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May 2001
Ph.D. Thesis
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Scanning Tunneling Microscopy Studies of the Structures and Dynamics of Molecular Monolayers on the Rh(111) and Pt(111) Single Crystal Surfaces

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Ph.D. Thesis

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Scanning Tunneling Microscopy Studies
of the Structures and Dynamics of Molecular Monolayers
on the Rh(111) and Pt(111) Single Crystal Surfaces

by

Yong Chen

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Professor Gabor A. Somorjai, Chair
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Spring 2001
Abstract

Scanning Tunneling Microscopy Studies

of the Structures and Dynamics of Molecular Monolayers

on the Rh(111) and Pt(111) Single Crystal Surfaces

by

Yong Chen

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Gabor A. Somorjai, Chair

The structures and dynamics of the chemisorbed overlayers of oxygen, nitric oxide, propylene and four cyclic aromatic hydrocarbon compounds on the Rh(111) and/or Pt(111) at room temperature were investigated by scanning tunneling microscopy (STM). The topography of the Rh(111) surface during the propylene thermal decomposition process was inspected. The STM tip catalyzed oxidation and hydrogenation of carbonaceous clusters were successfully performed on Rh(111).

Oxygen and nitric oxide both form (2×2) type overlayers on Rh(111) in ultrahigh vacuum. The (2×2) oxygen structure remains in the presence of up to 10 torr of O₂. However, at higher pressure, large disordered features were found on the surface, suggesting the concurrent nucleation of atomic oxygen localized around carbon impurities. The (2×2) nitric oxide overlayer has 1/3 of molecules on atop site and the remaining on hollow sites. In a perfectly ordered adsorption domain, only molecules on atop sites were imaged. However, the topography change due to the
absence of molecules on hollow sites was observed, indicating that the apparently large corrugation of molecules on atop site has both geometric and electronic density contribution from all molecules in the unit cell.

On Pt(111) propylene forms a stable (2×2) propylidyne overlayer, but upon exposed to CO it decomposes to disordered small fragments. On Rh(111), however, propylene briefly forms a unstable (2×2) propylidyne structure, which further decomposes into disordered mixture of ethylidyne and C-H species. When co-adsorbed with CO, ethylidyne segregates from the mixture and forms a stable c(4×2) overlayer.

The adsorption behaviors of benzene, naphthalene, phenanthrene and anthracene on Rh(111) and Pt(111) were systematically investigated. The characteristic shapes of all four molecules were differentiated. All molecules lie flat on the substrate. Benzene alone forms (3×3) and c(2√3×4) overlayers, and when co-adsorbed with NO, it arranges to a (3×3) overlayer. Naphthalene forms (3×3) and (3√3×3√3)R30° overlayers on Rh(111). The former structure can be converted into the latter by co-adsorption with CO. Low pressure of O₂ and H₂ do not change the structure of a naphthalene pre-covered Rh(111) surface, but the adsorption of naphthalene on an oxygen pre-covered Rh(111) shows a new (4×4) structure, and high pressure of H₂ completely destroys naphthalene overlayer. In all naphthalene adsorption structures, the long axis of naphthalene is always orientated to the close-packed direction of the Rh(111) substrate. On both Rh(111) and Pt(111), phenanthrene and anthracene have no long-range ordering, regardless of whether it is alone or co-adsorbed with other molecules. However, the C₂ axis of phenanthrene is always along one of the close-packed directions of the Rh(111) substrate, while anthracene is randomly orientated.
Topography images were taken after the propylene adsorbed Rh(111) surface was heated at 155°C, 265°C, 400°C and 600°C, where C_xH fragment, carbonaceous clusters, polymers, and graphite form, respectively. Compared with the results obtained from Pt(111) reported in literature, propylene thermal decomposition on Rh(111) generates more uniformly distributed particles in every stage before the formation of graphite, and the sizes of the particles are generally smaller. These differences are tentatively attributed to kinetic factors during the decomposition process.

Platinum STM tip-catalyzed hydrogenation and oxidation of carbonaceous species on the Rh(111) surface were observed for the first time. The reactions only took place when a Pt (not W or Au) tip was used in the presence of O_2 or H_2. The reaction rate rises with the increase of background pressure increase and/or the decrease of tunneling gap. The reactions on Rh(111) have similar behaviors to those on Pt(111) in the sense that reaction rates have the same order of magnitude, and the extents of the reaction are roughly the same. This indicates that on rhodium and platinum surface a common mechanism should account for the reactions. However, the reactions on Pt(111) are slightly faster. Kinetics considerations are needed to explain the rate differences between the reactions on the two substrates.
Scanning Tunneling Microscopy Studies of the Structures and Dynamics of Molecular Monolayers on the Rh(111) and Pt(111) Single Crystal Surfaces

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by

Yong Chen

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Dedicated to my parents.
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# Table of Contents

List of Figures vii

Chapter 1. Introduction 1

Chapter 2. Scanning tunneling microscopy: principle and apparatus 3

2.1 Introduction 3
2.2 Principle of operation 4
2.3 Design of the Ultrahigh Vacuum STM 11
2.4 Tip preparation 16

References 20

Chapter 3. Experimental methods and instrumentation 22

3.1 Introduction 22
3.2 Ultrahigh vacuum 22
3.3 Vacuum chamber 24
3.4 Crystal mounting and manipulation 29
3.5 Sample preparation 31
3.6 Auger electron spectroscopy (AES) 32
3.7 Low energy electron diffraction (LEED) 37

References 41

Chapter 4. STM studies of clean single crystal Rh(111) and Pt(111) surfaces 42

4.1 Introduction 42
4.2 Crystal structure of Rh(111) and Pt(111) 42
4.3 STM studies of a clean Rh(111) surface 44

4.3.1 Experimental 44
4.3.2 STM images with large scan area 46
4.3.3 STM images with atomic resolution 48

4.4 STM studies of a clean Pt(111) surface 50
4.5 Conclusions 51

References 54

Chapter 5. STM studies of oxygen and nitric oxide adsorption on the Rh(111) surface 55

5.1 Introduction 55
5.2 Oxygen adsorption on Rh(111) 56

5.2.1 Experimental 56
5.2.2 Rh(111)-O structure formed in low pressure O2 58
Chapter 8. The adsorption of benzene and small polycyclic aromatic hydrocarbons (naphthalene, phenanthrene and anthracene) on the Rh(111) and Pt(111) surfaces

8.1 Introduction 130
8.2 Experimental procedure 130
8.3 Benzene on Rh(111) 131
8.3.1 Benzene adsorption on Rh(111) 131
8.3.2 Benzene co-adsorption with NO on Rh(111) 132
8.3.3 Discussion 133

8.4 Naphthalene on Rh(111) 134
8.4.1 Naphthalene adsorption on Rh(111) 134
8.4.2 Naphthalene co-adsorption with CO on Rh(111) 135
8.4.3 Naphthalene co-adsorption with O_2 on Rh(111) 136
8.4.4 Naphthalene co-adsorption with H_2 on Rh(111) 137
8.4.5 The bias polarity effect on images 138

8.5 Phenanthrene on Rh(111) and Pt(111) 139
8.5.1 Phenanthrene adsorption on Rh(111) 139
8.5.2 Phenanthrene co-adsorption with CO and O_2 on Rh(111) 140
8.5.3 Phenanthrene adsorption on Rh(111) in the presence of NO 141
8.5.4 Phenanthrene adsorption on Pt(111) 142

8.6 Anthracene adsorption on Rh(111) and Pt(111) 143
8.7 Influences of high pressure of O_2 and H_2 on the adsorption of aromatic compounds 144
8.8 Summary 145

References 146

Chapter 9. Conclusions 148
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 (a)</td>
<td>A model of the tunneling barrier.</td>
<td>6</td>
</tr>
<tr>
<td>2.1 (b)</td>
<td>An atomic view of the tip-vacuum-metal configuration.</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Illustration of the two operation modes of STM.</td>
<td>7</td>
</tr>
<tr>
<td>2.3(a)</td>
<td>A representation of the response of a piezoelectric ceramic device to an external voltage bias.</td>
<td>8</td>
</tr>
<tr>
<td>2.3(b)</td>
<td>A simplified displacement versus voltage curve of a typical piezoelectric ceramic device.</td>
<td>8</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic of the feedback loop for STM operation.</td>
<td>10</td>
</tr>
<tr>
<td>2.5</td>
<td>An illustration of the operation principle of STM.</td>
<td>10</td>
</tr>
<tr>
<td>2.6</td>
<td>A photograph of the STM.</td>
<td>12</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic drawing of the STM.</td>
<td>13</td>
</tr>
<tr>
<td>2.8</td>
<td>A close look at the STM head (cross section).</td>
<td>13</td>
</tr>
<tr>
<td>2.9</td>
<td>A representation of the sample approaching mechanism.</td>
<td>15</td>
</tr>
<tr>
<td>2.10</td>
<td>Schematic diagram of the apparatus used to perform field emission of the STM tip.</td>
<td>19</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of the UHV chamber.</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic of the gas manifold.</td>
<td>26</td>
</tr>
<tr>
<td>3.3</td>
<td>Composition of residual gas in UHV chamber.</td>
<td>26</td>
</tr>
<tr>
<td>3.4</td>
<td>The heatable doser designed for low vapor pressure materials.</td>
<td>28</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic of the sample holder.</td>
<td>30</td>
</tr>
<tr>
<td>3.6</td>
<td>Schematic of the sample manipulator.</td>
<td>30</td>
</tr>
<tr>
<td>3.7</td>
<td>Schematic of the Auger electron process.</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 3.8  Schematic of an AES experimental setup using the retarding field analyzer (RFA).

Figure 3.9  Auger electron spectra of a clean (middle), carbon-contaminated (top), and sulfur-contaminated (bottom) rhodium (111) surface.

Figure 3.10  Schematic diagram of the LEED scattering process.

Figure 3.11  An illustration of the real space lattice and its diffraction pattern for an fcc (111)-(1x1) surface.

Figure 3.12  An illustration of the real space lattice and its diffraction pattern for an fcc (111)-(2x2) surface.

Figure 4.1  Face-centered cubic crystal structure and (111) surface plane structure of rhodium and platinum.

Figure 4.2  LEED pattern of a clean Rh(111) single crystal surface.

Figure 4.3  Large-scale STM image of the Rh(111) surface.

Figure 4.4  High resolution STM image of the Rh(111) surface.

Figure 4.5  Auger spectra of clean and carbon contaminated Pt(111).

Figure 4.6  LEED pattern of a clean Pt(111) single crystal surface.

Figure 4.7  High resolution STM image of the Pt(111) surface.

Figure 5.1  LEED patterns of a clean Rh(111) and Rh(111)-(2x2)-O structure.

Figure 5.2  High resolution STM image of the Rh(111)-(2x2)-O structure.

Figure 5.3  High resolution STM image of Rh(111) in 10 torr of oxygen.

Figure 5.4  High resolution STM image of Rh(111) in 100 torr of oxygen.

Figure 5.5  Schematic of the Rh(111)-(2x2)-O structure.
Figure 5.6 LEED pattern of the Rh(111)-(2×2)-3NO adsorption structure.

Figure 5.7 Auger electron spectrum of NO-covered Rh(111) surface.

Figure 5.8 STM image of a Rh(111) surface partially covered with the (2×2) NO structure.

Figure 5.9 100Å×100Å STM image of a Rh(111) surface almost completely covered with the (2×2) NO structure.

Figure 5.10 30Å×30Å STM image of a Rh(111) surface saturated with a (2×2) NO overlayer.

Figure 5.11 Schematic of Rh(111)-(2×2)-3NO and Rh(111)-(2×2)-3CO structures.

Figure 6.1 Pathways for the thermal decomposition of ethylene, propylene, methylacetylene and propadiene on Rh(111).

Figure 6.2 The formation of alkylidyne from small olefins.

Figure 6.3 H₂ thermal decomposition spectra of ethylene and propylene on Rh(111).

Figure 6.4 Illustration of the fcc (111) -(2√3×2√3)R30°-3 propilidyne structure.

Figure 6.5 Schematic diagram of various pathways for production of the c(4×2) arrangement of ethylidyne and CO on Rh(111).

Figure 6.6 Illustration of the Rh(111)-c(4×2)-C₂H₃+CO structure.

Figure 6.7 LEED patterns (all taken at 83 eV) for clean Pt(111)-(1×1), Pt(111)-(2×2)-propilidyne, and Pt(111)-(2×2)-propilidyne exposed to CO (disordered).

Figure 6.8 200Å×200Å STM images of the Pt(111)-(2×2)-propilidyne adsorption structure.

Figure 6.9 100Å×100Å STM image of the Pt(111)-(2×2)-propilidyne adsorption structure.
Figure 6.10  STM images taken on a Pt(111)-(2×2)-propylidyne structure before and after the exposure to 10L of CO. 92

Figure 6.11  LEED patterns for clean Rh(111)-(1×1), Rh(111)-c(4×2)-propylidyne+CO, Rh(111) surface 20 seconds after dosed with 10L propylene, and Rh(111) surface 60 seconds after dosed with 10L propylene. 94

Figure 6.12  STM image of a Rh(111) surface taken within 10 minutes after it was dosed with 10L of propylene. 96

Figure 6.13  Two STM images of Rh(111) co-adsorbed with 10L of propylene and 10L of CO. 98

Figure 6.14  100Å×100Å STM images of Rh(111) co-adsorbed with 10L of propylene and 10L of CO. 99

Figure 6.15  STM images taken at different stages of propylene thermal decomposition on the Rh(111) surface. 103

Figure 6.16  STM image of Rh(111) covered with graphite layers. 105

Figure 6.17  STM image of graphite grown on Rh(111) by thermally cracking propylene, showing Möire patterns. 106

Figure 7.1  Cartoon of the proposed mechanism for the tip-induced catalysis. 112

Figure 7.2  The gas phase pressure dependence of the tip catalysis reaction rates 113

Figure 7.3  A series of STM images show the progress of the tip induced oxidation of carbonaceous clusters on the Rh(111) surface. 116

Figure 7.4  Larger images taken before and after the tip underwent the reaction shown in Figure 7.3. 117

Figure 7.5  A series of STM images show the progress of the tip-induced oxidation of carbonaceous clusters on the Rh(111) surface in 3 torr of O₂. 119
Larger images were taken before and after the tip conducted the reaction shown in Figure 7.5.

A series of STM images show the progress of the tip-induced hydrogenation of carbonaceous clusters on Rh(111) surface.

The structure and dimensions of benzene and small polycyclic aromatic hydrocarbons.

The vapor pressure of naphthalene, phenanthrene and anthracene as a function of temperature.

The mass spectra for naphthalene and anthracene.

H₂ thermal desorption spectrum from benzene adsorbed on Rh(111) in both (3×3) and c(2√3×4) structures.

Schematic of Rh(111)-(3×3)-benzene and Rh(111)-c(2√3×4)-benzene structures suggested by LEED and HREELS.

The LEED patterns (left) and the corresponding models (right) for the structures of benzene adsorbed on Rh(111) (top) and benzene and NO co-adsorbed on Rh(111) (bottom).

STM image of benzene adsorption on the Rh(111) surface.

STM Image of benzene on Rh(111) with a (3×3) and a c(2√3×4) domain.

STM image of the Rh(111)-(3×3)-benzene domain.

High resolution image of benzene on Rh(111) in a (3×3) domain.

STM image of the Rh(111)-(3×3)-benzene+2NO structure.

Schematic of a proposed Rh(111)-(3×3)-benzene+2NO structure.

The molecular orbital diagram for benzene, NO and CO adsorbed on a Rh(111) surface.
Figure 8.14  H₂ thermal desorption spectrum from naphthalene adsorbed on Rh(111).

Figure 8.15  Schematic of the Rh(111)-(3×3)-naphthalene and Rh(111)-(3√3×3√3)R30°-3 naphthalene structures suggested by LEED.

Figure 8.16  LEED patterns for clean Rh(111), Rh(111)-(3×3)-naphthalene and Rh(111)-(3√3×3√3)R30° structures, taken at 74eV, 74eV and 100eV respectively.

Figure 8.17  STM image of the (3×3) naphthalene structure on Rh(111).

Figure 8.18  STM images of naphthalene on Rh(111) in a (3×3) domain with higher magnifications.

Figure 8.19  STM images of naphthalene on Rh(111) in a (3√3×3√3)R30° domain.

Figure 8.20  LEED patterns for Rh(111)-(3×3)-naphthalene and Rh(111)-(3√3×3√3)R30°-naphthalene+CO structures.

Figure 8.21  STM image of the Rh(111)-(3√3×3√3)R30° naphthalene+CO structure.

Figure 8.22  Schematic of a proposed model of the Rh(111)-(3√3×3√3)R30°-3 naphthalene+CO structure.

Figure 8.23  STM images of the surfaces of naphthalene-adsorbed Rh(111) exposed to O₂. The left and right images were taken respectively in 1×10⁻⁴ torr and 15 torr of O₂ at room temperature.

Figure 8.24  LEED patterns for the surfaces of clean Rh(111) with (1×1), Rh(111) adsorbed with oxygen and Rh(111) adsorbed in sequence with oxygen and naphthalene, respectively, in UHV and room temperature.

Figure 8.25  STM images of Rh(111) co-adsorbed with 60L of oxygen and 150L of naphthalene, in sequence.
| Figure 8.26 | STM images of the surface of naphthalene-adsorbed Rh(111) exposed to H\textsubscript{2}. |
| Figure 8.27 | The STM images change in the appearance as a function of the bias polarity. This series of four images are taken at the same area as the Rh(111)- (3\sqrt{3}×3\sqrt{3})R30°-naphthalene structure. |
| Figure 8.28 | STM images taken on a Rh(111)- (3\sqrt{3}×3\sqrt{3})R30°-naphthalene structure exposed to 1×10\textsuperscript{-4} torr H\textsubscript{2}, showing the same polarity effect as in Figure 8.27. |
| Figure 8.29 | STM image of phenathrene on Rh(111). |
| Figure 8.30 | High resolution STM images of phenathrene on Rh(111). |
| Figure 8.31 | STM images of phenathrene co-adsorbed with CO (left) and oxygen (right) on Rh(111). |
| Figure 8.32 | LEED pattern for a Rh(111) surface partially covered with phenanthrene (2L) and NO (100L). |
| Figure 8.33 | STM image of a Rh(111) surface co-adsorbed with phenanthrene (2L) and NO (100L). |
| Figure 8.34 | STM images of phenathrene co-adsorbed with CO on Pt(111). |
| Figure 8.35 | STM image of anthracene adsorbed on Rh(111). |
Chapter 1
Introduction

The physical and chemical properties of metal surfaces play an important role in heterogeneous catalysis. Studies of the structure and dynamics of chemisorbed atomic and molecular monolayers on surfaces provide a fundamental understanding into all surface processes. Since the early 1980's, the development of scanning tunneling microscopy (STM) has greatly enhanced the study of surfaces at the atomic/molecular level. Besides its applications in obtaining a topographic image of the surface species, STM is more often than ever being used to induce surface modifications/reactions and, at the same time, monitor the dynamics with atomic resolution. The capability of being operated in a wide range of pressures and temperatures makes STM an incomparable technique that can be utilized not only under ultrahigh vacuum and ultra low temperature conditions, but also in ambient and even industrial environments. The investigation of surface dynamics and reaction under high-pressure conditions, which is an unprecedented subject in traditional surface science studies, can thus be performed.

This dissertation work focuses on the structures and dynamics of atomic and molecular monolayers on Rh(111) and Pt(111) surfaces. These experiments have been performed using STM with the assistance of LEED (low energy electron diffraction). For an adsorbate overlayer on a metal surface in vacuum environment, the combination of STM images and LEED patterns gives an entire picture of the surface structures and the adsorbate-substrate interactions in both microscopic and macroscopic perspectives. Under high-pressure conditions, STM can be used to inspect the formation and dynamics
of some unique adsorption structures not seen in a UHV environment. Equipped with a catalytically active tip, STM can also be used to induce highly localized oxidation/hydrogenation reactions and image the process in situ.

The adsorption behavior of small gas molecules, such as O₂, NO and propylene, on Rh(111) and Pt(111) was first studied. Although most of their adsorption structures have been determined before, some more details were discovered. This information was also the basis of the following studies of their co-adsorption with aromatic molecules.

The thermal decomposition of propylene on Rh(111) was inspected. Based on this, the Pt tip-catalyzed oxidation and hydrogenation of carbonaceous clusters on Rh(111) were then carried out with success. The results were compared with published results obtained on Pt(111).

The adsorption of benzene, naphthalene, phenanthrene and anthracene on Rh(111) and Pt(111) was systematically investigated. Individual molecular shapes were discerned, and the adsorption overlayer structures were imaged. Their co-adsorption with CO, NO, O₂ and H₂ were then selectively examined, and some promotions and changes in the ordering of the surface structures were detected.

As an extension to the project of tip catalysis of carbonaceous clusters, the possibility of observing the similar reactions on individual aromatic molecules was explored. However, no positive result was obtained from these attempts.
Chapter 2.  

Scanning Tunneling Microscopy: Principle and Apparatus  

2.1 Introduction  

The scanning tunneling microscope (STM) was invented by Binnig and Rohrer in IBM's Zurich Laboratory in the early 1980's [1-2]. In the past two decades, it has been widely and extensively used to study a variety of surfaces, including metals and semiconductors, in almost every experimental environment (vacuum [3-6], air and in electrolyte [7]) at the atomic/molecular level. Now it is becoming a routine technique for surface studies. STM can be used to investigate the adsorption, co-adsorption and diffusion of atoms and molecules on metal surfaces [8-14], and the surface construction of metals [15] and semiconductors [16]. Most of the studies have been conducted in ultrahigh vacuum and/or low temperature conditions, where classical surface science originated and has achieved numerous valuable results. Recent applications of STM in high pressure high temperature conditions show that STM is of great use in investigating surface processes under industrial reaction conditions, which bridges both the pressure and temperature gap between the traditional surface science research regime and industrial application territory [17-21]. In this chapter, the principles of STM and the design of STM used in this dissertation work are discussed.
2.2 Principle of operation

The operation of STM is based on the electron tunneling effect. According to quantum mechanics, when two pieces of conducting objects are brought very close to each other, their electronic wave functions overlap considerably if the spacing is within a few angstroms. When a proper voltage is applied across the two objects, electrons have certain probabilities of tunneling through the classically forbidden energy gap, and form a small current, which can be detected macroscopically. This process is shown in Figure 2.1(a). The tunneling current normally has a magnitude of 100pA~10nA. It has an exponential dependence on the gap separation and the height of the energy barrier, which can be approximated with Wentzel-Kramer-Brillouin (WKB) theory,

\[
I \propto V \exp(-\Phi^{1/2} \cdot z)
\]

Where I is the tunneling current, V is the bias voltage, Z is the gap (or the separation between the two objects), and \( \Phi \) is the average work function of the two objects. This relationship is very sensitive to z as z shows in the exponential term. In fact, under normal condition (i.e., reasonable \( \Phi \) values, room temperature, and z around a few angstroms) with fixed bias voltage, the tunneling current will change by a factor of 10 if z changes by 1 angstrom. STM takes the advantage of this sensitive dependence of the current to the separation.

In figure 2.1(b) a general representation of a tip – vacuum – metal energy diagram is given. A sharp metallic tip and the metal sample behave as the two conducting objects, and the vacuum in between acts as the gap. A bias voltage is applied to the tip and sample externally. If one wants to keep the tunneling current constant, the distance between the tip and sample has to be kept constant. When the tip is scanned in the X-Y
direction over the sample and the tunneling current is monitored, the Z position of the tip is required to follow the contour of the sample in order to keep the current constant in the whole scanning process. A record of the X-Y-Z movement of the tip will be a replica of the sample surface in real space. In this scanning process, the sharp tip probes the sample surface while the current is kept constant. This is the most common operation mode of STM, and is exclusively used in this dissertation work. Another mode, constant height mode, is limited to scanning over an atomically flat surface. Both modes are illustrated and briefly explained in Figure 2.2.

In order to get atomic resolution, the movements of the tip with respect to the sample in all 3 dimensions require very precise control. This is achieved by the employment of piezoelectric ceramic ("piezo" for short) devices. Piezo ceramics, such as lead zirconate titanate (or PZT), are ferroelectric materials, which have asymmetric unit cells with an electric dipole moment. In a strong electric field, the unit cells will slightly change shape, by elongating (or shrinking) along the electric field direction and shrinking (or elongating) in the two perpendicular directions, as illustrated Figure 2.3(a). The response of this displacement with respect to the external field is very reproducible and normally quite linear, as shown in Figure 2.3(b). By combining several piezo device elements, very accurate three-dimensional control can be accomplished. In a modern STM design, an accuracy of 1Å in the X and Y directions, and 0.1Å in the Z direction is routinely obtained. Piezo element assemblies with dynamic ranges of 1 to 100μm in the X and Y directions, and 0.1 to 5 μm in the Z direction, are commercially available.
Figure 2.1(a) A model of the tunneling barrier.

Figure 2.1(b) An atomic view of the tip-vacuum-metal configuration.
Figure 2.2 Illustration of two operation modes of STM. Top: constant height mode, where the tip is held at a constant Z position and the measured current reflects the topography. Bottom: Constant current mode, where an electronic feedback loop maintains constant current by adjusting the z displacement of the tip. The z movement corresponds to the surface corrugation of the sample.
Figure 2.3(a) A representation of the response of a piezoelectric ceramic device to an external voltage bias.

Figure 2.3(b) A simplified displacement versus voltage curve of a typical piezoelectric ceramic device.
For constant current imaging mode, as the tip is rastering over the sample surface, a feedback loop is used to control the tip-to-sample distance such that the tunneling current is held to a preset value. The instantaneous tunneling current is measured during scanning and compared with the reference value, and the difference is sent to a negative feedback amplifier circuit. This circuit can compensate the current difference by extending or pulling back the tip accordingly. A typical feedback loop schematic is given in Figure 2.4.

A state-of-the-art STM takes advantage of the development of new microelectronics and computer data acquisition techniques. The rastering in the X and Y directions is handled by the data interface, as are the necessary parameters for feedback control and signal collection. Further processing of these data by the computer can produce the three-dimensional topographic image of the sample. An overlook of STM is shown in Figure 2.5.

It should be mentioned that although most of the time people refer to the image generated by STM as the surface “topography”, it is more accurate to be interpreted as a contour of the local electron density of state near the Fermi level of the sample. If the sample has a uniform electron density over the surface, then the image is a true topography of the surface, provided it is imaged with a clean and sharp tip. In reality, an STM image is a convolution of geometric and electronic density variations of the sample surface. Further consideration is often needed in order to explain complicated STM images.
Figure 2.4 Schematic of the feedback loop for STM operation.

Figure 2.5 An illustration of the imaging principle of STM.
2.3 Design of the Ultrahigh Vacuum STM

The microscope used for this dissertation work was home-built and based on an existing design, very similar to those described in Ref. 22 and 23. The photograph and schematic drawing of the STM are shown in Figure 2.6 and 2.7. The STM is mounted on an 8" conflat flange. The STM head has a double tube design that consists of two concentrically mounted piezo tubes. This design provides thermal compensation in the X and Y directions and minimizes the thermal drift. The outside electrode of each tube is sectored into quadrants to provide three-dimensional control. Figure 2.8 shows further details on the STM head. Both piezo tubes are soldered on copper supports. The outer piezo, with a diameter of 1", controls the offsets in X and Y positions, as well as the sample approach. The inner piezo, with a diameter of 1/8", controls the rastering in X and Y directions and tip-to-sample distance. The tip is held into a tip holder (made of Macor piece), which is glued onto the inner piezo tube. An anodized aluminum rail is soldered to the end of the outer piezo. A 0.0005" thin gold foil (mounted on top of the outer piezo tube), which touches the sample holder when it is on the rail, is used to make electric contact with the sample to supply bias voltage. Due to its extremely low mass and good deformability, the contact with the sample holder will not affect the sample approach or the scanning process. In this dissertation work, the bias voltage is always referred to with a polarity of sample versus tip.
Figure 2.6 A photograph of the STM. The STM head as well as the vibration isolation components are shown. The sample holder is on the rail extended from the outer piezoelectric tube.
Figure 2.7 Schematic drawing of the STM.

Figure 2.8 A close look at the STM head (cross section).
The approach of the sample to the tip is achieved by applying an asymmetric ramp waveform to the outer piezo tube, as illustrated in Figure 2.9. During the sharp rise of the triangle wave ("A-B"), the piezoelectric tube extends its length rapidly enough to break the static friction while the sample holder keeps still due to inertia. During the gentle down-slope of the triangle wave ("B-C"), the piezo retracts slowly and carries the sample holder towards the tip. This slip-stick motion repeats hundreds to thousands of cycles to bring the sample close to the tip. The fine approach mechanism behaves in a similar fashion but uses much lower frequencies, and involves the detection of the tunneling current. When the current reaches a preset threshold, the motion of the outer piezo stops. The final distance control is done manually to bring the sample to the tip within a few angstroms before scanning starts.

A set of RHK STM 100 (version 4, RHK Technology, Inc., Rochester Hills, MI) electronics is used to control the microscope. Through an interface board, commercial software can communicate with the controller, acquire the image, and process data offline.
Figure 2.9 A representation of the sample approaching mechanism.
The STM needs to be isolated from ambient vibrations so that the tunneling gap can remain stable. This is accomplished by three grades of vibration isolators: extension springs, vibration springs, and air legs. The whole vacuum chamber rests on a stiff stage that can be floated on three compressed air legs. The STM head is hung with four springs (extension springs) on the rack, extended from the 8” flange. The stainless steel plates on the STM head are spaced with Viton springs which help to dampen vibrations. When the STM is in operation, any ambient vibration would be greatly attenuated before propagating through the STM head. The noise level and its origin can be tested through measuring the background current signal and analyzing its frequency spectrum.

2.4 Tip preparation

The quality of the tip is very crucial in generating a genuine and reliable image of the surface under study. In the tunneling process, there are a large number of atoms on the tip that participate in tunneling, but only a few at the very end contribute significantly to the current. Therefore, STM tips are not required to have a curvature of only a few angstroms. Instead, one only needs a single atom jutting out at the end of the tip to achieve atomic resolution.

An STM tip can easily be contaminated during storage or scanning. Care has to be taken to keep a tip in good condition, and special treatment is needed to regenerate a clean and sharp tip from a blunt and/or contaminated one.

The tips used in this research are made of Φ0.01” wire of either tungsten or 87% platinum/13% rhodium alloy. W tips are used for general imaging since it has much greater hardness and is more durable under UHV conditions. Pt tips are used to take
images in the presence of moderate or high pressures of O₂ or H₂, for its ability to
dissociate those gases and initiate their reactions with the species adsorbed on the surface.

Both types of tips are electrochemically etched from wires. For making W tips,
the electrolyte is 2 mol/L aqueous solution of KOH, the anode is W wire, and the cathode
counter electrode is a Pt wire. Normal electrolysis voltage is ~1.5V, and a simple circuit
is used to automatically shut off the current when the W wire is etched across. For
making Pt tips, a molten NaNO₃ and NaCl (1:4) mixture serves as the electrolyte, and the
target Pt wire and a counter Pt wire are the anode and cathode, respectively. The
electrolysis voltage is around 5V. With these methods, it takes about 10 minutes to make
a W tip, and 1 minute for a Pt tip. The former can be controlled more precisely, and a W
tip made this way is typically of better quality both in sharpness and cleanliness. As-
prepared tips are then cleaned in de-ionized water and acetone, and examined under an
optical microscope before use.

Once inside the UHV chamber, the tip cannot be cleaned in a direct manner. Two
methods are generally used to reform (rather than "clean") the tip. One is used during
scanning by applying a pulse voltage jump between the tip and sample from ~1 to 10 V
for a fraction of a second. The other method is applying a high DC voltage (a few
hundred to three thousand volts) between the tip and another piece of metal within a
couple of millimeters away. The latter is often referred to as field emission. In both
cases, since the tip has a much larger curvature compared to the metal piece in front of it,
any contaminants or even some atoms of the tip material are expected to be removed by
either a sudden jump of high current density or a very strong electrostatic field. Figure
2.10 shows the schematic of the field emission apparatus used in this dissertation work.
A small piece of tantalum foil spot-weld on a long stainless steel wire (serving as the emission target), is controlled through a rotary motion feed-through and can be brought close to or away from the tip. The high voltage across the foil and the tip is applied with a high-voltage DC power supply. The field emission current is monitored through measuring the voltage on a sampling resistor in serial with the tip. In field emission, depending on the tip-foil separation and the actual condition of the sharpness and cleanness of the tip, the current is normally on the order of 10nA~1μA (considerably higher than a typical tunneling current). As mentioned above, both pulsing and field-emitting of the tip are non-direct treatment methods, so the extent of the cleaning or sharpening effect is unpredictable, and sometimes the tip may even be ruined. Changing tips is unavoidable, and even frequent, especially when conducting experiment in high-pressure gas.
Figure 2.10 Schematic diagram of the apparatus used to perform field emission of the STM tip.
References

Chapter 3.
Experimental Methods and Instrumentation

3.1 Introduction

This dissertation work was carried out in a typical ultrahigh vacuum (UHV) system. The UHV techniques involve UHV production, sample surface preparation and characterization, and gas environment analysis. For these purposes, the UHV system includes, respectively, a stainless steel chamber and variety of pumps, sample heating and sputtering apparatuses, a number of surface-specific characterization instruments, and a mass spectrometer for residual gas analysis.

3.2 Ultrahigh Vacuum (UHV)

In every surface related study, it is important to keep the surface at a clean or well-characterized status for at least the duration of the experiment. Most metal surfaces have a high surface energy [1], so they tend to adsorb or even react with gas molecules in the environment to minimize their surface energy by forming a layer of adsorbates. Therefore, it does not take long for a clean or well-characterized metal surface to become contaminated with undesired species present in a laboratory environment. In order to keep an as-prepared surface, the experiment should be carried out at very low gas pressure (i.e., a good vacuum is needed).
From the kinetic theory of gases, the quality of the required vacuum can be evaluated. In a given time, at a given temperature and pressure, the number of molecules \( r \) impinging on a surface is given by [2]

\[
r \text{ (atoms/cm}^2\text{·sec)} = N_a \cdot \frac{P}{(2\pi \cdot M \cdot RT)^{1/2}}
\]

which can be simplified as

\[
r = 3.51 \times 10^{22} \frac{P}{\sqrt{TM}}
\]

where \( P \) is pressure (in torr), \( T \) is temperature (in K) and \( M \) is the molecular weight (in atomic mass unit).

Using this equation, \( 10^{-6} \) torr of \( \text{N}_2 \) at room temperature \((300\text{K})\) should generate a flux equal to \( 3 \times 10^{15} \) molecules per cm\(^2\) per second. If we suppose all molecules hit and stick to the surface, this number is approximately equal to the concentration of the atoms on the surface. The surface would be covered completely by \( \text{N}_2 \) in just one second. This leads to the derivation of \textit{Langmuir} (L), a unit extensively used in gas-involved surface science studies. One Langmuir is defined as the exposure in a \( 10^{-6} \) torr gas environment for 1 second.

The previous calculation also gives us the magnitude of the pressure that ensures a clean environment for surface science studies. Typical experiments last for about one hour or so, so if the surface is required to be clean for 3600 seconds, the pressure must be no higher than \( 3 \times 10^{-10} \) torr. This pressure range is referred to as ultrahigh vacuum or UHV.

UHV is achieved in a stainless steel chamber by constantly pumping out the gas inside with numerous types of pumps.
3.3 UHV chamber

In this study, all experiments were conducted in a standard Varian chamber. A schematic of the chamber is shown in Figure 3.1. The chamber body is a bell jar mounted on a 250 L/s VaClon pump. A 260 L/s Turbo-molecular pump (Balzer Model TPU 260) is used during the sample cleaning process or quick pump down. The turbo pump is backed with a mechanical pump. To achieve a better vacuum, the ion pump is coupled with a titanium sublimation pump (TSP). A 6-way 2.75" cross (Fig 3.2), serving as a gas manifold, is mounted on the chamber through a bakeable angle valve. This manifold is also connected to a dual stage mechanical pump (Balzer DUO) for rough pumping, and gas lines for venting or filling high pressure gas. The vacuum level is monitored by an ionization gauge (for $10^{-4} \sim 10^{-10}$ torr range) and a baratron gauge (for $10^{-3} \sim 100$ torr range).

The UHV STM is mounted on one side of the chamber through an 8" port. The chamber is equipped with a modified MDC X-Y-Z-θ manipulator, a Varian four-grid retarding field analyzer optics (RFA) for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) analysis, a UTI 100C quadrupole mass spectrometer (MS) for residual gas analysis (RGA), and a Varian ion sputter gun for cleaning the sample.
Figure 3.1 (a) Schematic of the UHV chamber used in this dissertation work. For clarity, the LEED optics and turbo molecular pumps were not shown; (b) Cross-sectional view of the chamber showing the arrangement of the UHV setup.
Figure 3.2 A 6-way cross is mounted on the chamber, serving as a gas manifold.

Figure 3.3 Composition of residual gas in UHV chamber.
A good vacuum is obtained in three steps. Rough pumping (from atmosphere to 100 millitorr) is done by the mechanical pump through the gas manifold. The turbo molecular pump is used to get high vacuum (down to $10^{-6}$-$10^{-7}$ torr). The ultimate ultrahigh vacuum (low $10^{-10}$ torr) is achieved by ion pump and intermittent use of the TSP. Through a 24–48 hour bakeout of the chamber after each exposure to atmosphere or high pressure gas, the typical base pressure when running experiments is better than $2\times10^{-10}$ torr. Under STM experimental conditions, the ion pump alone can maintain this base pressure. All other pumps and the ion gauge are shut off to prevent vibrational or thermal noise that may incur. The background gas is mainly composed of hydrogen, water and carbon monoxide, with trace amounts of carbon dioxide, methyl and carbon as detected by RGA. The typical composition of residual gas in UHV chamber is shown in Figure 3.3.

There are several Varian-type leak valves on the chamber for dosing various gases into the chamber. These gases include those for sample preparation (Ar for sputtering, $O_2$ and $H_2$ for cleaning), and those for study (such as CO, $O_2$, NO, and organics). If the species is liquid or even solid at room temperature, preheating the reservoir is needed to allow the organics to reach a high enough vapor pressure before dosing. For those with very low vapor pressure, extra treatment needs to be taken. Figure 3.4 is the schematic diagram of a specially designed doser for less volatile materials. A regular leak valve is wrapped with heating tape. The outside wall of the leak valve can be heated to 200°C. At the UHV end of the leak valve, a thin and long tubing is mounted to induct the gas flow. This tubing can be heated resistively up to
300°C though passing 0~7A DC current. The organic reservoir can also be heated externally with a heat gun.

Figure 3.4 The heatable doser designed for low vapor pressure materials.
3.4 Crystal mounting and manipulation

The Pt(111) and Rh(111) single crystals used in this dissertation were cut from a single crystal boule. The boule was first oriented with Laue X-ray diffraction to the (111) index plane surfaces (miscut < ±0.5°), then sliced and polished. The polishing consists of two steps. Rough polish is done with silicon carbide sand paper of different grades, then diamond pastes (with particle size 30, 6, 1 and 0.25 micron) are used for fine polishing. The rest of the sample preparation is carried out in the UHV chamber.

The single crystal is mounted on a molybdenum sample holder as illustrated in Figure 3.5. The crystal is held by two tantalum strips that are spot-welded on four small stainless steel screws. The sample holder is clamped by two copper blocks to the manipulator, as shown in Figure 3.6. The copper helps to dissipate heat from the crystal.

The sample holder can be transferred back and forth between the manipulator and the rail of the outer tube of the STM. When it is on the manipulator, it can be translated in the X, Y and Z directions and can be rotated to face various preparation and analysis facilities in the chamber. It can also be heated to 1100 °C by an electron bombardment heater (emission 0~12 mA, acceleration voltage 0~1200V). When the sample holder is not on the manipulator, it is not possible to heat or cool the sample, which limits the STM study at only room temperature.
Figure 3.5 Schematic of the sample holder. A single crystal sample is tightly held to the sample holder by two tantalum wires. The thermocouple is spot-welded on the crystal and carried with the sample holder.

Figure 3.6 Schematic of the sample manipulator. The sample holder can be clamped to the manipulator. Each of the other half of the thermocouple wires is fixed to the manipulator.
The temperature on the crystal can be measured with a type K thermocouple. Each of the thermocouple wires is cut in half in the middle. One half is spot-welded on the crystal and carried with the sample holder, and the other half is fixed on the manipulator (Fig 3.5 and 3.6). When the sample holder is on the manipulator, the two halves of the thermocouple wires connect to form the entire loop, and thus the temperature on the sample can be measured. When the sample holder is on the STM stage, although temperature measurement is not possible, there is no direct contact between the sample and the manipulator, therefore no vibration can be passed from the manipulator.

3.5 Sample preparation

After the crystal is transferred from atmosphere into the UHV chamber, or after one experiment is finished, a routine cleaning procedure is taken to maintain a clean and well-oriented crystallographic surface. This procedure consists of repeated cycles of argon ion sputtering, high temperature oxygen treatment and vacuum annealing. Since the mechanical and chemical properties of Pt and Rh samples are similar, virtually similar cleaning processes are employed. A layer of contaminants can be removed by sputtering with Ar⁺, which has a kinetic energy of 0.5 to 2 keV, and beam intensity of 20mA. The Ar pressure is kept at 2–5×10⁻⁵ torr for 10–20 minutes for such a step. The crystal is then heated to 600 to 800 °C by electron bombardment in 5×10⁻⁸ – 1×10⁻⁷ torr oxygen partial pressure for 1–3 minutes to eliminate any carbon contaminants. The sample is then heated at 900 to 1000 °C in UHV for 30 seconds to 2 minutes to let the
crystal recover from any damage induced during sputtering and regenerate an atomically flat surface.

The cleanliness and ordering of the crystal is characterized by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), of which the principles will be introduced in the following sections. The sample cleaning cycle is repeated until no contaminants are detected by AES. The resulting surface has a very sharp LEED pattern, free of any background intensities.

For adsorption/co-adsorption experiments, gas species are introduced into the chamber through leak valves at the desired temperature and exposure. During the dosing process, RGA is used to monitor the gas composition. AES and LEED are checked afterward. As complementary techniques to STM, they offer macroscopic information about the surface composition, structure and ordering.

### 3.6 Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy (AES) provides a method of identifying the chemical composition of the surface species [3]. The Auger process is illustrated in Figure 3.7. When the surface is bombarded by high-energy electrons, some surface atoms are ionized by losing a core electron each. An electron in a higher energy orbital can then relax into the empty core hole. The excess energy given off by this relaxation can be emitted either as an X-Ray photon (X-Ray fluorescence) or through the ejection of a secondary electron, which is called an Auger electron. The kinetic energy of the Auger electron, which can be calculated by

\[ \Delta E = (E_K - E_{L1}) - E_{L3} \]
is only dependent upon the energies of the three involved energy levels, which are characteristic of the element. The Auger process is also very surface-specific because the Auger electron can only have a free path of less than $\sim10\text{Å}$, as given by the "universal curve" of electron mean free path in a solid surface as a function of its kinetic energy [4]. Therefore, the analysis of the kinetic energy of Auger electrons can be used to distinguish the element composition of surfaces.

In this dissertation work, the excitation electron beam generated from an electron gun (with an incident energy of 1−3 keV) is directed on to the sample, and electrons that are reflected and ejected from the sample are collected by the retarding field analyzer (RFA). The principle of operation for the RFA is illustrated in Figure 3.8. In order to eliminate the strong background in the plot of electron number density as a function of kinetic energy, or $N(E)$ vs. $E$ plot, the derivative of $N(E)$ with respect to $E$ as a function of $E$, or $dN(E)/dE$ vs. $E$ plot is being used instead. The derivation is achieved by modulating the voltage between the grids and the screen, and detecting the second harmonic of the signal with a lock-in amplifier. The spectra can be easily compared to reference spectra to determine the chemical composition of the surface species.
Figure 3.7 Schematic of an Auger electron process. The energetic electron ejects one electron in the core level of the atom, then one of the electrons in an outer level orbital decays. The extra energy is transferred to another electron in the outer level (the Auger electron).

Figure 3.8 Schematic of an AES experimental setup using the retarding field analyzer (RFA).
In Figure 3.9, three typical Auger spectra taken on a rhodium (111) surface under different conditions are shown. In the middle spectrum, the clean rhodium (111) surface shows a set of three characteristic peaks at 220eV, 256eV and 302eV. The small shoulder to the right of the rhodium 256eV peak is from a small amount of carbon contaminant. The carbon peak is clearly shown at 272eV in the upper spectrum, when the surface is covered with hydrocarbons. Another common contaminant in a rhodium surface is sulfur, which has a distinctive peak at 150eV as shown in the bottom spectrum.

By monitoring the Auger spectra of the surface, one can routinely obtain surface chemical composition information, and use that as a guide for further sample cleaning or following steps of the experiments. In addition to the qualitative information, quantitative analysis of the spectra can be performed to determine the surface coverage of specific elements by comparing the relative intensity of the adsorbate peaks to the substrate peaks.
Auger Spectra of Rh(111) surfaces

After dosing 10L naphthalene at room temperature

Clean Rh(111)

Auger Electron Spectrum of Rh(111) contaminated with sulfur

Figure 3.9 Auger electron spectra of a clean (middle), carbon-contaminated (top), and sulfur-contaminated (bottom) rhodium (111) surface.
3.7 Low Energy Electron Diffraction (LEED)

Low energy electron diffraction, or LEED, is also a very surface-specific technique to determine the structure of a surface [5, 6].

A simple LEED representation is illustrated in Figure 3.10. A monochromatic electron beam is scattered off the lattice of the sample. Due to its wave/particle dualism, a low energy electron with energy between 20–300eV has a wavelength between 2.7–0.7Å according to de Broglie relationship,

\[ \lambda = \frac{h}{(2mE)^{1/2}} \]

Because this range of wavelength is on the same order of a typical lattice constant, a monochromatic beam of electrons will diffract from an ordered surface, similar to X-Ray diffraction. However, only the top few layers of atom can contribute to the scattering process due to the small mean free path of the scattered electrons. The surface-specificity of LEED offers a great tool for analyzing only the surface structure.

A LEED pattern is a projection of the real space, two-dimension lattice in reciprocal space. Figure 3.11 shows the real space lattice and its diffraction pattern for an fcc(111)-(1×1) surface. The formation of an ordered overlayer generates additional spots in the diffraction pattern. A typical overlayer has a larger lattice constant, so the reciprocal lattice vectors are smaller than those of the substrate, indicated in the diffraction pattern as extra spots between the spots from the substrate. Figure 3.12 shows a (2×2) overlayer on an fcc(111) surface. The additional spots, which are generated from the adsorbate atoms, appear at “half-order” positions with respect to the substrate spots. In this example, the overlayer lattice has the same orientation as the substrate lattice, so the diffraction patterns from the two lattices have the same
orientation. If there is any difference in the relative orientations of the two lattices, then there will be a corresponding rotation of the set of spots in the diffraction pattern.

For qualitative application, LEED can be used to determine the symmetry of the surface and surface overlayer by simply inspecting the patterns. Quantitative application of LEED, which involves the interpretation and calculation of both the intensity and symmetry of the scattering patterns, can be used to determine the position in the three-dimensional space of the surface atoms (both adsorbate and substrate) to an accuracy of better than tenths of an angstrom.

In this dissertation work, LEED is used only as a qualitative technique. A visual inspection of the diffraction pattern can offer information on the surface geometric symmetry of the unit cell of both the substrate and the adsorbed overlayer, as well as the relative sizes of these unit cells.

LEED patterns were obtained with RFA. By changing control electronics, a RFA can be operated in either Auger or LEED mode. A beam of monoenergetic electrons is generated and focused on the sample. After the electrons are back-scattered, they need to pass four grids before they are captured by a positively biased phosphorescent screen. The four grids are biased at zero or negative voltage with respect to the sample. The set of grids function as a high pass filter, only allowing elastically scattered electron to pass and illuminate the screen. The pattern thus formed is inspected visually or recorded with a CCD video camera controlled by a computer.

LEED is a handy complementary technique to STM. Many surface structures have been determined by LEED in considerable detail [7]. However, the information obtained from LEED is an average over many equivalent atoms, often ignoring the
involvement of local defects. Also, for complex structures, LEED does not provide a direct identification of the model that solves the surface. By contrast, STM is capable of imaging single atoms and defects as well as large ordered domains, and can in favorable cases, directly indicate the structure model (or at least set severe restrictions on possible structural models) [8]. In addition, with computational modeling of STM images, one may extract more detailed structural information as well [9,10].

A simple comparison of STM and LEED is given in Table 3.1. The combination of these two techniques is powerful and versatile, as can be found in the latter chapters.

Table 3.1 The comparison of STM and LEED techniques

<table>
<thead>
<tr>
<th></th>
<th>STM</th>
<th>LEED</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Data</strong></td>
<td>3D topography image in REAL space</td>
<td>2D diffraction pattern in RECIPROCAL space</td>
</tr>
<tr>
<td><strong>Sampling area</strong></td>
<td>Micron or nanometer scales</td>
<td>~ 1mm$^2$ (size of the e$^-$ beam)</td>
</tr>
<tr>
<td><strong>Qualitative</strong></td>
<td>Local ordering, molecular clusters, single molecule imaging</td>
<td>Long-range ordering and symmetry</td>
</tr>
<tr>
<td><strong>information</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Quantitative</strong></td>
<td>(Scanning Tunneling Spectroscopy)</td>
<td>(LEED Crystallography)</td>
</tr>
<tr>
<td><strong>analysis</strong></td>
<td>Orbital structure, local density of electronic states</td>
<td>Bond length/angle determination through I-V curve analysis</td>
</tr>
</tbody>
</table>

39
Figure 3.10 Schematic diagram of the LEED scattering process. Monoenergetic electrons generated in the electron gun are scattered off the crystal lattice. Only elastically scattered electrons are able to pass through the retarding grids to illuminate the fluorescent screen on which the diffraction pattern is recorded.

Figure 3.11 An illustration of the real space lattice and its diffraction pattern for an fcc (111)- (1×1) surface.

Figure 3.12 An illustration of the real space lattice and its diffraction pattern for an fcc (111)- (2×2) surface.
References


Chapter 4.
STM Studies of Clean Single Crystal Rh(111) and Pt(111) Surfaces

4.1 Introduction
The ultimate goal of surface science studies is to elucidate the relationship between the properties of the surfaces/interfaces and the interactions between the interface components. The direct approach to this goal is to investigate the adsorption behavior of variety of substances on surfaces, where the understanding of substrate and simple adsorbate on this substrate is the usual start point. In this chapter, the application of STM on clean single crystal of Rh(111) and Pt(111) is discussed.

4.2 Crystal structure of Rh(111) and Pt(111)
As many metals, rhodium and platinum form face-centered cubic crystal structures [1-2]. This type of structure is illustrated in figure 4.1. On an (111) surface, atoms form a hexagonal close packed layer with six-fold symmetry. If the second layer is also considered, the surface has only a three-fold symmetry, and thus the six hollow sites around each atom are divided into two categories, those directly above second layer atoms and those overlapping hollow sites on the second layer. The first type is named an hcp hollow site, and the second type is named an fcc hollow site. Two other common adsorption sites include the one directly on top of an atom, or an atop site, and one right
in the middle of two adjacent atoms, or a bridge site. Those sites have different symmetries and bonding abilities, which give rise to the diversification and complexity of adsorption structures.

There are several important vectors related to the (111) surface often used later in this dissertation. They include one surface normal vector [111], a group of three along the close-packed direction [110], [101] and [011], and another group of three along the direction pointing to a second nearest neighbor atom [112], [121] and [211]. Each vector in the latter group is perpendicular to the respective one in the former group (e.g., [112] is perpendicular to [110]). Within each group, apparently three vectors are mutually 60° apart from one another.

Figure 4.1 Face-centered cubic crystal structure and (111) surface plane structure of rhodium and platinum.
If the adsorbed atoms or molecules form an ordered structure on a substrate, and this structure has a certain registry with the substrate, there is a simple notation to aid the description of this super-lattice. It is based on the relationship between the relative size and symmetry of the adsorbate unit cell with respect to the substrate unit cell. According to this notation, a clean surface has a (1×1) structure, so a complete notation of a clean single crystal Rh(111) surface is Rh(111)- (1×1). Carbon monoxide on Rh(111) can form an overlayer with lattice constants twice as large as those for the substrate, so the notation for this structure would be Rh(111)-(2×2)-CO. At high coverage, two more CO molecules would be squeezed into each of the above unit cells, and the structure thus formed is Rh(111)-( 2×2)-3CO. More examples of this notation can be found in Ref. 3, and in the following chapters.

4.3 STM studies of a clean Rh(111) surface

4.3.1 Experimental

The experiments were carried out in the UHV chamber described in Chapter 3. The base pressure for this clean surface study was better than 2×10⁻¹⁰ torr. The Rh(111) crystal was cleaned by repeated cycles of Ar⁺ sputtering followed by annealing in oxygen and in vacuum. Cleanliness of the crystal was determined by AES (as shown in Figure 3.9 middle), and the ordering of the surface was determined by the appearance of very sharp (1×1) diffraction spots in the LEED pattern (see Figure 4.2). Note one diffraction spot was not seen in the photograph due to the fact that the sample manipulator was
positioned between the RFA phosphorescent screen and the video camera and blocked the view of the camera. This is the major drawback of the front view LEED apparatus arrangement, and unfortunately, this problem existed throughout this dissertation work. All LEED patterns taken in this fashion always have one fraction invisible to the video camera.

The STM images were taken with a tungsten tip. The bias voltage was normally chosen to be anywhere between 30mV to 1V (sample versus tip), and the tunneling current was around 1nA. The images shown in this dissertation are either raw or taken only after brief low pass. Sometimes, a cross-section plot is drawn to show the corrugation.

Figure 4.2 LEED pattern of a clean Rh(111) single crystal surface. The incident electron energy is 74 eV. Due to the apparatus arrangement, one diffraction spot was blocked by the sample manipulator when taking the photograph. The six diffraction spots form a hexagon, indicating an fcc(111) surface.
4.3.2 STM images with large scan area

Figure 4.3 shows the topographic image of a clean Rh(111) surface with 2000Å \times 2000Å scan area, and the corresponding three-dimensional plot. It can be seen that there are several very large terraces separated by clear step edges. The steps are either parallel to each other or intercept one another at a 60° angle, which is characteristic of an fcc(111) surface. A surface with many intercepting steps is not often observed. In most large-scale images, almost all steps are parallel, indicating that during the polishing process the crystal was off-oriented by a small angle. The existence of intercepting steps offers a convenient reference for STM scanner skew calibration. As described in Chapter 2, the piezoelectric tube was sectored in quadrants, which were referred to as X+, Y-, X-, Y+ clockwise. If for any reason the sectoring is not perfectly done, the X+ and X- pair would not be absolutely orthogonal to the Y+ and Y- pair. In addition, the nonuniformity of the piezo material also plays a factor in this nonorthogonality, which leads to distorted images. With the reference of the intercepting steps in the STM image, the large-scale skew of the scan head can be calibrated by the control software.

Most of the steps in a well-annealed (111) single crystal have a monoatomic height. In the case of Rh(111), the height of these steps is known to be 2.2Å, which gives us the reference to calibrate the scanning piezo in the Z direction.
Figure 4.3 Large scale STM image of the Rh(111) surface. The scan size is 2000Å \times 2000Å. Tunneling conditions: bias voltage of 90mV, and current of 1.0nA. The corresponding 3D plot of the image is given at the bottom.
4.3.3 STM images with atomic resolution

The ability to take real space atomic resolution images is the exclusive advantage of STM as a surface science technique. To conduct the type of study, special care needs to be taken apparently, but there is no guarantee that a satisfactory image can be obtained.

For taking an atomic resolution image on clean metal surface, a very small gap (the ratio of bias voltage and tunneling current) is often required, which yields very small separation between tip and sample. Since the variation in the local density of state between atoms on a metal surface is very low, a small tip-to-sample distance improves the image contrast. However, it is still extremely difficult to routinely resolve atoms on clean metal surfaces. This is due to the reduced electronic corrugation in the surface unit cells. In metals, the free nature of the electrons in the conduction bands makes the surface essentially electronically smooth. As a result, atomic resolution of metals is much more difficult to achieve compared to semiconductors. Even so, some results have been reported on (111) surface of Pt [4], Cu[5], Au [6], Al[7], Ag [8] and Rh [9].

Figure 4.4 is a very high quality high resolution image of a Rh(111) surface. The scan size is 28Å × 28Å, taken with a bias voltage of 116mV and a current of 1.13nA. Hexagonal close-packed individual rhodium atoms are clearly seen. The cross section plot of ten atoms, indicated by the straight line drawn over them, is given at the bottom, and shows the corrugation between atoms is around 40pm, or 0.4Å. This number is 3~4 times bigger than the average corrugation for a clean metal surface. This phenomenon only happens when every condition of imaging (i.e., sharpness, symmetry and cleanliness
of the tip, the noise level of STM head, the ambient vibration level) is optimized, which is very rarely encountered.

Figure 4.4 High resolution STM image of the Rh(111) surface. The scan size is 28Å × 28Å. Tunneling condition: bias voltage of 116mV, and current of 1.13nA. Individual rhodium atoms are clearly imaged. The cross section plot along the straight line is given at the bottom, showing the corrugation between the atoms is around 0.4 Å.
It is also noticeable that not all atoms have the same contrast. Most are very clear, but some are blurry and others are even not resolved. The reason is not clear. Since the atoms with high contrast show up in clusters that are roughly equally spaced, this phenomenon can be tentatively attributed to the Moire interference between the metal lattice and the virtual lattice produced by digital sampling of the data acquisition.

The calibration of the scan head in the X and Y directions can take advantage of this atomically resolved image, since the spacing between atoms is known to be 2.7 Å.

### 4.4 STM studies of a clean Pt(111)surface

The experimental procedure of preparing and imaging the Pt(111) is very similar to that for the Rh(111). Figure 4.5 contains the Auger spectra of Pt(111) before and after carbon contaminants have been removed. Figure 4.6 is the LEED pattern of the cleaned Pt(111) surface.

Not surprisingly, under STM, the Pt(111) surface appear to be almost identical to Rh(111) except that the platinum lattice constant is slightly larger (2.78 Å for platinum compared to 2.69 Å for rhodium). In the X and Y directions, the STM can hardly tell the difference between features less than 0.1 Å.

Figure 4.7 shows a high resolution image of the Pt(111) surface. The scan size is 30Å × 30Å, taken with a bias voltage of −30mV and a current of 1.03nA. Compared with Figure 4.4, it is worse in quality. However the contrast in this image is very typical for a metal surface. In the cross section plot the corrugation is measured to be 0.05 ~ 0.08Å, well within the regular value range. Along the right edge of the image it appears fussy, with some feature extending parallel to the X direction (the fast scan direction). This is
believed to be due to the motion of some weakly bonded adsorbates on the surface. They are disturbed and swept off by the motion of the tip, and reciprocally affect the instantaneous tunneling condition, which causes spikes in the transient current if the interaction is of a much smaller time scale than the feedback control time constant. In the image, they appear as extremely bright features.

4.5 Conclusions

Clean Rh(111) and Pt(111) surfaces were characterized with LEED and STM. Atomically resolved metal surface images were obtained. Some features, such as variation in contrast of individual atoms and unusually large current spikes, were found, which can be tentatively explained by the imaging mechanism of the STM. The STM images, both in large scale and in atomic resolution, can be used to calibrate the scan head in all X, Y, and Z directions.
Figure 4.5 Auger spectra of a clean and a carbon contaminated Pt(111).

Figure 4.6 LEED pattern of a clean Pt(111) single crystal surface. The incident electron energy is 82 eV.
Figure 4.7 High resolution STM image of the Pt(111) surface. The scan size is 30Å \times 30Å. Tunneling condition is: bias voltage of -30mV, and current of 1.03nA. Quite a few individual platinum atoms are resolved. The cross-section plot along the straight line is given at the bottom, showing the corrugation between the atoms is less than 0.1 Å (or 10pm).
References


Chapter 5.

STM Studies of Oxygen and Nitric Oxide Adsorption on the Rh(111) Surface

5.1 Introduction

The adsorption of small inorganic molecules such as O\textsubscript{2}, NO and CO on metal surfaces has been extensively studied by various surface science techniques [1-9] due to the importance of the gas/metal surfaces in heterogeneous catalysis. Besides the individual adsorption behaviors, their co-adsorption with organic molecules, especially with those rich in electronic structures such as aromatic hydrocarbons, has drawn considerable attention [10-14]. Work function measurements on typical transition metal indicate that aromatic molecules are normally electron donors, as their adsorption reduces the work function of the substrate. CO, NO and O\textsubscript{2}, however, are electron acceptors, as they increase the work function of the metal [15-16]. The attraction between the donor and acceptor helps them to form a well-ordered and stable co-adsorption structure. In recent years the introduction of new surface specific techniques that are capable of running in a high pressure environment, such as sum frequency generation vibrational spectroscopy (SFG) and STM, has given exciting results on this old research topic of adsorption of small gas molecules on metal [7, 17, 18]. In this chapter, the Rh(111)-NO and Rh(111)-O systems as models of metal-adsorbate systems are discussed. In future
chapters, the results of their co-adsorption with organic molecules, and STM tip induced catalysis in the presence of high pressure O$_2$, will be reported.

5.2 Oxygen adsorption on Rh(111)

The interaction of oxygen with rhodium is important in understanding both partial and total oxidative catalysis over rhodium surfaces. To elucidate the oxidative reaction mechanisms, it is necessary to have a fundamental knowledge of the interactions and structure of oxygen at an atomic level on the rhodium surface.

5.2.1 Experimental

The experiments were conducted in the integrated UHV chamber with homemade STM and LEED/AES described in Chapter 3. The base pressure for this clean surface study was better than 2×10^{-10} torr. The Rh(111) crystal was cleaned by repeated cycles of Ar$^+$ sputtering followed by annealing in oxygen and in vacuum. Cleanliness of the crystal was determined by AES and no observable impurities were detected, as shown in Figure 3.9 (middle). The ordering of the surface was determined by the appearance of very sharp (1×1) diffraction spots in the LEED pattern as shown in Figure 5.1 (left).

The oxygen was introduced through a leak valve. At room temperature, it has been demonstrated that oxygen undergoes dissociative chemisorption on Rh(111) surface [19, 20]. An O structure in UHV were prepared through dosing oxygen to the Rh(111) crystal until a sharp (2×2) LEED pattern was observed [21, 22]. To form the oxygen structure on Rh with the presence of high pressure of O$_2$, the chamber was filled with low pressure (1×10^{-6} torr) of O$_2$ through leak valve, then the ion pump and ion gauge were
shut off, and more \(O_2\) was filled in through the gas manifold until the pressure indicated by the baratron gauge reached a desirable value.

The STM images were taken with either tungsten or platinum tips. Although the dissociation of \(O_2\) on Pt tip material was expected, no apparent effect on the imaging was observed. The imaging condition, normally a bias voltage between hundreds of millivolts to 1V and a tunneling current around 1nA, was optimized until best quality (good contrast and low noise level) was obtained. The images were raw data without filtering or smoothing.

Figure 5.1 LEED patterns of a clean Rh(111) (left) and Rh(111)-(2×2)-O structure (right). The incident electron energy is 70 and 74eV, respectively.
5.2.2 Rh(111)-O structure formed in low pressure $O_2$

When the clean Rh surface was exposed to oxygen, the LEED pattern showed a transition from (1×1) to a sharp (2×2) pattern at low coverage (~2L). The LEED pattern is shown in Figure 5.1(right). If the exposure pauses at this stage, the (2×2) pattern will gradually disappear, indicating the oxygen ad-atoms tend to migrate into the bulk. In order to stabilize the (2×2) pattern, prolonged exposure up to 30L is required. Due to the limitation of the RFA optics in use, the Auger peak of oxygen at 500eV was not detected.

Figure 5.2 shows a STM image of the Rh(111)-(2×2)-O structure. Since STM probes the local density of states at the Fermi level, and because the oxygen local density of states at the Fermi level is lower than that for the bare metal, the presence of oxygen atoms makes a negative contribution to the local density of states at the Fermi level and leads to black holes or depressions on the metal surface in a topographic image [23]. Therefore in Figure 5.2, dark spots represent oxygen atoms, and they form linear rows along three directions rotated 120° with respect to one another, reflecting the Rh(111) surface’s three-fold symmetry. The space between dark features is 5.4±0.5Å, which is consistent with LEED observation of (2×2) periodicity. The corrugation of the bright features varies from 0.2 to 0.4 Å.

With the increase of $O_2$ pressure in the chamber background, the Rh(111)-(2×2)-O structure does not change. This adsorption structure can be studied by both LEED and STM under the $O_2$ pressure up to $1\times10^{-6}$ torr, beyond which LEED cannot operate.
Figure 5.2 High resolution STM image of the Rh(111)-(2×2)-O structure. The scan size is 100Å × 100Å. Tunneling condition: bias voltage of 1.00V, and current of 1.2 nA. Dark features (oxygen atoms) forming rows with spacing of 5.38Å can be seen. The corrugation of the dark features is 0.2~0.4 Å.
5.2.3 Rh(111)-O structure formed in high pressure O₂

STM study of oxygen adsorption on Rh(111) in the presence of high pressure O₂ was conducted. The pressures of oxygen in the chamber ranged from $1 \times 10^{-4}$ to 100 torr. Typical STM images taken under 10 torr and 100 torr are shown in Figure 5.4 and 5.5 respectively. In Figure 5.4, beside (2×2) oxygen structure, some large bright features with 5~10 Å in size and 1~2 Å in height were also observed. These features were not seen on clean surface, and they were found to grow up with the increase of oxygen pressure. When the tip was scanning over these features, the tunneling condition was disturbed considerably, indicating a great change in the local electronic structure. When the pressure of O₂ was increased to 100 torr, the coverage of the bright features was so high that it was very difficult to get an acceptable image. The image in Figure 5.5 was taken in the one of few areas without bright features. It can be seen that, although the individual oxygen features are still resolved, they no longer form large domains of ordered (2×2) structure as in UHV condition or when O₂ background pressure is lower than 10 torr. In very small region, there are still small patches of oxygen features showing a poor local (2×2) symmetry, but in long range the surface is rather disordered.
Figure 5.3 High resolution STM image of Rh(111) in 10 torr of oxygen. The scan size is 100Å × 100Å. Tunneling condition: bias voltage of 410mV, and current of 1.02 nA. The structure is still Rh(111)-(2×2)-O. Several impurities with high corrugation exist at the surface.
Figure 5.4 High resolution STM image of Rh(111) in 100 torr of oxygen. The scan size is 100Å × 100Å. Tunneling condition: bias voltage of 500mV, and current of 1.09nA. The surface is much more disordered compared with Figure 5.3, but individual oxygen features can still be resolved.
5.2.4 Discussion

For the Rh(111)-O structure formed in UHV or in low pressure (<10^{-6} torr) of O_2, both LEED and STM studies showed that oxygen forms a (2\times2) structure. Quantitative analysis of LEED study has demonstrated that the oxygen atoms in this structure occupy the fcc hollow sites [24, 25]. The schematic of this structure is shown in Figure 5.5.

In literature, the structure of the oxygen layer on Rh(111) has long been an issue of controversy. Since the (2\times2) structure and (2\times1) structure gave the same LEED pattern, it was suggested that the observed (2\times2) LEED pattern actually corresponds to the three domains of the (2\times1) structure associated by the three-fold rotational symmetry [22]. A combined diffraction using thermal He atoms and low-energy electrons provided a strong support to this (2\times1) model [25]. However, a recent UHV STM study of oxygen on Rh(111) discovered that only the (2\times2) structure forms with a surface coverage of 0.25, and no structure transitions have been observed for higher oxygen exposure up to 27L [4]. Our result further supports this observation. Note that in the proposed (2\times1) model, all oxygen atoms occupy the fcc hollow sites. Since all oxygen atoms are equivalent and have identical contributions to the local electronic structure, in STM image they should appear with same corrugation. However, no STM result has shown any sign of (2\times1) periodicity. In a comment to Ref. 4, to solve the discrepancy between the LEED/He atoms diffraction results and the STM results, a suggestion was made that in the STM study the 27L oxygen dosage was simply not sufficient to saturate the surface [26]. As a reply to this comment, it was argued that the Auger peak of the oxygen on Rh(111) surface reached a plateau at an exposure of only 4~5L, and further exposure of

63
O₂ only slightly varied the oxygen coverage, so the surface was well-saturated with oxygen at a coverage of 27L [27].

A high pressure study of the Rh(111)-O system can obviously end this controversy. Unfortunately, no such studies had been done previously. In this dissertation work, STM images showed that the (2×2) structure did not change when the background O₂ pressure reached 10 torr. At even higher pressure, although the long range ordering was broken, the local correlation distance between the observed features remained ~5.4Å, which is equal to twice the Rh(111) lattice constant. Our study with the O₂ pressure ranging over 10 orders of magnitude clearly showed that oxygen can only form one (2×2) structure on the Rh(111) surface.

The larger bright features that developed on the surface with the increase in O₂ dosage were also observed in Ref. 4. It was tentatively attributed to the cluster-like structures formed by oxygen nucleation around carbon impurities. The interactions between oxygen and carbon are localized around the impurities. The electronic structures of those features are different from oxygen on the Rh surface and show a higher density of states near the Fermi level and thus give a very large corrugation. When the chamber is filled with a very high pressure of O₂, a considerable level of impurities in the gas background is unavoidable, which could cause the high surface contaminant concentration. The increasingly higher occurrence frequency of the features can be thus explained.
Figure 5.5 Schematic of the Rh(111)-(2×2)-O structure. Individual O atoms occupy the fcc hollow sites.
5.3 Nitric oxide adsorption on Rh(111)

The adsorption of nitric oxygen (NO) on rhodium is intensely studied due to the importance of the rhodium-based catalytic conversion of NO in automobile exhaust into N₂. In the NO+CO→ N₂ + CO₂ reaction in a heterogeneous catalytic converter, the NO adsorption and dissociation on Rh surface are the initial and essential steps [28, 29]. A real Rh catalyst consists of many Rh crystallites disbursed onto micro-porous supports. Rh(111) is the most energetically stable surface of rhodium crystal planes, so on the Rh crystallites, small (111) crystal planes should dominate. The STM study of the surface structure of adsorbed NO on Rh(111) is thus a natural approach to all related STM studies of the complicated heterogeneous catalytic system.

5.3.1 Experimental

The experimental procedure is essentially the same as described in Section 5.2.1. Nitric oxide was introduced through a leak valve. At room temperature, NO molecules adsorb dissociatively at low coverages and adsorb molecularly at high coverages [19]. NO also forms a (2×2) adsorption structure on Rh(111) [21]. Similar to oxygen adsorption on Rh(111), when the clean Rh surface was exposed to NO, the LEED pattern started to show a stable and sharp (2×2) pattern only after prolonged exposure to NO, which is an indication of dissociative chemisorption. The required exposure ranged from 10 to 30L (in 1×10⁻⁷ torr of NO for between 100 to 300 seconds), increasing with the initial temperature on the Rh(111) crystal. STM images were taken under similar conditions as described before.
5.3.2 Rh(111)-(2×2)-3NO structure

The LEED pattern of the Rh(111)-NO structure is shown in Figure 5.6. It has the same symmetry and structure as in the case of oxygen on Rh(111). The Auger spectrum is shown in Figure 5.7. The small peak at 390eV was due to nitrogen.

![LEED pattern](image)

Figure 5.6 LEED pattern of the Rh(111)-(2×2)-3NO adsorption structure. The incident electron energy is 100eV.

![Auger spectrum](image)

Figure 5.7 Auger electron spectrum of NO-covered Rh(111) surface. The six peaks below 310eV are due to Rh. The weak peak at 390eV is due to nitrogen.
Figure 5.8 shows an STM image of a Rh(111) surface partially covered with NO. In the left half of the image, a very ordered (2×2) structure can be seen. Each bright spot is attributed to one single NO molecule. The corrugation is 0.1~0.15Å, as can be measured in the cross-section plot. The space between bright features is 5.4±0.5Å, which is consistent with LEED observation of (2×2) periodicity. To the right of the (2×2) structure, except for two very bright clusters that can be attributed to impurities, no feature can be seen. The corrugation on the featureless area is less than 0.05Å, close to that of an exposed rhodium substrate. Surprisingly, the height difference between the top of the NO molecule and the Rh substrate is only ~0.25Å, considerably smaller than the dimension of the NO molecule along its molecular axis, even the N-O bond length of 1.15Å [30]. This gives an undeniable example that indeed the corrugation in STM images is a measure of the variation of the electronic density rather than merely the topographic difference.

Since the Rh lattice was not imaged, it was not possible to determine the adsorption sites of the NO molecules. However, it should be pointed out that if the adsorption site of NO can be determined by other technique(s), it is possible to use the NO lattice to locate the adsorption site of other adsorbates with unknown adsorption properties. One can dose sub-monolayers of the adsorbate, and then dose a certain amount of NO. Providing the two species form their own lattice (no co-adsorption), the NO lattice, which is relatively easy to image, can be used to deduce the network of substrate atoms. This network is then extended to the area that is covered with the adsorbates to be determined, and their adsorption sites will be readily clarified.
Figure 5.8 STM image of a Rh(111) surface partially covered with NO. The scan size is 100Å×100Å. The image was taken with a bias of 1.00V and a current of 0.98nA.
Figure 5.9 is an STM image of Rh(111) surface saturated with a (2×2) NO overlayer. Two cross-section lines were drawn, and letter labels were used to guide the inspection of the sites of interest. At the left bottom corner the triangular shape of very bright area is a terrace of Rh atoms one layer higher than the rest area. In the cross section the height difference between the two terraces, as indicated with “E” and “G”, is 2.1 Å. This number is in good agreement with the crystallography data (2.15 Å). There are quite a few black holes and bright spots scattered on the ordered (2×2) structure. The black holes are apparently vacancies in the lattice. The bright spots cannot be attributed to some random impurities since all of them are aligned with the (2×2) lattice, and are the same size and 0.4 Å (equal to the height difference between “F” and “G”) higher up than the majority of NO molecules on the surface. They can be attributed to some loosely bonded NO molecules. Near the center of the image, a patch of vacancies can be seen. There are some details in this area. For example, position “C” is 0.2 Å higher than “D”, but not as high as “B”. Suppose “D” is a true vacancy, then “C” has to be assigned to another type of NO than “B”. This suggests that there are at least two types of adsorption sites for NO to occupy on the Rh(111) surface. Their apparent height difference is 0.3 Å.
Figure 5.9 100Å×100Å STM image of a Rh(111) surface almost completely covered with the (2×2) NO structure. The image was taken with a bias of 1.00V and a current of 0.98nA. Two cross-section lines were drawn, and letter labels were used to guide the inspection of the sites of interest.
Figure 5.10 was taken at an even higher resolution. More details can be seen with the guide of an overlapped (2×2) grid of little “+”s. The bright spots (presumably individual NO molecules) “A”-“F” and “I” are all located on a “+” position, while “E” is 0.15Å lower than the rest. This corrugation difference cannot be explained by the instrument noise. It is noticeable that around “E” there are a considerable number of darker holes, one of which is labeled as “H”. In the (2×2) unit cell shaped by BEFD, suppose the four corners are NO adsorbed atop sites, then consequently, H and G should correspond to the two three-fold hollow sites in the Rh lattice. H and G have very different heights. Since in a clean Rh(111) surface no height difference between fcc and hcp hollow sites could be imaged, in this (2×2) unit cell there cannot be only one type of NO molecule. Therefore, a slightly more complicated structure than a plain (2×2) model should be taken into account in order to interpret the STM images.
Figure 5.10 30Å×30Å STM image of a Rh(111) surface covered with a (2×2) NO overlayer. The image was taken with a bias of 1.00V and a current of 0.98nA. Two cross section lines were drawn, and letter labels were used to guide the inspection of the sites of interest. More details in one (2×2) unit cell can be resolved, suggesting that the unit cell contains more than one molecule.
5.3.3 Discussion

NO adsorbed on Rh(111) has been previously studied by STM [8,9]. In Ref. 8, it was reported that molecular NO can not form an ordered overlayer, but it can co-adsorb with atomic O or N (which are the products of the NO dissociation) and form its own (4×4) island, while O and N form (2×2) or (2×1) structures respectively, segregated from NO. This result was contradictory with other literature [6, 9, 19].

LEED analysis [6] revealed that on a NO-saturated Rh(111) surface, the (2×2) unit cell contains three NO molecules. One is bonded to atop site, and two others are each located to one of the two types of three-fold hollow sites. The schematic of this Rh(111)-(2×2)-3NO structure is illustrated in Figure 5.11. As a comparison, an almost identical (except for the molecular dimensions and bond lengths) Rh(111)-(2×2)-3CO structure [5] is also shown.

It is well known that NO and CO have very similar dimensions and electronic structures, as a result, they often form identical adsorption structures on various metal surfaces. The CO structure has been investigated by STM [7], which sees only the atop site CO. An explanation for this was that atop site CO is closer to the tip and therefore dominates the tunneling current. The assignment was based on a recent STM image simulation that explains the very similar structure formed by CO on Pd(111). The calculation indicates that the tunneling probability is much larger at the position of the top CO site, making the other two CO molecules in the hollow sites invisible [30].
Figure 5.11 Schematic of NO and CO adsorption on a Rh(111) surface. Both NO and CO form (2×2) overlayers in which there are three molecules in one unit cell. The three molecules occupy different sites: one at an atop site, one at an fcc hollow site, and the other at an hcp hollow site.
The same argument explains the invisibility of NO molecules at hollow sites in the perfectly formed Rh(111)-(2×2)-3NO structure [9]. However, in this research, it was found that due to some surface defects, one or more NO molecules were missing in the unit cell. As a result, considerable depressions on the vacancies were observed, and the corrugation of the molecules around the vacancies was reduced. Again, this clearly shows that STM images are not merely the surface topography (actually, it is almost impossible to define the topography at the molecular level). It is a map of the convolution of both the geometric variation of surface atoms and the changing local electronic density of states. In the case of Rh(111)-(2×2)-3NO structure, the two factors have the same effect on minimizing the contrast of NO molecules in the hollow sites, and enhancing the protrusion of the atop site NO.

5.4 Conclusions

The oxygen and nitric oxide chemisorption on Rh(111) has been studied by STM and LEED in vacuum. Rh(111) exposed to high pressures of oxygen was also imaged by STM. Oxygen was found to form only one ordered structure, the Rh(111)-(2×2)-O structure, contradicting some previous reports of three domains of the (2×1) structure. Large disordered features with high corrugation were found on the surface when Rh(111) was exposed to elevated pressures (up to 10 torr) of oxygen, suggesting a concurrent nucleation of oxygen localized around carbon impurities with increasing oxygen pressure. Nitric oxide forms a Rh(111)-(2×2)-3NO structure, which has an identical two-dimensional unit cell arrangement to the Rh(111)-(2×2)-3CO adsorption structure. In a perfectly ordered area, due to the geometric and electronic density differences in the three
NO molecules in one unit cell, only the one at atop site can be imaged. However, one or more NO molecules missing in the unit cell could still be distinguished, suggesting that the apparently large corrugation of the NO molecules adsorbed on atop sites is due to the combined contributions of all three molecules in one unit cell.
References


Chapter 6.

The Adsorption and Decomposition of Propylene on Pt(111) and Rh(111).

6.1 Introduction

The adsorption of hydrocarbons on metal surfaces has long been an important area of research both in surface science and in catalytic industry. Light alkenes, such as ethylene, propylene and butadiene, have been often used as model molecules for hydrogenation and dehydrogenation reactions [1-4]. Hydrocarbons adsorbed on metal surface can undergo decomposition and sequentially form small C_xH fragments, carbonaceous clusters and graphite [5, 6]. These intermediate species are of interest in catalysis, as they play active roles in catalytic processes while graphitic carbon is generally thought to be a poison [7].

The adsorption and decomposition behavior of small olefins on both surfaces have been investigated through various techniques, such as high-resolution electron energy loss spectroscopy (HREELS) [6, 8, 9], thermal desorption spectroscopy (TDS) [5, 6, 10, 11], and LEED [5, 9, 10-18]. The adsorption models of these species have been well established and accepted.

On Pt(111), Rh(111), Pd(111) and some similar fcc (111) surfaces, small olefins undergo a series of changes with temperature. In Figure 6.1, the thermal decomposition pathways of several unsaturated C3 species as well as ethylene on Rh(111) are shown [6].
At low temperature (<100K), they adsorb on Rh(111) molecularly, with the double bond parallel to the substrate. At 200K, propylene changes to propylidyne and adsorbs on the metal through a C-Metal covalent bond. This process is similar to the formation of ethylidyne. The formation of alkylidyne is illustrated in Figure 6.2. At room temperature, propylidyne will dissociate into ethylidyne and another C-H fragment. Beyond 420K the ethylidyne will be further cracked into small CₓH fragments. At 530K, those fragments will polymerize into carbonaceous clusters, and at still higher temperature (800K) a graphitic carbon layer will form. H₂ is desorbed sequentially, as detected by TDS (shown in Figure 6.3). The carbon to hydrogen ratio increases over the whole process. On Pt(111), the thermal decomposition of propylene takes a similar route, except that propylidyne forms at 270K, and between the propylidyne and CₓH fragmentation stages, no ethylidyne is formed [5, 17].

Ethylidyne was found by LEED experiments to form a (2×2) structure on Rh(111) or Pt(111) below room temperature. For propylidyne, the two bottom carbon atoms also ordered into a (2×2) lattice. For large propylene exposures, a weak (2√3×2√3)R30° diffraction pattern was observed. This was due to the ordering of methyl groups [18]. The fcc(111)- (2√3×2√3)R30° - 3 propylidyne structure is illustrated in Figure 6.4.

The co-adsorption of ethylene/propylene and CO on Rh(111) or Pt(111) has been studied intensively by LEED [6, 9, 18]. It was found that CO can help propylidyne to form a very ordered (2√3×2√3)R30° structure by inserting itself into the lattice. At higher temperature, both ethylidyne and propylidyne are disordered on Rh(111), but they form a very ordered c(4×2) superlattice when co-adsorbed with CO, as shown in Figure
6.5. The adsorption structure of Rh(111)-c(4×2)-ethylidyne+CO, illustrated in Figure 6.6, is solved by quantitative LEED analysis [9].

Few STM studies of the olefin adsorption on metal surfaces have been done. The study of ethylidyne on Pt(111) generated no atomic resolution STM images, and the reason was attributed to the fact that at room temperature the mobility of the adsorbed molecules was too high [19]. The propylene thermal decomposition on Pt(111) was studied [19, 20]. However, no molecular resolution of propylene adsorption structure was obtained, and the same argument was used to explain the invisibility of the propylidyne.

In this dissertation work, the adsorbed propylene on both Pt(111) and Rh(111) at room temperature was imaged by STM, and the surface topography at each stage of the thermal decomposition route was also investigated and compared with the result on Pt(111) reported in literature.
Hydrocarbon Decomposition on Rh(111)

Figure 6.1 Pathways for the thermal decomposition of ethylene, propylene, methylacetylene and propadiene on Rh(111) (from Ref. 6). These decomposition intermediates, determined by HREELS and TDS, are stable in the indicated temperature ranges.
Formation of Alkylidyne

\[ \text{H}_2\text{C} = \text{CH}_2 \xrightarrow{\text{M}} \text{H}_2\text{C} = \text{C} \xrightarrow{\text{M}} \text{H}_2\text{C} = \text{CH}_2 \]

\[ \text{H}_2\text{C} = \text{CH}_3 \xrightarrow{\text{M}} \text{H}_2\text{C} = \text{C} \xrightarrow{\text{M}} \text{H}_2\text{C} = \text{CH}_3 \]

Figure 6.2 The formation of alkylidyne from small olefins. This process involves losing one hydrogen atom to the environment, and transferring another hydrogen from the terminal carbon to its neighbor. The alkylidyynes adsorb on fcc(111) metal surfaces at the three-fold hollow sites through metal-carbon covalent bonds.
Figure 6.3 $\text{H}_2$ thermal decomposition spectra of ethylene and propylene on Rh(111) (from Ref. 6).

Figure 6.4 The fcc (111) $-(2\sqrt{3} \times 2\sqrt{3})R30^\circ-3\text{ C}_3\text{H}_5$ (proplidyne) structure (from Ref. 17).
Figure 6.5  Schematic diagram of various pathways for production of the c(4×2) arrangement of ethylidyne and CO on Rh(111) (taken from Ref. 9).

Figure 6.6 Illustration of the structure of Rh(111)-c(4×2)-C\textsubscript{2}H\textsubscript{3}+CO in side view (top) and near perpendicular view (bottom), showing bond lengths (from Ref. 9).
6.2 Propylene adsorption on Pt(111)

6.2.1 Experimental

The experiments were conducted in the integrated UHV chamber with homemade STM and LEED/AES described in Chapter 3. The base pressure for this clean surface study was better than $2 \times 10^{-10}$ torr. The Pt(111) crystal was cleaned by repeated cycles of Ar$^+$ sputtering followed by annealing in oxygen and in vacuum. Cleanliness of the crystal was determined by AES and no observable impurities were detected, as shown in Figure 3.9, middle. The ordering of the surface was determined by the appearance of very sharp (1×1) diffraction spots in the LEED pattern as shown in Figure 5.1 (left).

Propylene and CO were introduced into the chamber through leak valves. Unless otherwise specified, the exposures were normally 10L and were achieved by filling the chamber with $1 \times 10^{-7}$ torr of gas for 100 seconds. The LEED experiment was then conducted immediately. All STM images were taken in UHV condition. The images were not filtered or smoothed.

6.2.2 Propylidyne adsorption on Pt(111)

When the clean Pt(111) surface was exposed to ethylene, the LEED pattern showed a transition from a (1×1) to a (2×2) pattern at low coverage (~3L). The intensity of the (2×2) increases with the dosage of propylene, and becomes very sharp at 10L. This is shown in Figure 6.7.
Figure 6.7 LEED patterns (all taken at 83 eV) for clean Pt(111)-(1×1), Pt(111)-(2×2)-propylidyne, and Pt(111)-(2×2)-propylidyne exposed to CO (disordered).
Figure 6.8 shows STM images of the Pt(111)-(2×2)-propyldyne structure. For the top image, the propylene exposure was 2 L. Many bright spots with a periodicity of 5.4 Å can be seen. Each spot is considered to be one propyldyne molecule. These molecules are preferentially adsorbed on the step edge. At the center of the terrace, not much detail can be seen, and image is blurry, which is a sign of the existence of a highly mobile surface species. For the bottom image, the propylene exposure was 10 L. The surface is completely covered with the (2×2) lattice. All propyldyne molecules were clearly resolved, which is the result of their low surface mobility. Therefore, there must be an attraction between the propyldyne molecules. When the coverage is low, they form small islands on the step edge, where more surface dangling bonds exist and thus a high degree of coordination from the metal is available to the adsorbates. When more propyldyne molecules adsorb on the surface, they nearly completely occupy all available sites. Both LEED and STM data showed no sign of the (2√3×2√3)R30° lattice, suggesting that the methyl groups are disordered at room temperature.

Figure 6.9 is an 100Å×100Å image of the high coverage Pt(111)-(2×2)-propyldyne surface. The corrugation of propyldyne molecules is 0.15–0.2 Å. Besides the individual propyldyne molecules adsorbed on (2×2) lattice, many defects with the size of one propyldyne molecule and patches of disordered areas can be seen. The defects and disordered areas can be attributed to the impurities.
Figure 6.8 200Å×200Å STM images of the Pt(111)-(2×2)-propylidyne adsorption structure. For the top image, the propylene exposure was 2 L, and image was taken with 1.0V bias and 0.98nA current. For the bottom image, the propylene exposure was 10 L, and image was taken with 211mV bias and 1.07nA current.
Figure 6.9 100Å×100Å STM image of the Pt(111)-(2×2)-propylidyne adsorption structure. Many defects with the size of one propylidyne molecule can be seen. The corrugation is 0.1–0.2 Å. The tunneling condition was 211mV and 1.07nA.
6.2.3 Propylidyne co-adsorption with CO on Pt(111)

Carbon monoxide has long been considered able to form ordered co-adsorption structures with organic molecules on metal surfaces. However, CO can destroy the Pt(111)-(2×2)-propylidyne structure. With only $1 \times 10^{-8}$ torr CO in the background, the very ordered (2×2) lattice can be broken in a few minutes. This process can be followed by changes in the LEED pattern (Figure 6.7) and STM image (Figure 6.10). After exposure to CO, a sharp (2×2) LEED pattern becomes a blurry (1×1) pattern with a strong background. In the STM image, the nice (2×2) lattice is smeared out quickly, and eventually the surface becomes completer disordered, with very few bright spots found at the step edges. This result suggests that CO can help dissociate propylidyne, and the product is not likely ethylidyne, as the latter could form an ordered co-adsorption structure with CO.

Figure 6.10 STM images taken on a Pt(111)-(2×2)-propylidyne structure before (left) and after (right) exposure to 10L of CO. The tunneling conditions were both 211mV and 1.12nA. The scan sizes are both 100Å×100Å.
6.3 Propylene adsorption on Rh(111)

Both LEED and STM data showed propylene on Rh(111) behaves very differently than on Pt(111). The experimental procedure is the same as described in Section 6.2.1, except here a Rh(111) crystal is used.

6.3.1 Propylidyne adsorption on Rh(111)

Figure 6.11 shows the LEED patterns for a clean Rh(111)-(1×1), Rh(111)-c(4×2)-propylidyne+CO, a Rh(111) surface 20 seconds after dosed with 10L propylene, and a Rh(111) surface 60 seconds after dosed with 10L propylidyne. It can be seen that, at the first few seconds of dosing propylene on Rh(111), a (2×2) pattern was formed. This structure decays very quickly. After a few minutes, the (2×2) spots become invisible. The decrease in the intensity of diffraction spots means the surface overlayer becomes disordered over time, possibly due to the dissociation of propylidyne. To check the influence of electron beam exposure on the decay of surface ordering, several LEED experiments were conducted in which the electron beam was turned on immediately, several tens of seconds, or several minutes after a 10L exposure of propylene was dosed onto the Rh(111) crystal. The result shows that the decay of the (2×2) structure is independent of the electron beam activity, so the dissociation of propylidyne is a consequence of the interaction of itself with the Rh(111) substrate.
Figure 6.11 LEED patterns (all taken at 65 eV) for clean Rh(111)-(1×1), Rh(111)-c(4×2)-propylidyne+CO, Rh(111) surface 20 seconds after dosed with 10L propylene, and Rh(111) surface 60 seconds after dosed with 10L propylene. In the first two patterns, the diffraction spots are very sharp and stable. In the third one, which was obtained 20 seconds after dosing with propylene, a clear and sharp (2×2) pattern appeared. Its intensity decreased very quickly. After 60 seconds the (2×2) spots were almost invisible. The decrease in intensity of diffraction spots indicates the surface overlayer became disordered over time, possibly due to the dissociation of the propylidyne.
An STM image was taken shortly after the Rh(111) was exposed to propylene. Although the LEED result shows that macroscopically the (2×2) structure decays very fast, some local remnant of the (2×2) structure was still imaged. Figure 6.12 shows an 100Å×100Å STM image of a Rh(111) surface taken within 10 minutes of dosing with 10L of propylene. A (2×2) domain can be seen, while disordered structure occupies the edge. The corrugation of the (2×2) feature is 0.05~0.1Å, smaller than that of propylidyne on Pt(111). This (2×2) domain was very difficult to find on the surface. Most of the images taken on the surface showed no ordered feature.

From TDS studies, it is believed that, propylidyne formed on Rh(111) start at room temperature to dissociate into ethylidyne and C-H fragments [6], both of which are disordered on the surface [9]. Therefore, the disordered surface is covered with highly mobile ethylidyne and C-H fragments. In Figure 6.12, the ordered (2×2) domain snapshot by STM could be comprised of not-yet-dissociated propylidyne molecules. Whether there is propylidyne on the surface cannot be determined by STM alone. Surface vibrational spectroscopy techniques such HREELS or sum frequency generation (SFG) should be able to solve this puzzle.
Figure 6.12 100Å×100Å STM image of a Rh(111) surface taken within 10 minutes after it was dosed with 10L of propylene. A (2×2) domain can be seen, while disordered structure occupies the edge. The corrugation of the (2×2) feature is 0.05~0.1Å. The tunneling condition was 406mV and 0.98nA.
6.3.2 Propylidyne co-adsorption with CO on Rh(111)

Unlike adsorption on Pt(111), propylidyne can co-adsorb with CO to form a very ordered c(4×2) structure on Rh(111). This structure can be prepared by exposing Rh(111) sequentially with 10L propylene and 10L CO. The corresponding LEED pattern is shown in Figure 6.11. This c(4×2) overlayer is stable at elevated temperatures up to 400K. Even after considerably long exposure to 1×10⁻⁶ torr of O₂, the LEED pattern will not change.

Figure 6.13 shows two STM images of Rh(111) co-adsorbed with 10L of propylene and 10L of CO. Rows of bright features can be seen. In many images three rotation domains were observed, and two of them are displayed in Figure 6.13. The orientations of the rows are 60° with respect to one another. Each bright feature is one hydrocarbon adsorbate (presumably ethylidyne) in one C(4×2) unit cell. In Figure 6.14, an STM image taken at higher resolution is shown, where individual C(4×2) unit cells with rectangular shapes can be seen. The corrugation is 0.1~0.2 Å. The orientation of the rectangle can be determined by the direction of a majority of step edges, as discussed in Chapter 4. As shown by the arrows in the figure, the longer lattice vector is along [110], and the shorter one is along [112], consistent with the model in Ref. 9.

It can also be found in the STM images that the surface is only partially covered with c(4×2) domains. Quite a large portion of the surface is still very disordered and represented by an appearance similar to the upper right corner of the left image in Figure 6.13. If one accepts that the disordered surface consists of the mixture of ethylidyne molecules and C-H fragments when only propylene is exposed to Rh(111), then it can be
proposed that when CO is dosed to this system, the ethylidyne and C-H fragments will segregate, and the former will form ordered c(4×2) domains with CO.

Figure 6.13 Two 200Å×200Å STM images of Rh(111) co-adsorbed with 10L of propylene and 10L of CO. Rows of bright features can be seen. Three rotation domains are observed, and two of them can be seen in the above images. The orientations of the rows are 60° with respect to one another. Each bright feature is one hydrocarbon adsorbate (presumably ethylidyne) in one C(4×2) unit cell. The tunneling conditions were both 60mV and 1.0nA.
Figure 6.14 100Å×100Å STM images of Rh(111) co-adsorbed with 10L of propylene and 10L of CO. Individual C(4×2) unit cells with rectangular shape can be seen. The corrugation is 0.1–0.2 Å. The tunneling condition was 60mV and 1.0nA.
6.3.3 Comparison of propylene adsorption on Rh(111) and Pt(111)

In previous sections, quite large differences in behavior have been shown for propylene adsorption on Rh(111) and Pt(111) at room temperature. Propylidyne adsorbs stably on Pt(111) in a (2×2) fashion, but upon exposure to CO, it will decompose into small fragments, as it does at above 400K. On Rh(111), however, propylene decomposes to propylidyne and forms a (2×2) overlayer briefly, then undergoes further decomposition and breaks into ethylidyne and C-H fragments. Ethylidyne can co-adsorb with CO and form a stable c(4×2) overlayer.

Due to STM’s inability to chemically differentiate between species, other techniques are desired to explain these differences. HREELS and TDS results suggested that at the decomposition temperature, surface hydrogen, which is instrumental in the conversion of propylidyne to ethylidyne, is present on Rh(111) but not on Pt(111) [6]. Dynamic LEED analysis of ethylidyne on Pt(111) and Rh(111) gave the bond length difference in the metal-carbon bonds: Pt-C bond (1.91Å) vs. Rh-C (1.96 Å). Since the Pt bulk radius is 0.04 Å larger than Rh, the Pt-C bond appears to be shorter and thus stronger than the Rh-C bond [15]. However, no data can be used to explain why propylene on Rh(111) decomposes at lower temperatures and what role CO plays in the decomposition of propylidyne. Some kinetic investigation may solve these questions, but are beyond the scope of this dissertation work.
6.4 Thermal decomposition of adsorbed propylene on Rh(111)

6.4.1 Experimental

Rh(111) was first exposed to 10L propylene, then heated to a desired temperature, on the order of 155°C (432K), 265°C (538K), 400°C (673K) and 600°C (873K), and then cooled back to room temperature before STM measurements were carried out. As illustrated in Figure 6.1, at these four temperatures, the adsorbed propylene on Rh(111) is cracked into CₓH, carbonaceous clusters, polymers and graphite, respectively. STM images were taken for each stage.

6.4.2 Formation of hydrocarbon fragments and clusters

Figure 6.15 shows the STM images taken on the surface thermally treated at the first three temperatures. The STM images are not difficult to interpret when considering the surface composition formed at a specific temperature. In the first image, the surface has many small grainy features with a characteristic size of 5~10Å and an average height of 0.1~0.2 Å. Essentially, the surface is quite smooth, corresponding well to a small CₓH fragment-covered surface. At higher temperatures, those fragments start to polymerize and, as a result, much larger and higher particles are formed. The average size of the particle grows as temperature increases, as seen in the second and third images. In the second image, many incompletely separated clusters can be found on the middle terrace. Surprisingly, those clusters have similar sizes and they form a quite ordered layer. The average size and height of the clusters is 20~30Å and 0.5~1Å, respectively. The appearance of the “ordered” structure formed by thermal cracking of hydrocarbons has
never reported before, and it is very appealing to attempt to elucidate the formation mechanism. In the third image, many isolated, large particles are the only features visible to STM. The size of the particles ranges from 10 to 30Å. Their height is well over 1Å, and some even reach 2 Å. It can be imagined that when the temperature rises, the clusters seen in the second image start to congregate, and fuse together to form the large cluster (or the polymer particles seen in the third image), so the surface has fewer but larger and higher clusters.

Compared with the ethylene [21] and propylene [20] decomposition behavior on Pt(111), the propylene decomposition on Rh(111) generates more uniformly distributed particles over the surface in every stage before the formation of graphite, and the sizes of the particles are generally smaller. This is tentatively attributed to a kinetic effect, as dynamic LEED analysis suggested a stronger bonding (thermodynamic data) of adsorbed ethylidyne to Rh(111) than to Pt(111) [15]. The kinetic effect, as well as bonding strength, plays a very important role in the reactivity of the particles in the tip-catalyzed oxidation/hydrogenation on the metal surface. The details will be discussed in the next chapter.
Figure 6.15 STM images taken at different stages of propylene thermal decomposition on the Rh(111) surface. The tunneling conditions were all 0.5–1.0V in bias and 1.0 nA in current. The scan sizes are all 500Å×500Å. From top to bottom, the three surfaces were prepared by heating the Rh(111) pre-exposed to 3L propylene to 155°C, 265°C and 400°C, respectively, then cooling back to room temperature in UHV.
6.4.3 Formation of graphite

At very high temperature (>800K) on both Pt(111) and Rh(111), the polymer clusters will eventually lose all hydrogen in its composition and fuse into graphite. Figure 6.16 shows a STM image of Rh(111) covered with graphite layers. The layers of sheet-like features can be assigned to graphite by the fact that the top of the layer is very flat and there are very bright boundaries between the layers, both of which are characteristic of the topography of graphite.

At higher resolution, features at the atomic level can be seen. Figure 6.17 shows an 100Å×100Å STM image taken on top of a graphite layer. Two domains with ordered features are clearly shown. The local fast Fourier transform pattern and cross-section plot of each domain are given to the right of the image. The two domains have different ordering structure in terms of the periodicity and orientation. The periodicity is too large to be of a graphite lattice (2.46 Å). The formation of those ordered structures can be attributed to the Moire interference between a graphite lattice and a rhodium lattice underneath. The graphite lattice is incommensurate with the Rh(111) or Pt(111), so there is no correlation between the orientation of the two lattice substrate. The differences in the contrast, corrugation, and orientation between the two Moire patterns are caused by the randomly oriented graphite layers on top of the metal lattice.
Figure 6.16  STM image of Rh(111) covered with graphite layers. The sample was prepared by heating the Rh(111) pre-exposed to 3L propylene at 600°C in UHV for 30 seconds, then cooling back to room temperature before taking the image. The tunneling condition was 1.0V in bias and 0.7nA in current. The scan size is 500Å×500Å.
Figure 6.17 100Å×100Å STM image of graphite grown on Rh(111) by thermally cracking propylene. The tunneling condition was 1.0V in bias and 1.07 nA in current. Two domains with ordered features are clearly shown. The local fast fourier transform pattern and cross-section plot of each domain are given to the right of the image. The two domains have different ordering structure in terms of the periodicity and orientation. The periodicity is too large to be from a graphite lattice. The formation of those ordered structures can be attributed to the M"oire interference between a graphite lattice and a rhodium lattice underneath.
6.5 Conclusions

In this chapter, the adsorption and decomposition behavior of propylene on Rh(111) and Pt(111) were investigated by STM with the assistance of LEED. It was found that at room temperature, propylidyne, which is the product of partial dehydrogenation of propylene, adsorbs stably on Pt(111) in a (2×2) fashion, but it will decompose to disordered small fragments upon exposure to CO. On Rh(111), however, propylene decomposes to propylidyne and forms a (2×2) overlayer briefly, then undergoes further decomposition and breaks into ethylidyne and C-H fragments. Ethylidyne can co-adsorb with CO and form a stable c(4×2) overlayer. On both metals CO seems to expedite the decomposition of propylidyne into small species.

At each stage of thermal decomposition of propylene on Rh(111), STM images were taken and compared with the result on Pt(111) reported in the literature. At 155°C, 265°C, 400°C and 600°C, the adsorbed propylene on Rh(111) decomposes into \( \text{C}_x\text{H} \) fragments, carbonaceous clusters, polymers and graphite, respectively. Compared with propylene thermal decomposition on Pt(111), the propylene decomposition on Rh(111) generates more uniformly distributed particles over the surface in every stage before the formation of graphite, and the sizes of the particles are generally smaller. These differences are tentatively attributed to some unclear kinetic factors during the cracking process of propylidyne.
References


Chapter 7
The STM Tip-Catalyzed Oxidation and Hydrogenation of Carbonaceous Clusters on Rh(111) Surfaces

7.1 Introduction

Not long after its invention in the early 1980's, STM proved not only an important tool for imaging surface structure, but also a means of modifying or manipulating atoms or molecules on the surface through the controllable interaction between the STM tip and surface species. The interactions include mechanical force, electron bombardment or a highly localized electrostatic force. Numerous experiments have been done using STM tips to manipulate surfaces [1]. In the territory of surface chemistry, a natural extrapolation of this application is to use the tip to induce surface reactions at a molecular level. This type of research has become increasingly popular. Some more recent results include manipulating CO on Cu(111) [2] and Cu(211) [3, 4] and dissociating O₂ on Pt(111) [5]. Most experiments reported in the literature involved the use of tunneling electrons or electric fields generated by the tip to induce a reaction. As of yet, the possibility of using the tip as a catalyst to induce reaction of the surface species has been rarely explored.

Since 1990, extensive work has been done on using a Pt STM tip to catalyze the oxidation or hydrogenation of decomposed propylene on Pt(111) [6-8]. A clean Pt(111) crystal was first exposed to propylene, then heated to 200–500 °C. In this temperature
range the adsorbed propylene will dissociate into small C\textsubscript{x}H fragments then polymerize to form carbonaceous clusters. The crystal was then transferred to a high-pressure reaction cell which was equipped with an STM. When a Pt STM tip was used to scan the surface in the presence of O\textsubscript{2} or H\textsubscript{2} in the background, some clusters on the surface were removed and the clean substrate underneath was then exposed. Since no material was found piled up at the edge of the STM scanned area, it was believed that the carbonaceous clusters reacted away or gasified by the O\textsubscript{2} or H\textsubscript{2}. The reaction was initiated by applying a 0.1~1V voltage pulse between the tip and the crystal to “activate” the tip.

A reaction mechanism for the gasification of clusters was proposed, as illustrated in Figure 7.1. The catalytic action by an active tip, which is presumably clean Pt, consists of atomizing H\textsubscript{2} or O\textsubscript{2} [9-12] from the gas phase and hydrolyzing or oxidizing C-C or C-H bonds of the clusters beneath it. The mechanism by which the hydrogen or oxygen transfer occurs appears to be a local proximity effect. The clusters will be broken down into smaller fragments. Eventually, the hydrocarbon fragments are either desorbed or remain on the surface but are sufficiently small to diffuse quickly over the surface and disappear under the scope of STM. Further studies included the investigation of the dependence of the reaction rates on the O\textsubscript{2}/H\textsubscript{2} pressure (shown in Figure 7.2), the propylene decomposition temperature and tunneling conditions. However, some questions still remain open: possibility of reacting away atomic or molecular adsorbates which could be resolved with STM, the possibility of performing site specific reaction studies on catalytic systems which are known to be structure sensitive, and the possibility of replacing the substrate with metals other than Pt or another crystal face and comparing their reactivity. The first attempt will be discussed in Chapter 8. The second one is very
appealing, yet the experiment is extremely difficult to perform even for a state-of-art STM instrument due to spatial resolution. In this chapter, to answer the third question, similar oxidation/Hydrogenation reactions were conducted with a Rh(111) crystal, and the results were compared with those obtained with Pt(111) as reported in Ref. 8.

![Figure 7.1 Cartoon of the proposed mechanism for the tip-induced catalysis (from Ref. 8). The catalytic action by the active Pt tip consists of atomizing O$_2$ or H$_2$ from the gas phase and oxidizing or hydrolyzing the carbonaceous clusters under it. The oxygen or hydrogen atom transfer from the tip to the cluster is due to a local proximity effect. Once reacted, the carbonaceous fragments produced from the clusters are either desorbed or diffuse quickly over the surface, and eventually disappear from the view scope of STM.]
Figure 7.2 The gas phase pressure dependence of the tip catalysis reaction rates (from Ref. 8). The plot was made after examining the number of STM scans required to remove approximately 80% of the hydrocarbon clusters in an area as a function of oxygen or hydrogen gas pressure.
7.2 Tip-catalyzed oxidation on Rh(111)

The carbonaceous species which covered Rh(111) was prepared by heating a Rh(111) crystal that was pre-adsorbed with 10 L of propylene under UHV. Different temperatures for this treatment were investigated as a function of the tip-catalysis reaction rate. After a desired temperature was reached, the sample was cooled down to room temperature. O$_2$ with a pressure of $1 \times 10^{-6}$, $2 \times 10^{-4}$, 0.1 or 3 torr was then leaked into the chamber. Pressures below $2 \times 10^{-4}$ torr were measured by the ion gauge, while pressures higher than 0.1 torr were measured by a barotron gauge.

STM images were taken under constant current mode, with a bias voltage between a range of 50mV and 1V, and a tunneling current between a range of 0.5 to 2 nA. Normally the surface was stable and the images taken at the same area were without any noticeable change after several scans, except for some inevitable thermal drift. The surface was found covered with many particles with a characteristic size corresponding to the temperature at which the sample was treated. To initiate the tip-catalysis reaction, a pulse with a magnitude between several hundreds of millivolts to several volts was intentionally applied between the tip and sample, to “zap” the tip and presumably clean the tip (tip activation). Usually right after the pulse was applied, the tunneling gap became very unstable and huge current spikes were observed. On the image, directly under the area where the pulse was applied, a large and high bump was always found. Occasionally (and more often when there is high pressure in the background), a certain number of particles disappeared after each consecutive scan. When this happened, a series of images were taken at the same spot, until the surface was “cleaned” (gasification.
completed) or no additional particles could be removed for an extended period of time (tip de-activation).

Low pressure condition

In Figure 7.3, a series of STM images show the progress of the tip-induced oxidation of carbonaceous clusters on the Rh(111) surface in $2 \times 10^{-4}$ torr of $O_2$. The sample was prepared by dosing 10 L of propylene on Rh(111) and heating to 200°C. Consecutive images were taken two minutes apart, with a bias voltage of 90mV (tips vs. sample), and a current of 0.80 nA. Gradually from image #1 to image #10 (note there were some drifts), the clusters on the surface were mostly removed. At the edge of image #10, only some very large clusters, mostly on the step edges, are left on the surface. On the lower left terrace nearly all the clusters were removed. The large bright feature near the top of each image was formed by “activating” the tip by applying a pulse to it.

Before and after the tip carried on the reaction, zoom-out images were taken (as shown in Figure 7.4). The white squares represent #1 and #10 in Figure 7.3, respectively. Clearly, clusters were removed only in previously scanned areas, which indicates that the tip participated in the process. During the course of many experiments, the build-up of clusters was never observed, as shown in the right image that there was no materials piling up at the edges of the square.
Figure 7.3 A series of \(1000\text{Å} \times 1000\text{Å}\) STM images show the progress of the tip induced oxidation of carbonaceous clusters on the Rh(111) surface. The sample was prepared by dosing 10L of propylene on Rh(111) and heating to 200°C. The images were taken in \(2\times10^{-4}\) torr \(\text{O}_2\). Consecutive images were taken two minutes apart. Tunneling conditions are: bias voltage of 90mV (tip vs. sample), and current of 0.80 nA. From Image 1 to Image 10, nearly all the clusters on the lower left terrace were removed. Note there was some image drift. The large bright feature near the top was formed when “activating” the tip by applying a pulse to it.
Figure 7.4 Before (left) and after (right) the tip underwent the reaction shown in Figure 7.3, larger images were taken. The white squares represent #1 and #10 in Figure 7.3, respectively. During the course of many experiments, the build-up of clusters was never observed, as shown in the right image that there are no clusters piling up at the edges of the square. The scan sizes are both $2000\AA \times 2000\AA$. Tunneling conditions are both: bias voltage of 90mV and current of 0.80nA.
**High pressure condition**

In Figure 7.5, a series of STM images show the progress of tip-induced oxidation of carbonaceous clusters on Rh(111) surface in 3 torr of O2. Consecutive images were taken two minutes apart. From Image 1 to Image 8, the clusters in the lower half of were almost completely removed, and clean and smooth terraces were gradually exposed.

Larger images were taken before (Image #1) and after (Image #2) the tip underwent the reaction, shown in Figure 7.6. The white squares represent the scanned areas of Image #1 and Image #8 in Figure 7.5, respectively. The lower half of the area was completely cleaned by oxidizing clusters. Image #3 was taken on a cleaned terrace in Image #2. No clusters or any other features could be seen. Image #4 is a high resolution image taken on an area in Image #3, which shows more or less ordered black features with an average distance of 5.4 Å (twice the lattice constant of the Rh(111) substrate). These black holes and a roughly (2x2) periodicity are characteristic of an oxygen overlayer on the surface, as discussed in Section 5.2.3 and shown in Figure 5.4. The formation of an oxygen overlayer is undoubtedly an indication of complete removal of all carbonaceous species on the surface. The fact that this overlayer was not found in any low-pressure experiments suggests that the extent of the reaction (related to the chemical equilibrium) strongly depends on the O2 pressure in the background.

In high pressures of O2 the number of STM scans required to remove the same percentage of particles was less than in low pressure of O2, indicating a faster reaction rate.
Figure 7.5 A series of STM images show the progress of the tip-induced oxidation of carbonaceous clusters on the Rh(111) surface in 3 torr of O2. Consecutive images were taken two minutes apart. The scan sizes are all 500Å × 500Å. Tunneling conditions are all: bias voltage of 90mV and current of 0.80nA. From Image 1 to Image 8, the clusters on the lower half were gradually removed.
Figure 7.6 Larger images were taken before (#1) and after (#2) the tip conducted the reaction shown in Figure 7.5. The white squares represent #1 and #8 in Figure 7.5, respectively. The lower half of the area was completely cleaned by oxidizing the clusters. #3 was taken on a cleaned terrace in #2. #4 is a high resolution image taken within area #3, which shows roughly ordered black features with an average distance of 5.4 Å (twice the lattice constant of the Rh(111) substrate). The scan sizes are 1000Å x 1000Å for #1 and #4, 180Å x 180Å for #3, and 30Å x 40Å for #4. Tunneling conditions are all: bias voltage of 90mV and current of 0.80nA.
7.3 Tip-catalyzed hydrogenation on Rh(111)

The sample preparation and STM experimental procedure were the same as described in Section 7.2, except H₂ was used instead of O₂. Unlike in O₂, no reaction was observed in low pressure H₂. A considerably high pressure was needed to initiate the hydrogenation reaction.

In Figure 7.7, a series of STM images show the progress of the tip-induced hydrogenation of carbonaceous clusters on the Rh(111) surface. The sample was prepared by dosing 10L of propylene on Rh(111) and heating to 265°C. The images were taken in 3 torr of H₂. Consecutive images were taken one minute apart. At first, the surface (Image #1) was covered with medium-sized incompletely separated particles and a few larger ones. As scans continued, those medium size clusters were removed gradually, but not the large ones. At the end, medium sized clusters could only be seen at the step edge (Image #15), and several large clusters remained unreacted. The fact that it took 15 scans to get the same degree of cleaning as in an oxidative environment with much lower pressure suggests a much lower reaction rate. The existence of many leftover particles also reflects the incompleteness of the hydrogenation reaction.
Figure 7.7 A series of 500Å × 500Å STM images show the progress of the tip-induced hydrogenation of carbonaceous clusters on Rh(111) surface. The sample was prepared by dosing 10L of propylene on Rh(111) and heating to 265°C. The images were taken in 3 torr of H₂. Consecutive images were taken one minute apart. Tunneling conditions are all: bias voltage of 176mV, and current of 2.03nA.
7.4 Reaction condition dependencies of tip catalysis

7.4.1 Propylene decomposition temperature

According to the propylene TDS and STM images taken at different stages of the propylene thermal dissociation process discussed in the previous chapter, carbonaceous species with different size can form depending on the temperature. It was found that only when the sample was heated between 200 and 260 °C could the tip catalysis reaction be imaged by STM. 200~260 °C is the temperature range for the formation of incompletely separated middle size particles (10~30 Å in diameter and 1~2 Å in height). The surfaces prepared at lower and higher temperatures belong to two different cases in terms of imaging in high-pressure gases by STM. At lower temperature (<150 °C), adsorbed propylene is cracked into small CₓH fragments. The surface could not be imaged with high resolution. The blurry images indicate that the mobility of the surface species is too high in the presence of a high pressure of background gas. At this condition, even if there is a tip-catalyzed reaction happening, one is unlikely to see individual particles being removed. At higher temperature (>400 °C), the cracked propylene will polymerize into large (>20 Å in diameter and >2 Å in height) and discrete clusters. In contrast to those formed at lower temperature, the large particles were very stable under STM scanning and could not be removed.

It was proved that surface CₓH species formed by cracked propylene at different temperatures had different compositions. Their catalytic hydrogenation/oxidation behavior as well as their mobility on the surface can be related to their composition, or the carbon to hydrogen ratio. At lower temperature, both the cracked fragments and x in the formula of CₓH, are smaller (higher hydrogen content), so the surface species are
more mobile and reactive, both of which can make the surface difficult to image. By contrast, at higher temperature, the clusters are larger and have less hydrogen, so they are more mechanically and chemically inert. As a result, although they can be imaged easily, their oxidation/hydrogenation is hard to initiate. Therefore, an appropriate temperature to form carbonaceous species is equally critical for the STM tip to induce and image the catalytic reactions.

7.4.2 Tunneling condition

The influence of tunneling conditions was investigated, but no apparent effect was found. By intuition, the tip catalysis reaction should depend on the tunneling condition, but the fact that it does not is not surprising because there are many other factors can more heavily affect the entire reaction process. While the tunneling condition can be set precisely, other parameters, especially the “activity” of the tip, are nearly impossible to control, so a reaction rate versus tunneling condition plot would have a huge error bar.

7.4.3 Tip material

The Pt STM tip was replaced with a tungsten or gold tip and the experiments in both oxygen and hydrogen were repeated. No removal of the carbonaceous clusters was found in any combination of experimental conditions. On the edge of the image, no new features piled up. Therefore, the mechanical effects of the tip on the clusters could not account for the removal of the clusters. Furthermore, since neither gold nor tungsten is shown to be able to dissociate O_2 or H_2 at room temperature, having a source of atomic oxygen or hydrogen proved necessary for the tip-induced reactions.
7.4.4 Other Background gas

Besides $O_2$ and $H_2$, similar experiments were conducted with other gases as control experiments, to further confirm the tip-catalyzed oxidation/hydrogenation reaction mechanism. Various pressures of CO, $N_2$ and argon were tested, and no disappearance of carbonaceous clusters was observed. This ruled out the possibility that the removal of the clusters was merely caused by the high frequency mechanical impact from background gases.

7.5 Comparison of the reactions on Pt(111) and Rh(111)

The results obtained from the Rh(111) surface were mostly similar to those reported for Pt(111) in Ref. 8. The basic trends are the same, i.e., an oxidation reaction is less demanding than hydrogenation (Figure 7.2) and the reactions are faster in a higher pressure gas environment. The former is due to the activation energy difference between the oxidation and hydrogenation of hydrocarbons. The oxidation of hydrocarbons on Pt is widely acknowledged to have a lower activation barrier ($\sim 15$ kcal/mol) than the hydrogenation ($50\sim80$ kcal/mol) [13]. The latter, i.e., the positive pressure dependence on the reaction rate can be simply explained by the Le Chatlier’s Principle.

There is also a large difference between the two substrates in terms of reaction rate. Under the same conditions, oxidation reactions on Rh(111) are slower than on Pt(111). On Pt(111), the oxidation could be initiated at an $O_2$ pressure as low as $1\times10^{-6}$ torr, whereas on Rh(111) this threshold was $2\times10^{-4}$ torr. For hydrogenation, the difference is not as noticeable: on each surface the reaction was not observed until the $H_2$ pressure reached a torr range. On Pt(111), the lowest pressure at which hydrogenation
occurred was 0.5 torr, and for Rh(111) the number was 3 torr. Moreover, the extent of hydrogenation (the cleanliness of the surface after reaction) on Pt(111) the reaction was more complete. Reasons for the differences between Rh(111) and Pt(111) are discussed at the end of this chapter.

7.6 Further discussion and conclusions

This chapter presents for the first time that a platinum STM tip catalyzes (with nanometer spatial resolution) the hydrogenation and oxidation of carbonaceous species on a Rh(111) surface. The pressure, tip composition and tunneling gap dependencies of the tip catalysis were investigated. It was found that the reactions only underwent in the presence of \( \text{O}_2 \) or \( \text{H}_2 \) and when a Pt (not W or Au) STM was used. The reaction rate slightly increases as the background pressure increases and tunneling gap decreases.

In comparison with the study on Pt(111) previously reported in Ref. 8, the tip-induced catalytic reactions behave similarly in the sense that the reaction rates have the same order of magnitude, and the extent of the reaction is roughly the same. This indicates that on both rhodium and platinum surfaces a common mechanism should account for the reactions.

The reaction rate was also found to be heavily dependent on the activity of the STM tip. At a fixed pressure, the ability of the tip to gasify the clusters can vary to a great extent, which directly proves that the generation of a catalytically active tip is the rate-determining step in the gasification reaction. When the Pt STM tip was exposed to a high pressure of reactive gas during the tip catalysis reaction, the tip was mainly covered with two types of adsorbates, i.e., the atomic oxygen or hydrogen and carbonaceous
species. Atomic oxygen and hydrogen, which are the active reactants in the initial step of the tip-induced catalysis, are formed by the adsorption/dissociation of the respective gas. The carbonaceous species, which inhibits the tip-catalysis reaction, is adsorbed on the tip through transport from the metal surface during STM scanning. These two adsorption pathways are competing processes, and the dominant one undoubtedly determines the overall reaction rate of the gasification of the carbonaceous species on the surface. When the background gas pressure increases, the adsorption of carbonaceous species onto the tip is suppressed, and the tip catalysis rate becomes faster. This is because under higher gas pressure, the greater collision rate of those species with $O_2$ or $H_2$ makes them less likely to contact and adsorb on the tip. One may argue that at higher pressure the adsorption/dissociation of $O_2$ or $H_2$ becomes faster and overwhelming, so the overall catalysis reaction is quickened. This possibility can be safely ruled out by considering that on the very small area at the end of a STM tip, all adsorption processes are essentially limited by the number of available sites on the tip surface, and so are virtually zero ordered with respect to the gas pressure. In tip catalysis, the carbonaceous species is both the reactant and a poison to the catalyst. Keeping the tip "fresh", or free of any carbonaceous contaminant, is very crucial to the reaction. Although the adsorption behavior of small gas molecules has been well studied on Pt surfaces, similar experimental data for cracked hydrocarbons are rarely reported due to the difficulties of quantitative analysis and the lack of kinetic characterization.

The difference between reaction rate on Pt(111) and Rh(111) could be explained in terms of kinetic effects as well as thermodynamics. The entire tip catalysis process can be divided into the following steps: a) the dissociative adsorption of $O_2$ or $H_2$ on Pt tip; b)
the transport of atomic oxygen or hydrogen from the tip to the carbonaceous species during STM scanning; c) the oxidation or hydrogenation of the carbonaceous species; d) the desorption or migration of smaller carbonaceous species formed in (c) after the C-C or C-H bonds in larger ones are reacted away. The first three steps are virtually unrelated to the metal substrate, while the substrate does play an important role in the last step.

One may seek the answer to the question why Rh(111) and Pt(111) behave somewhat differently in the tip-catalysis through comparing the strength of the metal-carbon bonds. A dynamic LEED study suggested that the Pt-C bond is shorter and thus stronger than Rh-C bond in the metal/ethylidyne structure, but no exact number was given [14]. However, this result does not seem applicable to the case of the carbonaceous species absorbed on the metal, otherwise the carbonaceous clusters would bond to Pt(111) more strongly, and thus be less reactive in the oxidation or hydrogenation catalysis. In the previous chapter, carbonaceous species were shown to form more easily on Rh(111) by the fact that hydrocarbons dissociate into small C_xH species at lower temperature on Rh(111) than on Pt(111). Therefore, it appears that the kinetics, rather than thermodynamics, governs the tip catalysis process. On either substrate, the reaction progress after steps (a), (b) and (c) presumably reaches the same extent. At step (d), however, the intermediate species has less probability to desorb from or migrate on Rh(111) than on Pt(111). As indicated in the apparent reaction rate measurement data, more repeated STM scans or higher initiation pressure are needed to remove the carbonaceous clusters on Rh(111) than on Pt(111). In other words, the carbonaceous species on Rh(111) is kinetically less reactive, more inert or more resistive to the gasification reactions.
References


Chapter 8.
The Adsorption of Benzene and Small Polycyclic Aromatic Hydrocarbons (Naphthalene, Phenanthrene and Anthracene) on the Rh(111) and Pt(111) surfaces

8.1 Introduction

The atomic spatial resolution available to the scanning tunneling microscopy allows its exclusive capability to obtain real-space images of molecules adsorbed on a conducting surface. Since the invention of the STM in the early 1980’s, considerable interest has arose in using of STM for imaging the structure, atomic components of large molecules, and even directly manipulating the structure. Especially in the case where the molecule shows an internal structure, the possibility of identifying a molecule with the STM is an important step in the manipulation and transformation of a single molecule by an STM tip and related applications. It also has important implications for surface chemistry and heterogeneous catalysis.

Numerous studies have been performed on the adsorption of conjugated cyclic compounds on metal surfaces. The molecular systems that have been investigated include benzene co-adsorbed with CO on Rh(111) [1, 2], benzene on Pt(111) [3], o-xylene and p-xylene on Rh(111)[4], naphthalene on Pt(111) [5, 6], two-ring systems with/out heteroatom such as naphthalene, azulene and substituted azulenes [7], a Cyporphyrin complex on Cu(100), Au(110) and Ag(110) [8], Cu-phthalocyanine [9], etc. In
addition to the traditional UHV STM studies, electrochemical STM has also been extensively used in this subject. Very high resolution images have been obtained for benzene, naphthalene and anthracene on Rh(111) and Pt(111) in HF solution [10, 11] and Cu(111) in HClO₄ solution [12]. With the development of computational chemistry, theoretical calculations of STM images have been used to explain or predict the shape and adsorption sites for these molecules. Those calculations, mostly based on the Extended Hückel Theory [13-15] or \textit{ab initio} methods [16], can often show qualitative agreement with experimental results.

In surface science, benzene and small polycyclic aromatic hydrocarbons such as naphthalene, phenanthrene and anthracene, are among the most frequently studied organic molecules. Numerous studies have been done by means of traditional surface analysis techniques, such as LEED [17-23], work function measurements [17, 24], TDS[18, 20, 21], and HREELS [20, 21, 24, 25]. However, a systematic STM investigation and comparison of their adsorption behavior on metal surfaces, and their co-adsorption with CO, NO and O₂, have yet been performed.

In this chapter, the adsorption behaviors of benzene, naphthalene, phenanthrene and anthracene on Rh(111) and Pt(111) have been studied by STM with the assistance of LEED. Individual adsorption property of each compound on Rh(111) was specifically investigated. Their co-adsorption with CO, NO, O₂ and H₂ on Rh(111) was selectively studied. Phenanthrene and anthracene adsorption on Pt(111) was conducted and compared with that on Rh(111). As an extension of the tip catalysis work discussed in Chapter 7, the possibility of using a Pt STM tip to induce the oxidation/hydrogenation of
individual molecules on Rh(111) and Pt(111) in the presence of a high pressure of O₂ or H₂ was also explored.

8.2 Experimental procedure

The structure and dimension of the four molecules under study are illustrated in Figure 8.1. The bond lengths and van der Waals radii were taken from Ref. 17, and the dimensions of the molecules have been recalculated. Of each molecule, all atoms are in the same plane, and the entire molecule is a large conjugated system where each π electron (contributed from each carbon atom) is delocalized and shared by the entire ring system. It is expected that all molecules are flat when adsorbed on the metal surface, and the ring is parallel to the substrate. Under STM, they each should have a distinct shape that corresponds to the molecular geometry.

All chemicals used in the experiments were reagent grade. Figure 8.2 shows the vapor pressures of naphthalene, phenanthrene and anthracene as functions of temperature. For benzene and naphthalene, the vapor pressures around room temperature are high enough so one can use standard organic dosers to introduce them into the chamber. The chemicals were stored in a glass vessel that was connected to a stainless steel manifold, which was then connected to a leak valve and pump. Prior to the adsorption experiment, the chemical samples were degassed by several freeze-pump-thaw cycles. The vapor pressure of benzene is ~100 torr at room temperature. Naphthalene had to be melted at ~355K to maintain its partial pressure at 20 torr at the leak valve.
Figure 8.1 The structure and dimensions of benzene and small polycyclic aromatic hydrocarbons.
Figure 8.2 The vapor pressures of naphthalene, phenanthrene and anthracene as functions of temperature. Data are taken from the CRC Handbook.
The vapor pressures for phenanthrene and anthracene are very low, so special treatment is needed to introduce them into the UHV chamber. The chemicals, in forms of white or yellowish powder at room temperature, were stored in a \( \frac{1}{4} \) " stainless steel Swagelok cap. The cap was then mounted directly to the inlet of the leak valve through stainless steel tube fittings. The pre-pumping and the freeze-pump-thaw cycles were achieved by opening the leak valve and pumping the doser from inside the UHV chamber. Before dosing the organics, the whole gas line needed to be warmed or heated up to avoid clogging any organics in it. The design of the heatable organic doser is illustrated in Figure 3.4. During the dosing process, the organic doser, the leak valve and the inducting tube inside the UHV chamber were heated to \( \sim 200^\circ\text{C} \) to ensure a quick and controllable deposition of organics. However, because the opening of the inducting tube is close to the crystal, during the deposition, the local pressure of the organics was presumably much higher than that measured by the ion gauge, so the numbers of phenanthrene and anthracene exposure used later in the chapter were not as meaningful as those for benzene, naphthalene or other small gas compounds. When dosing the organics, the gas component was monitored by mass spectrum to check the purity of the introduced gas. The mass spectra of naphthalene and anthracene are shown in Figure 8.3. The mass spectrum of phenanthrene is almost identical to that of anthracene.
Figure 8.3  The mass spectra for naphthalene (top) and anthracene (bottom). The mass spectrum for phenanthrene is almost identical to that of anthracene.
The base pressure in the UHV chamber before each experiment was better than $2 \times 10^{-10}$ torr. The Rh(111) crystal was cleaned by repeated cycles of Ar$^+$ sputtering followed by annealing in oxygen and in vacuum. Cleanliness of the crystal was determined by AES, and the ordering of the surface was determined by the appearance of very sharp (1×1) diffraction spots in the LEED pattern. The organic was then introduced to the surface at a certain dosage and desired temperature. The LEED pattern of the crystal surface was inspected. When conducting co-adsorption experiments, the order of dosing the two compounds was sometime very critical. The LEED and AES inspections were normally done after dosing each compound. After the UHV chamber was filled with over $1 \times 10^{-7}$ torr of the organic shortly (<several tens of seconds), the base pressure became very poor, and it then needed at least 30~60 minutes to get down to low $10^{-9}$ or high $10^{-10}$ torr range.

STM experiments were conducted after the crystal was cooled to room temperature. The STM images were normally taken with a tungsten tip. Bias voltage was normally chosen to be anywhere between 30mV to 1V, and the tunneling current was around 1nA. The images shown were either raw or taken after brief low pass.

8.3 Benzene on Rh(111)

In the literature, benzene was found to form several types of ordered overlayers on Rh(111) between 300~400K, depending on the benzene coverage[25]. Two structures were often reported [1,2, 17-20, 23, 24]. A well-ordered c(2√3×4) structure formed at around room temperature and it was stable up to 358K. Above 363K, it began to transform into a (3×3) structure. The phase transition was irreversible, which allowed
one to perform an STM study on either one at room temperature. In fact, a mixture of both structures was often obtained at room temperature. Figure 8.4 shows the H$_2$ thermal desorption spectrum for benzene adsorbed on Rh(111) in both the (3×3) and c(2√3×4) structures [18]. The schematic of the Rh(111)-(3×3)-benzene and Rh(111)-c(2√3×4)-benzene structures suggested by LEED and HREELS studies [25] is illustrated in Figure 8.5.

The co-adsorption of CO and benzene was found to greatly promote the ordering of the benzene arrangement [1, 2, 19-24]. This is due to the fact that benzene is an electron donor, as its adsorption reduces the work function of the metal surface, while CO is an electron acceptor (as it increased the work function of the metal), so the donor-acceptor attraction between the two species stabilizes the benzene adsorption, as indicated by the fact that the benzene desorption peak appears at 20°C higher when it is co-adsorbed with CO [26]. The co-adsorption structures include (3×3) and c(2√3×4), which are identical to the two most common adsorption structures formed when benzene alone is on Rh(111). It is claimed that benzene is disordered on Rh(111) or forms a c(2√3×3) overlayer when it is alone, and the (3×3) and c(2√3×4) overlayers are merely the result of the co-adsorption with CO [2, 21], because as one of the most common residual gases in UHV chamber, a trace amount of CO in the background is unavoidable. However, an electrochemical STM study of benzene on Rh(111) in HF solution found the existence of both (3×3) and c(2√3×3) overlayers with no co-adsorbed species. Therefore, whether the (3×3) and c(2√3×4) overlayers can be formed in a CO-free environment seems still an open question. In this section, the benzene adsorption on Rh(111) was re-examined, and the co-adsorption of benzene with NO was studied for the first time.
Figure 8.4  H$_2$ thermal desorption spectrum from benzene adsorbed on Rh(111) in both (3×3) and c(2√3×4) rect structures (taken from Ref. 18).
Figure 8.5 Schematic of Rh\((111)-(3\times3)\)-benzene and Rh\((111)-c(2\sqrt{3}\times4)\)-benzene structures suggested by LEED and HREELS (taken from Ref. 25). All benzene molecules adsorb on hcp hollow sites.
8.3.1 Benzene adsorption on Rh(111)

In the upper left of Figure 8.6, the LEED pattern for benzene on Rh(111) shows a mixture of (3×3) and c(2√3×4) domains. A schematic of the pattern is illustrated on the right-hand side. The corresponding STM image of this structure is shown in Figure 8.7. Individual benzene molecules are clearly imaged. All four adsorption domains, one of (3×3) and three of c(2√3×4), can be distinguished. Those domains are highlighted in the bottom miniature by superimposing the four lattice meshes.

To obtain information on the relative adsorption sites of the two structures, images of higher resolution were taken in an area where the (3×3) and one c(2√3×4) domains co-existed, as shown in Figure 8.8 (A). At the upper left corner, a (3×3) lattice can be seen. The rest of the image is covered by one domain of the c(2√3×4) structure, where the unit cell has rectangular shape. Two meshes of lattice points marked by “+”s are superimposed on the miniature plot (C) to guide the viewer’s vision. In plot (D), the molecular position are highlighted by circles, and all circles are translated to plot (E) and superimposed on a net representing the Rh(111) lattice. It can be seen that all circles are centered at the same locations within the unit cells, suggesting that all benzene molecules adsorb on the same site on Rh(111), regardless of what super-lattice they form. This gives a support to the suggestion that all benzene molecules adsorb on hcp hollow sites [25]. A cross section plot along seven molecules shows that the corrugation of benzene molecules is 0.3–0.4 Å. Attempts were made to image the Rh(111) lattice underneath to determine what site the benzene molecules actually occupy, but were unsuccessful.
LEED for benzene on Rh(111) showing a mixture of (3×3) and c(2√3×4) patterns.

Figure 8.6 The LEED patterns (left) and the corresponding models (right) for benzene adsorbed on Rh(111) (top) and benzene and NO co-adsorbed on Rh(111) (bottom). The electron beam energies in LEED measurements were 56eV and 65 eV, respectively.
Figure 8.7 260Å x 260Å STM image of benzene on the Rh(111) surface. Tunneling condition is: bias voltage of −33.1mV, and current of 1.09nA. Individual benzene molecules are clearly imaged. All four adsorption domains, one (3×3) and three c(2√3×4), can be distinguished. Those domains can be more clearly seen in the bottom image, on which four lattice meshes are superimposed to guide the viewer’s vision.
Figure 8.8  (A) Image of benzene on Rh(111) with a \((3\times 3)\) and a \(c(2\sqrt{3}\times 4)\) domain. The scan size is \(80\,\text{Å} \times 80\,\text{Å}\). Tunneling condition is bias voltage of \(82\,\text{mV}\) and current of \(1.0\,\text{nA}\). (B) Cross-section plot along the line in the image. The corrugation of the benzene molecules is \(0.3\sim 0.4\,\text{Å}\); (C) Two meshes of lattice points marked by “+”s are superimposed on the image. On the upper left corner, a \((3\times 3)\) lattice and hexagonal units can be seen. The rest of the image is covered by one domain of a \(c(2\sqrt{3}\times 4)\) structure. The unit cell has rectangular shape; (D) The positions of molecules are highlighted by circles; (E) A net representing the Rh(111) lattice is superimposed on the set of circles which have the same relative positions as in (D). It can be seen that all circles are centered at the same locations on the lattice, suggesting that all benzene molecules adsorb on the same site on Rh(111), regardless of what super-lattice they form.
Under certain optimized tunneling conditions, the distinct shape of molecules can be imaged. The image in Figure 8.9 was taken on a (3×3) benzene domain. Individual benzene molecules are clearly seen. On each molecule there is a depression at the center, corresponding to the ring structure. At still higher resolution, the benzene rings are well resolved. As can be seen in Figure 8.10, each benzene molecule has a crater shape. The corrugation of the benzene molecules is 0.5–0.8Å, and the depression at the center of each molecule, which corresponds to the ring, is ~0.2Å deep. These corrugation numbers are in agreement with literature values [1, 2].
Figure 8.9 100Å x 100Å STM image of the Rh(111)-(3×3)-benzene domain. Individual benzene molecules are clearly seen. On each molecule there is a depression at the center, corresponding the ring structure. Tunneling condition is: bias voltage of 15mV, and current of 1.10nA.
Figure 8.10 (A) 30Å × 30Å STM image of benzene on Rh(111) in a (3×3) domain. The benzene rings are well resolved. Tunneling condition is bias voltage of 82mV and current of 1.0nA. (B) the cross-section plot along the line in (A). The corrugation of the benzene molecules is 0.5~0.8Å, and the depression at the center of each molecule, which corresponds to the phenyl ring, is ~0.2Å deep. (C) the three-dimensional plot of (A). Each benzene molecule has a volcano-like shape.
8.3.2 Benzene co-adsorption with NO on Rh(111)

The (3×3) co-adsorption of benzene and CO has been studied by STM [1,2]. In high-resolution images, although every single benzene molecule is clearly resolved, no feature that can be associated with CO was imaged. In the investigation of the benzene adsorption on CO-precovered Rh(111), it was found that as benzene coverage increases, row-like features associated with CO disappear, indicating CO displacement from the surface. Since CO and NO have very similar molecular sizes, and both are electron acceptors and have similar adsorption behavior on metal surfaces, it would be interesting to compare their co-adsorption with benzene.

The experiments were done with different dosing sequences of benzene and NO, and the surface structure was first checked by LEED. When benzene was dosed first, a LEED pattern (upper half of Figure 8.6) showed the existence of a mixture of (3×3) and c(2√3×4) structures. As NO was introduced, this LEED pattern changed to a simple (3×3) pattern (lower half of Figure 8.6). An Auger spectrum indicated the existence of nitrogen on the surface, which confirmed benzene and NO co-adsorbed on the surface. If the dosing sequence was reversed, a completely different process occurred. When the surface was saturated with NO first, a sharp (2×2) LEED pattern appeared. As benzene was introduced, this pattern did not change, indicating that benzene can not replace NO on Rh(111) and thus no co-adsorption can take place.

The STM study was conducted for the case where the co-adsorption occurred. Figure 8.11 shows an STM image of the Rh(111)-(3×3)-benzene+NO structure. The sample was prepared by dosing 2L of benzene and 5L of NO in sequence. Individual benzene molecules can be seen. The surface has a certain disordering with some
impurities adsorbed on. In the cross-section plot, one can see the corrugation of benzene molecules is still as high as 0.2~0.4Å, but no fine structure is resolved in between which can be attributed to NO.

Figure 8.11 50Å x 50Å STM image of the Rh(111)-(3×3)-benzene+2NO structure. The sample was prepared by dosing 2L of benzene and 5L of NO in sequence. Individual benzene molecules can be seen, but NO was not visible. The surface has certain disordering with some impurities adsorbed on. In the cross-section plot, the corrugation of the benzene molecules is still as high as 0.2~0.4Å, but no fine structure is resolved in between. Tunneling condition is bias voltage of 82mV and current of 1.0nA.
8.3.3 Discussion

The molecular shape of benzene in STM images has been investigated by both experiment and theoretical calculation. Benzene molecules with flat-topped cylindrical [1], ring-like [2], triangular [1,10], and dumbbell [10] shape were obtained experimentally. The conditions for getting each shape seem unpredictable and irreproducible. Theoretical simulations were in agreement with only some of the results. In this dissertation work, only round shapes with one depression at the center was found for benzene molecules.

The co-adsorption structure of benzene and CO on Rh(111) determined by LEED was Rh(111)-(3×3)-benzene+2CO [23]. Due to the similarity between CO and NO, it is reasonable to propose the same arrangement pattern exist for the benzene+NO system. Figure 8.12 shows a schematic of the proposed Rh(111)-(3×3)-benzene+2NO structure. In the lower box, the determined adsorption structure of Rh(111)-(3×3)-benzene+2CO is given (taken from Ref. 23). All molecules adsorb on hcp sites. As a comparison, the Rh(111)-c(2√3×4) –benzene structure is shown on the right hand side.

When the benzene is alone on the Rh(111) surface, it can form both (3×3) and c(2√3×4) overlayers, and the latter has slightly higher coverage. Upon exposure to NO, in order to fit more NO molecules on the surface, benzene molecules need to change their arrangement to make room for more hcp hollow sites. In a c(2√3×4) unit cell, there is only one available hcp site, while in a (3×3) unit cell there are two. Therefore, when the benzene-covered Rh(111) is saturated with NO, the surface turns to an exclusively (3×3) arrangement.
Figure 8.12 Schematic of a proposed Rh(111)-(3×3)-benzene+2NO structure. In the bottom box, the adsorption structure of the Rh(111)-(3×3)-benzene+2CO structure is given (taken from Ref. 23). The Rh(111)-c(2√3×4)-benzene structure has higher coverage than the Rh(111)-(3×3)-benzene, so in order to fit more NO molecules on the surface, benzene molecules need to change their arrangement to make room for more hcp sites. When the benzene-covered Rh(111) is saturated with NO, the surface has an exclusively (3×3) arrangement.
As in the benzene-CO co-adsorption structure, no NO molecules were visible. A popular explanation of this contrast difference considers the apparent height differences, i.e., tunneling probability of the two co-adsorbed species. Benzene adsorbed on an hcp site has a corrugation of 0.4-0.8 Å. In the STM images shown in Chapter 5, NO adsorbed on atop site showed a corrugation of only 0.1~0.25 Å, and NO adsorbed on the hollow site was even not visible. Therefore, it is expected that when both molecules adsorbed on hcp site, the large corrugation between benzene molecules dominated the overall image contrast. The apparent height differs from the geometry height. In fact, in the determined Rh(111)-(3×3)-benzene+2CO structure shown in Figure 8.12, the CO molecule is even higher than the benzene by ~0.4 Å. The apparent height difference originates from the distinctive electronic states of the two molecules. Figure 8.13 shows the molecular orbital diagram for benzene, NO and CO adsorbed on a Rh(111) surface. The data were obtained by various techniques, including angle resolved UV photoemission (ARUPS) [26], Extended Hückel Theory calculations [27], periodic density-functional calculations [28], and inversion photoemission [29]. As stated in Chapter 2, an STM image is the surface profile of the local density of the states near the Fermi level (E_F). On the Rh(111) surface, the benzene 1e_{2u} orbital is only a few tens of millivolts above E_F, while the 2π* orbital for NO is higher, and the same orbital for CO is a few volts above E_F. The electron density has a finite distribution around the orbital, so among the three molecules, benzene has the highest density of state near E_F, NO has lower density, and CO has nearly zero density. Therefore, benzene is relatively easier to image by STM than NO, and CO is much more difficult to image. The interaction between benzene and CO in the mixed overlayer was not very pronounced [26], so it is
reasonable to assume that the co-adsorptions do not change the molecular orbitals considerably. Therefore, in the co-adsorption overlayer, benzene will by preferentially imaged by the STM tip compared with NO or CO.

Figure 8.13 The molecular orbital diagram for benzene, NO and CO adsorbed on a Rh(111) surface.
The adsorption energy data can be used to explain the fact that on a Rh(111) surface pre-covered with CO or NO, benzene can replace CO but not NO. On Rh(111), the desorption energy ($E_d$) for benzene and CO on Rh(111) is 1.0 eV [25] and 1.34 eV [30], respectively. For NO, however, two values were reported, 1.2 eV as determined by TDS [31] and 2.2 eV calculated by DFT [28]. The discrepancy may be due to the dissociative adsorption nature of NO on Rh(111). CO and benzene have comparable bonding energies to Rh(111), so each can replace the other when it is in excess in the gas phase. For NO, the situation is complicated. When benzene is pre-adsorbed on Rh(111), there are still plenty of available hcp hollow sites for NO to occupy non-dissociatively. When a clean Rh(111) is saturated with NO, there is a considerable amount of atomic oxygen on the surface which bonds to the substrate extremely strongly, as indicated by its high TDS peak starting at 600°C. Both NO and oxygen form (2×2) structures that cannot be distinguished by either LEED or STM. When NO-saturated Rh(111) is exposed to benzene, although the replacement of NO by benzene is energetically favorable (if the 1.2eV $E_d$ value for NO is used), the strongly bonded oxygen atoms on the surface can not be replaced and they may block sites which are required by benzene adsorption, the replacement of NO by benzene is then greatly hindered. If $E_d$ for NO is 2.2eV, as calculated, which is more than double that for benzene, then replacement of NO by benzene is even thermodynamically unlikely.
8.4 Naphthalene on Rh(111)

Naphthalene adsorption on metal surfaces has been investigated on Pt(111) [5-7, 11, 17], Pt(100) [17], Rh(111) [11, 18], and Cu(111) [12] by means of LEED [5, 17, 18], TDS [18], work function measurements [17], UHV STM [5-7] and electrochemical STM [11]. On Pt(111) or Rh(111), the centers of molecules occupy a (3×3) lattice. Depending on the sample preparation conditions or other unclear factors, naphthalene on Pt(111) can form a (6×3) [5-7], (6×6) [17] or disordered [11] overlayer, and on Rh(111) it can form a (3×3) or (3√3×3√3) overlayer [18]. All overlayers on Pt(111) have been imaged by STM, while on Rh(111) only the (3√3×3√3) overlayer was observed by electrochemical STM. No result from naphthalene co-adsorption with other molecules has been published. In this dissertation work, the two types of naphthalene overlayers on Rh(111) were prepared and imaged by STM. The dynamics of the overlayer structure in the presence of various pressure of CO, O₂, H₂ was investigated.

8.4.1 Naphthalene adsorption on Rh(111)

An early study by TDS and LEED established that naphthalene can adsorb molecularly on Rh(111) below 520K [18]. Depending on the temperature, it forms two ordered overlayer structures. Between room temperature and 400K, it forms a (3√3×3√3)R30° overlayer. When the temperature is increased to between 400K and 423K, the overlayer changes to a simple (3×3) structure. The overlayer disordered permanently upon further heating to 450K. The phase transitions were largely found to be irreversible, which allowed one to perform STM study on every single overlayer structure at room temperature. Figure 8.14 shows the H₂ thermal desorption spectrum from naphthalene adsorbed on Rh(111). The schematic of the proposed models of
Rh(111)-(3×3)-naphthalene and Rh(111)-(3√3×3√3)R30°-3 naphthalene structures is illustrated in Figure 8.15. It was suggested that all naphthalene molecules lie flat and do not overlap. They are centered on atop sites, with the long molecular axes all along the [110] direction or its equivalents. In these two arrangements, naphthalene molecules have the same coverage (0.11 monolayer), with all molecular centers occupying a (3×3) lattice. In every (3√3×3√3)R30° unit cell, each of the three molecules has a 60° orientation shift with respect to one another. By this arrangement, there is one atop Rh completely exposed, while in the (3×3) arrangement all Rh atoms are “covered”. The models were proposed by the least-overlap space-filling method and symmetry considerations, but were not confirmed by dynamic LEED analysis yet. By electrochemical STM, the Rh(111)-(3√3×3√3)R30°-3 naphthalene structure was well imaged in HF solution, and the preferential orientations of the molecules were confirmed to be along [110] type by comparing the direction of the molecular long axes and the lattice of Rh atoms. However, the (3×3) structure was not observed.

Figure 8.14 H$_2$ thermal desorption spectrum from naphthalene adsorbed on Rh(111) (taken from Ref.18).
Figure 8.15 Schematic of the Rh(111)-(3\times3)-naphthalene and Rh(111)-(3\sqrt{3}\times3\sqrt{3})R30^\circ-naphthalene structures suggested by LEED (from Ref. 18). All naphthalene molecules are centered on atop sites, and the long molecular axes are all along the [1\bar{1}0] direction or its equivalents. Note that the two structures are closely related. They have the same coverage of naphthalene (0.11 monolayer), and all molecular centers occupy a (3\times3) lattice. In the (3\sqrt{3}\times3\sqrt{3})R30^\circ unit cell, each of the three molecules has a 60^\circ orientation shift with respect to one another. By this arrangement, there is one atop Rh completely exposed, while in the (3\times3) arrangement, all Rh atoms are “covered”.
In this dissertation work, the two ordered structures were prepared by exposing the cleaned Rh(111) surface to 10L naphthalene at 150° for the (3×3) structure, or at room temperature for the (3√3×3√3)R30° structure, respectively. All measurements were taken at room temperature. LEED patterns were checked and recorded. In Figure 8.16, the LEED patterns are shown for clean Rh(111), Rh(111)-(3×3)-naphthalene and Rh(111)-(3√3×3√3)R30° structures, taken at 74eV, 74eV and 100eV, respectively.

Figure 8.17 shows the STM image of a (3×3) naphthalene structure on Rh(111). The (3×3) lattice can be unambiguously drawn due to the high ordering. The lattice vectors, which are indicated by LEED (the same as the Rh(111) substrate), are given at the upper right corner in the image. The “∞” shaped molecules are well resolved. Each half of the molecule, (i.e., one phenyl ring) shows up as a bright feature, while the center of the molecule is dark in contrast. The two phenyl rings have the same brightness, indicating that the molecules lie flat on the surface. Most molecules are along the [101] direction. This demonstrates that the long axes of the molecules are preferentially orientated to one of the close-packed directions of the Rh(111) lattice underneath. Some molecules with altered orientations can be found around the surface defects. In images with higher magnifications (Figure 8.18), each molecule still shows up as oval in shape with only one depression at the center. No two-ring like shape was observed.

In Figure 8.19, the two STM images were obtained from the (3√3×3√3)R30° structure. The surface is characterized by the existence of dark triangular holes. In the right image, one unit cell is highlighted by a black rhombus. In each unit cell, three molecules stagger with a 60° angle to one another, and the dark triangle is enclosed by the
long axes of three adjacent molecules. These images conform to the model proposed in Ref. 18.

Figure 8.16 LEED patterns for clean Rh(111), Rh(111)-(3×3)-naphthalene and Rh(111)-(3√3×3√3)R30° structures, taken at 74eV, 74eV and 100eV respectively. The naphthalene-covered Rh(111) samples were prepared by exposing the clean Rh(111) surface to 10L naphthalene at 150° for the (3×3) structure, and at room temperature for the (3√3×3√3)R30° structure.
Figure 8.17 100Å × 100Å STM image of the (3×3) naphthalene structure on Rh(111). The “∞” shaped molecules are well resolved. Each half of the molecule (i.e., one phenyl ring) shows up as a bright feature, while the center of the molecule is dark in contrast. The two phenyl rings have the same brightness, indicating that the molecules are flat on the surface. Most molecules are along the diagonal of the image. The fact that one (3×3) lattice vector is also running along this direction demonstrates that the long axes of the molecules are along one of the [110] type directions of the Rh(111) lattice underneath. Some molecules with altered orientations can be found around surface defects. Tunneling condition: bias voltage of 202mV and current of 1.07nA.
Figure 8.18 50Å × 50Å (top) and 25Å × 25Å (bottom) STM images of naphthalene on Rh(111) in a (3×3) domain with higher magnifications. Images were both taken with a bias voltage of 202mV and a tunneling current of 1.07nA.
Figure 8.19 STM images of naphthalene on Rh(111) in a \((3\sqrt{3} \times 3\sqrt{3})R30^\circ\) domain. The unit cell can be defined by the dark holes with triangular shape. In the right image, one unit cell is highlighted by a black rhombus. The scan sizes are 100Å \(\times\) 100Å and 50Å \(\times\) 50Å, and the images were taken with a bias voltage of 452mV and 383mV, and a tunneling current of 1.12nA and 1.02nA, respectively.
8.4.2 Naphthalene co-adsorption with CO on Rh(111)

In the Rh(111)-(3\sqrt{3}\times3\sqrt{3})R30°-naphthalene structure, a dark hole exists in each unit cell, which can be attributed to a naked Rh atom. This site does not exist in the (3×3) structure. It is very appealing to see whether any small molecule adsorbs preferentially to this Rh atom, and can thus induce the phase transition between the two structures if the foreign molecule. CO was checked first as it is well-known to adsorb molecularly requiring only one site, and on Rh(111) the atop site is preferred at low coverage [32, 33].

For this purpose, a (3×3) naphthalene on Rh(111) structure was prepared by exposing the cleaned Rh(111) surface to 10L naphthalene at 150°. A sharp (3×3) LEED pattern was obtained. When the structure was then exposed to 6L of CO, the LEED pattern changed to a (3\sqrt{3}\times3\sqrt{3})R30° pattern. This LEED pattern transition is shown in Figure 8.20. The reverse process, which is the transition from (3\sqrt{3}\times3\sqrt{3})R30° to (3×3) in the presence of CO, was not observed. Note that without CO, the transition from (3\sqrt{3}\times3\sqrt{3})R30° to (3×3) was achieved by heating the crystal, but the transition from (3×3) to (3\sqrt{3}\times3\sqrt{3})R30° was not possible, as reported in Ref. 18. The abnormal behavior in the phase transition in the presence of CO provides solid evidence of the existence of a naphthalene and CO co-adsorption structure.
Figure 8.20 LEED patterns for Rh(111)-(3×3)-naphthalene (left) and Rh(111)-(3√3×3√3)R30°-naphthalene+CO (right) structures, all taken at 74eV. The (3×3) structure was prepared by exposing the clean Rh(111) surface to 10L naphthalene at 150°. When it was exposed to 6L of CO, the LEED pattern changed to a (3√3×3√3)R30° pattern.
Figure 8.21 shows the STM image of the Rh(111)-(3√3×3√3)R30° naphthalene +CO structure. The image appears identical to the pure naphthalene adsorption structure. One unit cell is highlighted by a rhombus. Individual naphthalene molecules with staggered orientations are resolved. The black hole in the unit cell can still be seen. However, there is no indication of the existence of CO in the hole. The same argument as in the case of benzene and CO co-adsorption could be used to explain the invisibility of CO.

Figure 8.22 is the schematic of a tentatively proposed model of a Rh(111)-(3√3×3√3)R30°-3 naphthalene+CO structure. The CO adsorbs at the top site of the Rh atom that is not covered by naphthalene. In the presence of CO, the (3×3) naphthalene structure undergoes a phase transition to the (3√3×3√3)R30° arrangement to make room for CO adsorption. This model can explain the STM images and LEED pattern perfectly. Some surface vibrational spectroscopy techniques, such as HREELS and SFG, are desired for further confirmation. If the C-O stretch on atop site on Rh(111) is observed, then the final determination of naphthalene adsorption on Rh(111) can be made.
Figure 8.21 50Å × 50Å STM image of the Rh(111) - (3√3×3√3)R30° naphthalene+CO structure. One unit cell is highlighted by a rhombus. Individual naphthalene molecules with staggered orientations are resolved. The black hole in the unit cell can be seen, but there is no indication of the existence of CO inside. The image was taken with a bias voltage of 1.0V and a tunneling current of 1.03nA.
Figure 8.22 Schematic of a proposed model of the Rh(111)-(3√3×3√3)R30°-3 naphthalene+CO structure. The CO adsorbs at the top site of the Rh atom that is not covered by naphthalene. In the presence of CO, the (3×3) naphthalene structure undergoes a phase transition to the (3√3×3√3)R30° arrangement to make room for CO adsorption.
8.4.3 Naphthalene co-adsorption with O$_2$ on Rh(111)

Attempts to use O$_2$ to induce the phase transition between the two Rh(111)-naphthalene adsorption structures were made. It was found by both LEED and STM that low pressure O$_2$ in the background did not seem to have any effect to the naphthalene pre-covered Rh(111) surface. This is not surprising because O$_2$ adsorbs dissociatively [30], and on the naphthalene-covered Rh(111) there are no adjacent sites to accommodate two oxygen atoms. In high pressure of O$_2$ the surface became very rough and the arrangement of naphthalene was more disordered. Figure 8.23 shows STM images of the surfaces of the naphthalene-adsorbed Rh(111) in the presence of O$_2$. The left and right images were taken, respectively, in $1 \times 10^{-4}$ torr and 15 torr of O$_2$ at room temperature. In both images, individual naphthalene molecules were resolved. In the presence of low pressure O$_2$, the surface kept the $(3 \sqrt{3} \times 3 \sqrt{3})$ structure. Under high pressure O$_2$, the naphthalene molecules lose their preferential alignment, but still roughly have a translational correlation length three times that of the Rh-Rh distance. Although there are more defects on the surface, overall O$_2$ does not change the Rh(111) surface pre-adsorbed with naphthalene. In either image, no feature can be attributed to the adsorbed oxygen atom.
Figure 8.23 STM images of the surfaces of naphthalene-adsorbed Rh(111) exposed to O₂.

The left and right images were taken respectively in 1×10⁻⁴ torr and 15 torr of O₂ at room temperature. In both images individual naphthalene molecules are resolved. In the presence of low pressure O₂, the surface kept the (3√3×3√3) structure. Under high pressure O₂, the surface became very disordered, but the naphthalene molecules still roughly have a translational correlation length of three times the Rh-Rh distance. This suggests that, overall O₂ does not change the Rh(111) surface pre-adsorbed with naphthalene. The scan sizes are both 200Å × 200Å. Images were taken with a bias voltage of 476mV and 570mV and a tunneling current of 1.17 and 0.96nA, respectively.
Surprisingly, if the Rh(111) is pre-covered with an oxygen overlayer, the naphthalene adsorption is entirely different. A sample was prepared by saturating Rh(111) with oxygen then exposing it to 150L of naphthalene. The dosing of naphthalene was rather ineffective, so a considerably large exposure was needed before any change could be observed in LEED. During the whole sample preparation process, the LEED pattern underwent a change from (1×1) to (2×2), and then to (4×4), as shown in Figure 8.24. The LEED (4×4) pattern for naphthalene was not reported in literature.

Figure 8.25 shows STM images of the Rh(111) surface co-adsorbed with oxygen and naphthalene in sequence. In the left image, individual molecules were resolved. The surface local ordering is poor, but in the long range, the molecules have hexagonal symmetry, as shown in the fast Fourier transform plot at the upper right corner of the first image. The average intermolecular distance is 10.8Å, equal to four times Rh lattice constant and in agreement with the LEED pattern. In the right image, which has a higher resolution, the shape and orientation of individual naphthalene molecules can be distinguished. All molecular long axes are still along [1\bar{1}0] type directions. In the space between adjacent naphthalene molecules, there is no oxygen species visible.
Figure 8.24 LEED patterns for the surfaces of clean Rh(111) with \((1\times1)\), Rh(111) adsorbed with oxygen and Rh(111) adsorbed in sequence with oxygen and naphthalene, taken at 74eV, 74eV and 65eV, respectively, in UHV and room temperature. The sample preparation condition is listed above each pattern. The three LEED patterns, in turn, have \((1\times1)\), \((2\times2)\) and \((4\times4)\) symmetry.
Figure 8.25  STM images of Rh(111) co-adsorbed with 60L of oxygen and 150L of naphthalene, in sequence. The shape and orientation of individual naphthalene molecules can be distinguished. The local ordering is poor, but in the long-range the molecules have hexagonal symmetry, as shown in the fast Fourier transform plot at the upper right corner. The average intermolecular distance is 10.8Å, equal to four times Rh lattice constant and in agreement with the LEED pattern. In the space between adjacent naphthalene molecules, there is no O species visible. Some features are twice as large as most others, but their contrast in the image is identical. The scan sizes are 200Å × 200Å and 100Å × 100Å, respectively. Both images are taken with a bias voltage of 240mV and a tunneling current of 1.13nA.
Some parts of the image look blurry, with stripe-like noise running parallel to the horizontal direction (the slow scan direction of the tip). This is well known to be due to the motion of the surface feature under the sweeping of the tip. The movement of naphthalene molecules on bare Rh(111) induced by the tip under similar tunneling conditions was not observed. This suggests that naphthalene attaches less strongly to the oxygen-covered Rh(111) than to a bare Rh(111). This can also be proven by the fact that naphthalene is less ordered and has less coverage on the oxygen-covered Rh(111) surface even though the naphthalene exposure was very high during the preparation.

A (4×4) arrangement of naphthalene molecules was also observed by electrochemical STM on Cu(111) surface in HClO₄ solution [12]. The surface has long-range ordering, and all molecules have the same orientation, presumably along the close-packed direction of the Cu(111) surface. Combining the results in this dissertation work for the Rh(111) surface, in Ref. 12 for Cu(111) surface, and Ref. 5-7 and Ref 11 for Pt(111), the bonding energy of naphthalene on these surfaces can be summarized as Rh(111) > Pt(111) > Cu(111) > oxygen-covered Rh(111).

8.4.4 Naphthalene co-adsorption with H₂ on Rh(111)

The motivation of the study presented in this section was to investigate the stability of the Rh-naphthalene adsorption structure in various pressures of H₂. The structure in the presence of a low pressure of H₂ was only inspected briefly. Figure 8.26 shows the STM images of the surface of naphthalene-adsorbed Rh(111) exposed to H₂. The left and right images were taken, respectively, in 1×10⁻⁴ torr and 2 torr of H₂ at room temperature. In the low pressure range this particular surface has the (3√3×3√3)R30° structure. No apparent effect of low pressure H₂ (<1×10⁻⁴ torr) on the phase transition of
naphthalene overlayers was observed. Similar to the O\textsubscript{2} case, this is also due to the dissociative adsorption nature of H\textsubscript{2} on Rh(111).

Under a high pressure of H\textsubscript{2}, the surface became completely disordered. No naphthalene molecules were discerned any more. The surface was covered with randomly distributed bright features. This suggests that H\textsubscript{2} with a pressure in the torr range of H\textsubscript{2} may destroy the adsorption of naphthalene on Rh(111), possibly through simple desorption of naphthalene or even a hydrogenation/hydrogenolysis reaction.

Figure 8.26 STM images of the surface of naphthalene-adsorbed Rh(111) exposed to H\textsubscript{2}. The left and right images were taken respectively in 1×10\textsuperscript{-4} torr and 2 torr of H\textsubscript{2} at room temperature. In the low pressure range the surface kept the (3\sqrt{3}\times3\sqrt{3})R30° structure (as indicated by the holes in the unit cell). Under high pressure H\textsubscript{2}, the surface became completely disordered, and only randomly distributed bright features can be seen. This suggests that H\textsubscript{2} with a pressure in the torr range can possibly destroy the adsorption of naphthalene on Rh(111) through simple desorption of naphthalene or even a hydrogenation/hydrogenolysis reaction. The scan sizes are all 200Å × 200Å. Images were taken with a bias voltage of 476 and 424mV and a tunneling current of 1.17nA and 1.15nA, respectively.
8.4.5 The bias polarity effect on image

An interesting phenomenon was often observed when imaging the \((3\sqrt{3}\times3\sqrt{3})R30^\circ\) naphthalene structure on the Rh(111) surface. The topography changes as a function of the bias polarity. In Figure 8.27, a series of four images taken with the same area as the Rh(111)-\((3\sqrt{3}\times3\sqrt{3})R30^\circ\)-naphthalene structure are shown. At +404mV bias, black holes representing naked Rh atoms are clearly seen as occupying a \((3\sqrt{3}\times3\sqrt{3})R30^\circ\) lattice. At −404mV bias, however, the positions where black holes were previously located had much smaller corrugation, and the surface appeared similar to a \((3\times3)\) arrangement. The switching between the two appearances was very reproducible on a time scale of 30–60 minutes, and could be repeated from one experiment to another. In Figure 8.28, the two STM images were taken on a Rh(111)-\((3\sqrt{3}\times3\sqrt{3})R30^\circ\)-naphthalene structure exposed to \(1\times10^{-4}\) torr H\(_2\), showing the same phenomenon. At +476mV bias voltage, triangular holes can be seen, while at −476mV bias they are not visible and the surface shows the \((3\times3)\) symmetry. This phenomenon could be seen at a bias range from tenths of millivolts to several volts without an apparent threshold, but the contrast was optimized at around 400mV. However, it was not observed on Rh(111) with coadsorbed naphthalene and CO.

This reproducible image conversion can be attributed to two possible changes that can happen under the tip with the flip of the bias. One is the alignment/recovery of all naphthalene molecules in the \((3\sqrt{3}\times3\sqrt{3})R30^\circ\) unit cell, and the other is the shift of the tip at the Fermi level with respect to the profile of local electronic density on the bare Rh atom. The first involves a physical change of the naphthalene overlayer, and the second is a pure electronic effect. By plain STM images, none of the two possibilities can be
easily ruled out. The fact that switching was not observed for the CO co-adsorption case offers no help in eliminating one of the two possibilities, because although without a doubt the adsorption of CO can hinder the rotation of the naphthalene molecules, it can also greatly change the local density of states over the Rh atom. Further inspection by scanning tunneling spectroscopy may be very useful in giving an answer.

Figure 8.27 The STM images change in the appearance as a function of the bias polarity. This series of four images are taken at the same area as the Rh(111)-(3\sqrt{3}x3\sqrt{3})R30°-naphthalene structure. At positive bias, black holes representing naked Rh atoms are clearly seen. At negative bias, however, the positions where black holes used to be located at have much smaller corrugations, and the surface appears similar to a (3x3) arrangement. This reproducible image conversion can be attributed to the rotation of naphthalene molecules in the unit cell, or a pure electronic effect. The scan sizes are all 100Å x 100Å. Images were all taken with a tunneling current of 1.04nA.
Figure 8.28  STM images taken on a Rh(111)- (3√3×3√3)R30°-naphthalene structure exposed to 1×10⁻⁴ torr H₂, showing the same polarity effect as in Figure 8.27. At +476mV bias voltage, triangular holes can be seen, while at -476mV bias they are not visible and the surface shows the (3×3) symmetry. The scan sizes are both 200Å × 200Å. Both images were taken with a tunneling current of 1.14nA. A similar phenomenon was not observed on Rh(111) with coadsorbed naphthalene and CO.
8.5 Phenanthrene on Rh(111) and Pt(111)

No phenanthrene adsorption study has been published. Compared with benzene (D$_{6h}$), naphthalene (D$_{2h}$) and anthracene (D$_{2h}$), phenanthrene has the lowest symmetry (C$_{2v}$), so by intuition, it is expected to have lower ordering when adsorbed on a single crystal metal surface. In this dissertation work, phenanthrene adsorption on Rh(111) and Pt(111) were examined. Then, at an elevated temperature and/or in the presence of CO, O$_2$ and NO, its adsorption was inspected again to find out whether there is any change or promotion in the ordering.

8.5.1 Phenanthrene adsorption on Rh(111)

The sample was prepared by exposing the clean Rh(111) to 15L of phenanthrene at room temperature. The sample showed no ordering in the LEED pattern. Figure 8.29 shows a STM image of the sample. The kidney-shaped molecules, without overlapping with others, cover the whole surface. All molecules appear to be flat on the surface, as the contrast on each molecule is the same and it is uniform over the whole image. Note that the C$_2$ axis of each molecule is along one of the [110] directions. This can be more clearly seen in STM images with higher resolution. In Figure 8.30, at those resolutions, each of the molecules show up as a feature consisting of three non-separated bright lobes, which is consistent with the three-ringed molecular geometry. However, the rings were not resolved. The corrugation of the molecules is 0.3~0.6Å, similar to those of benzene and naphthalene.
Figure 8.29  200Å × 200Å STM image of phenanthrene on Rh(111). The sample was prepared by exposing the cleaned Rh(111) to 15L of phenanthrene. The kidney-shaped molecules cover the whole surface. All molecules appear to be flat on the surface, and the C$_2$ axis of each molecule is aligned with one of the [110] directions. The image was taken with a bias voltage of 1.0V and a tunneling current of 1.13nA.
Figure 8.30 High resolution STM images of phenathrene adsorbed on Rh(111). No preferential orientation for the molecules can be found. Each of the molecules shows up as a feature consisting of three non-separated bright lobes, well consistent with the three-ringed molecular geometry. However, the rings were not resolved. Unambiguously, the C\textsubscript{2} axis of each molecule is along one [110] direction. The corrugation is 0.3~0.6Å. The scan sizes are 100Å \times 100Å for the left, and 50Å \times 50Å for the right image. Both images were taken with a bias voltage of 1.0V and a tunneling current of 1.13nA.
8.5.2 Phenanthrene co-adsorption with CO and O₂ on Rh(111)

In the presence of CO and O₂, regardless of whether the phenanthrene is dosed before or after the gas is introduced, LEED inspections of the surface showed no indication of ordering. STM studies gave the same results as in the case of pure phenanthrene adsorbed on the surface, i.e., the surface had no long-range ordering, but each molecule had its C₂ axis oriented with one of the [110] directions. Figure 8.31 shows STM images of phenathrene co-adsorbed with CO (left) and oxygen (right) on Rh(111). The samples were prepared by exposing a clean Rh(111) surface to 10L or 5L of phenanthrene, and then to 2×10⁻⁷ torr of CO or 1×10⁻⁷ torr of O₂, respectively. The surface coverage as a function of the phenanthrene dosage is clearly shown, as the coverage of the right image is much smaller than the left one, in accordance with the 10L and 5L dosage, respectively. The corrugation is as large as 0.5~0.7Å. No co-adsorbed CO or oxygen was resolved in either image. However, in both images, there are some fuzzy features between the phenanthrene molecules, which can be attributed to highly mobile small co-adsorbed molecules.
The samples were prepared by exposing a clean Rh(111) surface to 10L or 5L of phenanthrene, and then to $2 \times 10^{-7}$ torr of CO or $1 \times 10^{-7}$ torr of O$_2$ for 60 seconds, respectively. The surface coverage as a function of the phenanthrene dosage is clearly shown, as the coverage of the right image is much lower than the left one (in accordance with the 10L and 5L dosage respectively). No co-adsorbed CO or oxygen was resolved. The corrugation of the molecules is as large as 0.5~0.7Å. Since the molecules are well separated from each other, this corrugation represents the apparent "height" of the phenanthrene, or the "thickness" of the phenyl ring. The images were taken with a bias voltage of 390mV and 1.0V, and a tunneling current of 1.09nA and 1.07nA, respectively.
8.5.3 Phenanthrene adsorption on Rh(111) in the presence of NO

The adsorption of both phenanthrene and NO on Rh(111) shows phase separation. The sample was a Rh(111) surface partially covered with phenanthrene (2L) and NO (100L). It generated a very sharp (2x2) pattern, corresponding to the NO adsorption lattice, as shown in Figure 8.32. The STM image of this sample showed clear (2x2) domains of NO. All rows of NO molecules are along the [110] direction. Many large bright features, corresponding to individual phenanthrene molecules, are randomly distributed on the empty spaces or between NO domains. To the right, a (2x2) lattice, which is extrapolated from the NO lattice, was superimposed on the same image to guide the viewer's vision. It can be seen that the positions of the phenanthrene molecules have no correlation with those lattice points, indicating that they adsorb on the Rh(111) with no preferential site.

Figure 8.32 LEED pattern for a Rh(111) surface partially covered with phenanthrene and NO, taken at 100eV. A sharp (2x2) pattern, corresponding to the NO adsorption lattice is highlighted by a hexagon.
Figure 8.33  (A) 100Å×100Å STM image of a Rh(111) surface co-adsorbed with phenanthrene (2L) and NO (100L). The (2×2) domains of NO are clearly imaged. Many large bright features, corresponding to individual phenanthrene molecules, are randomly distributed in the empty space or between NO domains. The NO molecular rows and the C₂ axes of phenanthrene molecules are all along the [110] directions. The image was taken with a bias voltage of 1.0V and a tunneling current of 0.98nA. (B). A (2×2) lattice, which is extrapolated from the NO lattice, was superimposed on the same image to guide the viewer’s vision. The positions of the phenanthrene molecules have no correlation with those lattice points, indicating that they adsorb on Rh(111) with no preferential site. However, the C₂ axis of each molecule remains along one of the [110] directions.
8.5.4 Phenanthrene adsorption on Pt(111)

Phenanthrene adsorption on Pt(111) was briefly investigated. It was found that it was very similar to phenanthrene adsorption on Rh(111), i.e., regardless of whether it was alone on the surface or co-adsorbed with CO, O₂ or NO, no long-range ordering was observed. More aggressive sample preparation conditions were tried to promote the surface ordering, but met with no success. Figure 8.34 shows STM images of phenathrene co-adsorbed with CO on Pt(111). The sample was prepared by heating the crystal to 200°C and dosing 10L phenanthrene in the presence of 1×10⁻⁷ torr CO and then cooling to room temperature before taking STM images. Compared with Rh(111), phenanthrene adsorbs on Pt(111) largely in the same fashion, and CO does not seem to promote surface ordering. The corrugation is 0.3~0.6Å, as on Rh(111).
Figure 8.34 STM images of phenanthrene co-adsorbed with CO on Pt(111). The sample was prepared by heating the crystal to 200°C and dosing 10L phenanthrene in the presence of $1\times10^{-7}$ torr CO and then cooling to room temperature before taking STM images. Compared with on Rh(111), phenanthrene adsorbs on Pt(111) largely in the same fashion, and CO does not seem to promote surface ordering. The corrugation is 0.3–0.6Å, as on Rh(111). The scan sizes are 100Å × 100Å for the left, and 50Å × 50Å for the right one. Both images were taken with a bias voltage of 0.74V and a tunneling current of 0.99nA.
8.6 Anthracene on Rh(111) and Pt(111)

No study has been published for the anthracene adsorption on a metal surface under UHV conditions. However, electrochemical STM has been used to image anthracene on Rh(111) [11] and Cu(111) [12] in solutions. On Rh(111) in HF solution, anthracene molecules adsorb with their long axes preferentially along the close-packed direction of Rh, i.e., the [110] direction. There is no ordering in the long range. On Cu(111) in HClO$_4$ solution, anthracene molecules occupy a (4×4) lattice, and the long axes of all molecules are along the [110] direction of the Cu(111) substrate to form straight molecular chains formed with a side-by-side configuration. In both cases, the internal molecular structure was elucidated with clear identification of three craters per molecule.

In this dissertation work, anthracene adsorption on Rh(111) and Pt(111) was studied. However, the dosing of anthracene was found to be very difficult to perform. The coverage of anthracene, checked with STM afterwards, was very hard to control. The mass spectrum taken during the dosing process often showed major peaks at mass 128 and 140 instead of 178 (the anthracene mass), which strongly suggested that either there are considerable amount of impurities in the anthracene source, or anthracene was cracked even before being dosed on the crystal. To prepare a sample that had anthracene adsorbed on without a doubt, the leak valve and the induct tube needed to be heated and pumped several times to get rid of any residual impurities with small masses before the anthracene reservoir was heated. However, this process involved using the UHV chamber to pump the leak valve from inside, which could contaminate the crystal significantly, and increase the base pressure by a factor of ten, if not more.
acceptable sample was verified by the mass spectrum, which showed a high molecular peak at 178, as shown in Figure 8.3.

Figure 8.35 is the image of anthracene adsorbed on Rh(111). The sample was prepared by exposing the clean Rh(111) to 40L of anthracene at room temperature. The shape of individual molecules is resolved. Each molecule has a depression along the long axis, instead of a three-ring feature. The long axes of the molecules are pointed to random directions. All molecules appear to be flat on the surface. The corrugation is 0.3–0.6 Å, similar to that of phenanthrene on Rh(111).

This UHV STM result revealed the random nature of the molecular adsorption, which considerably disagrees with the result obtained in HF solution [11]. Obviously the sample preparation played an important role. The adsorption energy of anthracene on Rh(111) is presumably very large, so the adsorbate – adsorbate repulsion force is not enough to make the adsorbed molecule translate or rotate to arrange in an aligned overlayer. In solution, however, the adsorbate is surrounded by ~10^23/cm^3 solvent molecules. The constant collisions from the solvent molecules will help the organic molecules on the surface overcome the translation or rotation barrier, so they can more likely form an ordered structure than in a UHV environment. Increasing the temperature can certainly improve the mobility of the organic molecules, but it also causes decomposition, so at certain point, it would become extremely difficult to use traditional UHV techniques to perform the adsorption studies of the compounds with low vapor pressures. However, transferring the compounds into solution and then conducting STM studies seems a very promising approach to circumvent the difficulty.
Figure 8.35 100Å × 100Å STM image of anthracene adsorbed on Rh(111). The shape of individual molecules is resolved. Each molecule has a depression along the long axis, but the three-ring structure is not seen, neither is the three-lobe shape of phenanthrene. The long axes of the molecules are along random directions. All molecules appear to be flat on the surface. The corrugation is 0.3~0.6 Å, similar to that of phenanthrene on Rh(111). The image was taken with a bias voltage of 1.0V and a tunneling current of 1.27nA.
8.7 Influences of high pressure $O_2$ and $H_2$ on the adsorption of aromatic compounds

As an extension of the tip catalysis work discussed in Chapter 7, the possibilities of using a Pt STM tip to induce the oxidation/ hydrogenation of individual molecules on Rh(111) and Pt(111) in the presence of a high pressure of $O_2$ or $H_2$ were also explored. The motivation was to perform the tip-catalyzed reaction on a molecular level, i.e., to use the tip to both induce the reaction on a particular molecule, and image any change the molecule may undergo. If the reaction can be imaged at all, the molecular changes one may expect to see include a molecular shape or the orientation change, polymerization/cracking, and desorption/re-adsorption. In any case, a distinctive molecular shape visible to STM is of great value. In this sense, to conduct a high-resolution study of tip catalysis, aromatic molecules would be reasonable to start with. However, preliminary results showed no success. It is presumably due to the significant replacement of the organic molecules by high pressure $O_2$ or $H_2$, the mobility of the molecules on the surface, and certainly, the oxidation/hydrogenation reactivity of these molecules.

The stabilities of benzene, naphthalene and phenanthrene adsorption structures on Rh(111) in the presence of a high pressure of $O_2$ and $H_2$ were inspected. Pre-adsorbed benzene can be replaced by $O_2$ even when the $O_2$ pressure is as low as $1 \times 10^{-6}$ torr. Benzene adsorption structure cannot survive high pressure $H_2$ either. Naphthalene adsorption structure on Rh(111) is stable in 15 torr of $O_2$ (Figure 8.23), but not in 2 torr of $H_2$ (Figure 8.26). Phenanthrene on Rh(111) is stable in high pressure of both $O_2$ and
H₂. There is a clear trend that as the molecule becomes larger, it can survive a higher gas pressure. This is a natural outcome of stronger bonding to the substrate.

When the molecules were found to be stable in high pressure of either O₂ or H₂, the tip-induced reaction was tried with the procedure as described in Chapter 7. However, no convincing indication of a reaction was observed. The surface features were found to be either too mobile to get repeatable images, or too inert to detect any change after imaging long after. The former is due to the high-pressure environment, where the strong interaction and mass flow between the adsorbate and gas phase species greatly affect the tunneling condition. The latter can be attributed to the fact that the high stability of these four molecules may prevent oxidation/hydrogenation at room temperature, so there is essentially no reaction happening. It is then recommended that to further explore the possibility of high resolution tip catalysis, a reaction with lower activation energy be conducted. A reaction that happens naturally at room temperature and requires no high-pressure reactant gas would be a promising candidate.

8.8 Summary

In this chapter, the adsorption of benzene, naphthalene, phenanthrene and anthracene on Rh(111) and Pt(111) at room temperature was systematically investigated. It was found that:

1. The distinctive shapes of all four molecules were imaged. They have a shape of crater, dumbbell, kidney with three non-separated lobes, and long ellipse with one depression, respectively. All molecules lie flat on the substrate.
2. Benzene forms (3×3) and c(2√3×4) overlayers on Rh(111). All adsorption domains were imaged, and the adsorption sites were found to be uniform. When co-adsorbed with NO, benzene arranges in a (3×3) overlayer.

3. Naphthalene forms (3×3) and (3√3×3√3)R30° overlayers on Rh(111). The former structure can be transformed into the latter one by co-adsorbing naphthalene with CO. The adsorption model of naphthalene on Rh(111) can be proposed with great confidence.

4. While low pressures of O₂ and H₂ cannot change the structure of a naphthalene pre-covered Rh(111) surface, the naphthalene adsorption onto an oxygen pre-covered Rh(111) shows a new (4×4) structure. In all naphthalene adsorption structures, the long axis of naphthalene is always along the close-packed direction of the Rh atoms.

5. Electronic effects of STM imaging were used to explain the fact that in every co-adsorption structure, only the organic molecules could be imaged. A similar effect, combined with a tip-induced phase transition of naphthalene overlayers, could be the cause of a “bias polarity-tuned” conversion of the naphthalene image between the two appearances.

6. Phenanthrene has no long-range ordering regardless of whether it is along or co-adsorbed with other molecules. However, its C₂ axis is always along one of the [110] directions of the Rh(111) substrate.

7. Anthracene is disordered with random molecular orientation on Rh(111).

8. The stabilities of benzene, naphthalene and phenanthrene adsorption structure on Rh(111) in the presence of a high pressure of O₂ and H₂ increase as the
molecules become larger. Attempts to conduct the tip-induced catalytic oxidation/hydrogenation of those molecules on Rh(111) and Pt(111) were largely unsuccessful because STM could not image the highly mobile surface species and/or induce the reactions of the inert organics.
References

Chapter 9
Conclusions

In this dissertation work, the structures and dynamics of molecular monolayers on Rh(111) and Pt(111) were studied by scanning tunneling microscopy.

Oxygen and nitric oxide chemisorption on Rh(111) in vacuum was examined by STM and LEED. Rh(111) exposed to high pressure oxygen was also imaged by STM. Oxygen was found to form only the (2×2) ordered structure in low exposure of oxygen and in up to 10 torr O₂ in the background, contradicting some previous reports of three domains of (2×1) structures. Large disordered features with high corrugation were found on the surface when Rh(111) was exposed to a high pressure of oxygen, suggesting a concurrent nucleation of atomic oxygen localized around carbon impurities with increasing oxygen pressure. Nitric oxide forms a Rh(111)-(2×2)-3NO structure, which has an identical two-dimensional unit cell arrangement to the Rh(111)-(2×2)-3CO adsorption structure. In a perfectly ordered area, due to the geometric and electronic density differences in the three NO molecules in one unit cell, only the one at the atop site can be imaged. However, one or more NO molecules missing in the unit cell can still be distinguished, suggesting that the apparently large corrugation of NO molecules adsorbed at the atop site has the combined contributions from all three molecules in the unit cell.

The adsorption and decomposition behavior of propylene on Rh(111) and Pt(111) were investigated by STM with the assistance of LEED. It was found that, at room temperature, propylidyne adsorbs stably on Pt(111) in a (2×2) fashion, but upon exposure
to CO, it decomposes to disordered small fragments. On Rh(111), however, propylene decomposes to propylidyne and forms a (2×2) overlayer briefly, then undergoes further decomposition and breaks into ethylidyne and C-H fragments. Ethylidyne can co-adsorb with CO and form a stable c(4×2) overlayer. On both metals, CO seems to expedite the decomposition of propylidyne into small species. At each stage of thermal decomposition of propylene on Rh(111), STM images were taken and compared with the result for Pt(111) reported in the literature. At 155°C, 265°C, 400°C and 600°C, the adsorbed propylene on Rh(111) decomposes into CₓH fragments, carbonaceous clusters, polymers, and graphite, respectively. Compared with propylene thermal decomposition on Pt(111), the propylene decomposition on Rh(111) generates more uniformly distributed particles over the surface in every stage before the formation of graphite, and the sizes of the particles are generally smaller. These differences are tentatively attributed to kinetic factors during the cracking process of propylidyne.

Pt STM tip-catalyzed hydrogenation and oxidation reactions of carbonaceous species on the Rh(111) surface were presented for the first time. The pressure, tip composition and tunneling gap dependencies of the tip catalysis were investigated. It was found that the reactions only proceeded in the presence of O₂ or H₂ and when a Pt (not W or Au) tip was used. The reaction rate slightly increases as the background pressure increases and tunneling gap decreases. In comparison with the study on Pt(111) previously reported, the tip-induced catalytic reactions have similar behaviors in the sense that reaction rates are the same order of magnitude, and the extent of the reaction is roughly the same. This indicates that on both Rh(111) and Pt(111) surfaces a common mechanism should account for the reactions. It appears that the kinetics rather than
thermodynamics dominate in the tip catalysis process in order to explain the rate differences between the reactions on Pt(111) and Rh(111).

The adsorption of benzene, naphthalene, phenanthrene and anthracene on Rh(111) at room temperature was systematically investigated. The distinctive shapes of all four molecules were imaged by STM. All molecules lie flat on the substrate. Benzene forms (3×3) and c(2√3×4) overlayers on Rh(111). When co-adsorbed with NO, benzene arranges in a (3×3) overlayer. Naphthalene forms (3×3) and (3√3×3√3)R30° overlayers on Rh(111). The former structure can be transformed into the latter one by co-adsorbing naphthalene with CO. The adsorption model of naphthalene on Rh(111) can be proposed with great confidence. Low pressure of O₂ and H₂ cannot change the structure of a naphthalene pre-covered Rh(111) surface, but the naphthalene adsorption onto an oxygen pre-covered Rh(111) shows a new (4×4) structure. In all naphthalene adsorption structures, the long axis of naphthalene is always along the close-packed direction of the Rh atoms. Phenanthrene and anthracene have no long-range ordering, regardless of whether it is alone or co-adsorbed with other molecules. However, the C₂ axis of phenanthrene is always along one of the [110] directions of the Rh(111) substrate, while anthracene is randomly oriented.

The stabilities of benzene, naphthalene and phenanthrene adsorption structures on Rh(111) in the presence of high pressure O₂ and H₂ increase as the molecules become larger. Attempts to conduct the tip-induced catalytic oxidation/hydrogenation of those molecules on Rh(111) and Pt(111) were largely unsuccessful, presumably due to the difficulties in imaging the highly mobile surface species and/or inducing the reaction of the inert organics.