so much that the kinetic rate of formation of oxygenated species is higher than that of adsorption of ethylene molecules. This produces more carbon monoxide than at room temperature. Secondly, the chance for the formation of two-dimensional cluster of ethylene becomes smaller at elevated temperatures and one ethylene molecule can be laterally surrounded by more adsorbed water molecules which increase the possibility of oxygenation process. Due to the strong adsorption ability of carbon monoxide on platinum surface, as shown above, it will stick there once it is produced and cannot be replaced again by the on-coming ethylene molecules. The assumption that change of the environment of the adsorbates with temperature is also reflected by the different frequency shift rates of carbon monoxide IR peaks with potential (81 cm\(^{-1}\)/V at room temperature and 55 cm\(^{-1}\)/V at 60°C), which will have a specific discussion in the next part.

Based on the experimental results and the above analysis, the adsorption of ethylene in the hydrogen
region of platinum produces carbon monoxide and alcohol-like species. The rate of formation of carbon monoxide is potential and temperature dependent. This partial oxidation of ethylene takes place with a mechanism of C-C bond rupture and oxygenation processes.

5.3.3. Unusual Frequency Shift of Carbon Monoxide IR Peaks.

Fig. 5-11 shows the frequency shift of the carbon monoxide IR peaks in Fig. 5-5 with potential. The two curves have different slopes. The frequency shift at 25°C (b) is 81 cm⁻¹/V and that at 60°C (a) is 55 cm⁻¹/V. Both numbers are much larger than that reported (30 cm⁻¹/V)[6]. The potential induced frequency shift of carbon monoxide has been interpreted on the basis of a first order Stark effect[17] or reduced back-donation of metal electrons into the antibonding 2π* orbital of the adsorbed CO[20-21]. In the case of carbon monoxide produced from the partial oxidation of ethylene, the situation is complicated. The first complication is that the coverage of carbon monoxide in the case of partial oxidation of ethylene is changing with potential as shown in Fig. 5-6. It is well known that the frequency of carbon monoxide is also a function of
Fig. 5-11. The frequency shifts of CO$_L$ with potentials at two temperatures: (a) 60°C. (b) 25°C. The data are originated from Fig. 5-5.
coverage which has been interpreted as the lateral dipole-dipole coupling effect of adsorbed CO[22-24]. To what extent the coverage change can contribute to the frequency shift, however, is not well examined. Secondly, there are different types of adsorbates on the surface for the adsorption of ethylene. To what extent the lateral interaction between these different adsorbates can contribute to this shift is also not known.

In order to examine the contribution of coverage of carbon monoxide to the frequency shift, the new flux FTIR cell has been used. This cell permits the author to change the coverage of carbon monoxide without suffering the variation of potential. As the coverage of carbon monoxide is changing, the IR spectra can be continuously collected and the frequency shift caused just by the coverage changing can be calculated out. As the electrode potential was held at 0 V vs. SCE with CO-free electrolyte flowing into the thin layer at a rate of 1.35 ml/min., the reference spectrum with 16 scans was collected. The sample spectra were continuously collected after the flowing electrolyte was changed to the electrolyte saturated with 1% CO. The sample spectra collected at different times were later subtractively normalized to the reference
Fig. 5-12. The intensity change of CO IR peaks with time at the potential 0 V vs SCE on platinum in 0.1 M HClO₄ saturated with carbon monoxide at 0.1 atm and 25° C. Flow rate of electrolyte: 1.35 ml/min. Resolution: 4 cm⁻¹. Scan number: 16.
Fig. 5-13. The frequency shift of CO$_2$ with coverage at the potential of 0 V vs SCE on platinum in 0.1 M HClO$_4$ saturated with carbon monoxide at 0.01 atm and 25 °C. Flow rate of electrolyte: 1.35 ml/min. Resolution: 4 cm$^{-1}$. Scan number: 16.
spectrum and gives the spectra showing the "absolute" CO bands. Integration of the CO IR peaks obtained at different times gives Fig. 5-12. When the intensity of CO band doesn't change, it is considered that the saturation coverage of carbon monoxide has been obtained and the intensity is defined as the saturation intensity. Ratioing the intensities at different times (on the average line) to this saturation intensity gives the relative coverage of carbon monoxide. Plotting the band frequency with the relative coverage gives Fig. 5-13. A straight line is obtained with a slope of 20 cm\(^{-1}\)/monolayer. This result shows that the maximum frequency shift cannot be larger than 20 cm\(^{-1}\).

Based on measurements discussed above, the unusual frequency shift of CO for the partial oxidation of ethylene is not just originated from the coverage change of carbon monoxide as the potential was swept from 0.2 V in the positive-going direction. Several other possible interpretations may also work for the unusual frequency shift observed for the partial oxidation of ethylene:

1. The Stark tuning rate has been reported to be a function of coverage. The lower the coverage, the larger the stark tuning rate\[^{23}\]. A 50 cm\(^{-1}\)/V frequency shift at low coverage of CO\(_L\) has been
obtained[23]. In the case of partial oxidation of ethylene at room temperature, the coverage of CO\textsubscript{L} is very low, which may cause a higher Stark tuning rate.

2. Another possible effect causing the higher Stark tuning rate of CO frequency may be the lateral interaction between adsorbed carbon monoxide and other types of adsorbates. This type of interaction may also depend on the potential. The more positive the potential, the stronger the interaction. As the temperature was elevated, more carbon monoxide was formed on the surface and the possibility of interaction between carbon monoxide and other type of adsorbates becomes less. The Stark tuning rate of carbon monoxide frequency, therefore, decreases at 60° C.

3. The Stark tuning rate has also been reported to be potential dependent[25]. A higher Stark tuning rate can be expected in the negative potential region. The adsorption of different types of species on the surface may make the pzc of platinum negative[26], which increases the Stark tuning rate[25].

5. 3. 4. Ex Situ NMR Studies of the Soluble Intermediates and Products.
As mentioned before, the oxidation of ethylene may involves some sort of intermediates which can desorb from the electrode surface and come into the electrolyte. It will be valuable to pick up these species in the electrolyte to enhance the understanding of the electrocatalytic oxidation of ethylene. The oxidation of ethylene was conducted under potentiodynamic condition. The electrolyte after the experiment was studied using both potentiodynamic and ex situ NMR techniques. Fig. 5-14 shows the voltammetry curve of platinum obtained in the electrolyte used for the oxidation of ethylene at 80°C for 4 hours. This figure clearly shows that the used electrolyte does contain some sort of organic molecules, which can be oxidized on platinum in the double layer region of platinum.

In order to increase the concentration of the organic molecules in the electrolyte, the oxidation of ethylene has been carried for 28 hours in 0.1 M D$_3$PO$_4$ in D$_2$O. The used electrolyte has been examined by H$^1$ NMR. The resulted NMR spectrum is shown in Fig. 5-15 (a). For comparison the NMR spectrum of blank solution was shown in this figure (b). Two types of organic molecules have been observed: ethylene glycol and small amount of acetic acid.
Fig. 5-14. A voltammetry curve of platinum at 80°C in 0.1 M H₃PO₄ (dashed line) and 0.1 M H₃PO₄ used for the oxidation of ethylene at the same temperature for 4 hours under potentiodynamic condition (solid line). Sweep rate: 100 mV/s.
Fig. 5-15. H\(_1\) NMR spectra: (a). blank electrolyte (0.1 M D\(_3\)PO\(_4\) in D\(_2\)O). (b). 0.1 M D\(_3\)PO\(_4\) in D\(_2\)O used for the oxidation of ethylene at 80°C for 28 hours under potentiodynamic condition.
Acetic acid cannot be strongly adsorbed on the platinum surface in the hydrogen region\[^{27}\]. The original organic molecules responsible for the anodic peaks in the double layer in Fig. 5-14, therefore, are ethylene glycol.

By intentionally adding $10^{-4}$ M ethylene into fresh 0.1 M H$_3$PO$_4$ at 80°C, the voltammetry curve of platinum is shown in Fig. 5-16. The dash-dotted line is for the oxidation of ethylene glycol and the solid line is copied from Fig. 5-14. The two voltammetry curves matches very well, which indicates that the species in the used electrolyte for the oxidation of ethylene is ethylene glycol.

The desorption of ethylene glycol into the electrolyte can be understood by considering the weaker adsorption ability of ethylene glycol than that of ethylene. Once the ethylene glycol was formed on the surface, some of it will be replaced by the coming ethylene molecules before they are further oxidized. Even the ethylene glycol molecule can be more easily oxidized than ethylene. The ethylene glycol once dissolved in the electrolyte will never come back to the electrode surface to be oxidized again in the presence of ethylene. The ethylene glycol will be gradually accumulated in the electrolyte.
Fig. 5-16. Voltammetry curves of platinum at 80°C in 0.1 M H\textsubscript{3}PO\textsubscript{4} (dashed line), 0.1 M H\textsubscript{3}PO\textsubscript{4} with 10\textsuperscript{-4} M C\textsubscript{2}H\textsubscript{4}(OH)\textsubscript{2} (dash-dotted line) and 0.1 M H\textsubscript{3}PO\textsubscript{4} used for the oxidation of ethylene at the same temperature for 4 hours under potentiodynamic condition (solid line). Sweep rate: 100 mV/s.
The detected acetic acid may be most probably from the further oxidation of ethanol-like species that just has one oxygenated carbon. The failure in detection of other types of alcohol species such as ethanol may be due to the low boiling point of ethanol and the small proportion of these side reactions. Once it is dissolved into the solution it will be vaporized.

5.3.5. The Possible Mechanism for the Oxidation of Ethylene

The identification of the adsorbed species on the electrode surface by the in situ FTIR measurements and the species in the solution phase using both in situ FTIR and ex situ NMR techniques have supplied more information about the mechanism of the oxidation of ethylene on platinum. The following reaction steps have been proposed and will be discussed in this part.

\[
\begin{align*}
4 \text{[H}_2\text{O(l) } & \rightarrow \text{H}_2\text{O(ad)]]} \\
\text{C}_2\text{H}_4\text{(g) } & \rightarrow \text{C}_2\text{H}_4\text{(ad) (2)} \\
\text{C}_2\text{H}_4\text{(ad) } + 2\text{H}_2\text{O(ad) } & \rightarrow \text{C}_2\text{H}_4(\text{OH})_2\text{(ad) } + 2\text{H}^+ + 2\text{e}^- \\
\text{C}_2\text{H}_4(\text{OH})_2\text{(ad) } & \rightarrow 2\text{CO} + 6\text{H}^+ + 6\text{e}^- \quad (3) \\
2 \text{[CO(ad) } + \text{H}_2\text{O(ad) } & \rightarrow \text{COOH(ad) } + \text{H}^+ + \text{e}^-] \quad (5) \\
2 \text{[COOH(ad) } & \rightarrow \text{CO}_2\text{(g) } + \text{H}^+ + \text{e}^-] \quad (6) \\
or
\end{align*}
\]
\[ 2 \text{[H}_2\text{O(ad)} \rightarrow \text{OH(ad)} + \text{H}^+ + \text{e}^-] \quad (7) \]
\[ 2 \text{[CO(ad)} + \text{OH(ad)} \rightarrow \text{CO}_2(g) + \text{H}^+ + \text{e}^-] \quad (8) \]

\[ \text{C}_2\text{H}_4(g) + 4\text{H}_2\text{O(l)} \rightarrow 2\text{CO}_2(g) + 12\text{H}^+ + 12\text{e}^- \quad (9) \]

The oxygen supplier for the oxidation of ethylene is water molecules adsorbed on the platinum surface (1) but it may not be necessary to be the first step of the series of reaction. The adsorption of ethylene on platinum (2) takes place very rapidly at the expense of loss of \( \pi \) bond in the molecule. The evidence for the formation of alcohol-like species has been obtained by the in situ FTIR studies and the assignment of this alcohol-like species to be ethylene glycol (3) is based on the \( H_1 \) NMR result. The further oxidation of ethylene glycol gives carbon monoxide (4) which has been detected by in situ FTIR measurements. The further oxidation of carbon monoxide can take place in step (5) or step (8), which depends on the temperature. At lower temperature, the oxidative desorption of carbon monoxide cannot take place until the water is discharged (7). The discharge of water (7) will be the rate-determining step, which has been suggested by Dahms and Bockris\[28\]. At higher temperature, as demonstrated in the last chapter(IV), the reaction of
carbon monoxide with bond-stretched water to yield COOH(ad) (6) will be rate-determining.

5. 4. Conclusion

Two types of adsorbed species originated from the adsorption of ethylene in acid media have been identified by means of both in situ FTIR and ex situ NMR spectroscopic studies. Type I species is linearly bonded carbon monoxide and Type II species is alcohol-like species, most probably ethylene glycol with two carbon atoms bonded to the platinum electrode surface.

The formation of carbon monoxide is temperature dependent. The higher temperature will help the formation of carbon monoxide by the mechanism of enhancement of C-C bond rupturing and oxygenation processes.

Unusual potential induced frequency shifts of carbon monoxide have been observed, 81 cm⁻¹/V at room temperature and 55 cm⁻¹/V at 60°C. The unusual values have been interpreted by the Stark effect, the dipole-dipole coupling, the variation of Stark effect with coverage and potential and the lateral interaction of adsorbed carbon monoxide and other different types of adsorbates.
The coverage-induced frequency shift has been measured under well potential control using a special designed thin layer FTIR flow cell. The maximum frequency shift induced by coverage is about 20 cm\(^{-1}/V\).

The further oxidation of carbon monoxide has been considered as going in two different ways, which depends on the temperature. At lower temperature, the oxidative reagent on the surface is OH(ad) and its formation will be the rate-determining step. At the higher temperature, the oxidative reagent may be the bond-stretched water molecule and the reaction between CO and this water molecule is probably the rate-determining step.
References


26. Discussion with Professor A. B. Anderson.


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E. CHAPTER V


26. Discussion with Professor A. B. Anderson.
