Fundamental Studies of Nitrogen and Hydrocarbons on Metal Surfaces

BY

JUN YIN
B.A. (University of Central South University) 1999
M.S. (University of Central South University) 2003

THESIS

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>1.1</td>
<td>NO\textsubscript{x} emission and regulations</td>
</tr>
<tr>
<td>1.2</td>
<td>NO\textsubscript{x} removal in stationary sources</td>
</tr>
<tr>
<td>1.3</td>
<td>NO\textsubscript{x} removal in mobile sources</td>
</tr>
<tr>
<td>1.3.1</td>
<td>Background</td>
</tr>
<tr>
<td>1.3.2</td>
<td>Technology review</td>
</tr>
<tr>
<td>1.3.2.1</td>
<td>Lean NO\textsubscript{x} trap</td>
</tr>
<tr>
<td>1.3.2.2</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>1.3.2.3</td>
<td>Selective Catalytic Reduction</td>
</tr>
<tr>
<td>1.4</td>
<td>Hydrocarbon SCR catalysts</td>
</tr>
<tr>
<td>1.5</td>
<td>Reaction mechanism</td>
</tr>
<tr>
<td>1.5.1</td>
<td>Decomposition mechanism</td>
</tr>
<tr>
<td>1.5.2</td>
<td>Reaction intermediates</td>
</tr>
<tr>
<td>1.6</td>
<td>Elementary steps-microscopic level</td>
</tr>
<tr>
<td>1.6.1</td>
<td>NO adsorption on Pt surfaces</td>
</tr>
<tr>
<td>1.6.2</td>
<td>NO dissociation on Pt surfaces</td>
</tr>
<tr>
<td>1.6.3</td>
<td>NO\textsubscript{2} and oxygenate hydrocarbon species</td>
</tr>
<tr>
<td>1.6.4</td>
<td>Summary</td>
</tr>
<tr>
<td>1.7</td>
<td>Surface science: Unraveling reaction mechanisms through model systems</td>
</tr>
<tr>
<td>1.7.1</td>
<td>Motivation</td>
</tr>
<tr>
<td>1.7.2</td>
<td>The recent development of surface science</td>
</tr>
<tr>
<td>1.7.2.1</td>
<td>Bridging the pressure gap</td>
</tr>
<tr>
<td>1.7.2.2</td>
<td>Bridging the material gap</td>
</tr>
<tr>
<td>1.8</td>
<td>Experimental Preview</td>
</tr>
<tr>
<td>2</td>
<td>EXPERIMENTAL</td>
</tr>
<tr>
<td>2.1</td>
<td>Construction a UHV system with high pressure capabilities</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Background</td>
</tr>
<tr>
<td>2.1.2</td>
<td>System description</td>
</tr>
<tr>
<td>2.1.3</td>
<td>Pumping scheme</td>
</tr>
<tr>
<td>2.2</td>
<td>Experimental methods</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>2.2.4</td>
<td>Reflection Absorption Infrared Spectroscopy</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3 PROOF OF PRINCIPLE EXPERIMENTS-HIGH PRESSURE STUDY</strong></td>
<td></td>
</tr>
<tr>
<td>3.1 N\textsubscript{2} adsorption on Ni(110)-a high pressure study</td>
<td>46</td>
</tr>
<tr>
<td>3.1.1 Motivation</td>
<td>46</td>
</tr>
<tr>
<td>3.1.2 Background</td>
<td>47</td>
</tr>
<tr>
<td>3.1.3 Experimental</td>
<td>49</td>
</tr>
<tr>
<td>3.1.4 Results and discussion</td>
<td>50</td>
</tr>
<tr>
<td>3.1.4.1 Cleaning procedure</td>
<td>50</td>
</tr>
<tr>
<td>3.1.4.2 RAIRS study of nitrogen adsorption on the Ni(110) surface</td>
<td>51</td>
</tr>
<tr>
<td>3.1.4.3 NO baking of the stainless steel chamber</td>
<td>54</td>
</tr>
<tr>
<td>3.1.4.4 RAIRS study of nitrogen adsorption on the Ni(110) surface after a NO bake out</td>
<td>55</td>
</tr>
<tr>
<td>3.2 Hydrogenation of the N layer on Pt(111)</td>
<td>60</td>
</tr>
<tr>
<td>3.2.1 Background</td>
<td>60</td>
</tr>
<tr>
<td>3.2.2 Results and discussion</td>
<td>61</td>
</tr>
<tr>
<td><strong>4 FORMATION OF π BONDED ETHYLENE</strong></td>
<td>70</td>
</tr>
<tr>
<td>4.1 Summary</td>
<td>70</td>
</tr>
<tr>
<td>4.2 Background</td>
<td>70</td>
</tr>
<tr>
<td>4.3 Experimental</td>
<td>73</td>
</tr>
<tr>
<td>4.4 Computational Methodology</td>
<td>74</td>
</tr>
<tr>
<td>4.5 Results and discussion</td>
<td>74</td>
</tr>
<tr>
<td>4.6 Conclusion</td>
<td>86</td>
</tr>
<tr>
<td><strong>5 AMMONIA FORMATION BY HYDROGENATION OF N ATOMS ON PT(111)</strong></td>
<td>88</td>
</tr>
<tr>
<td>5.1 Background</td>
<td>88</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>91</td>
</tr>
<tr>
<td>5.3 Results and discussion</td>
<td>92</td>
</tr>
<tr>
<td>5.3.1 Ammonia formation from the reaction of acetylene with nitrogen covered Pt(111)</td>
<td>92</td>
</tr>
<tr>
<td>5.3.2 Hydrogenation of N layer by deuterium</td>
<td>97</td>
</tr>
<tr>
<td>5.3.3 Ammonia formation from ethylene reaction with nitrogen covered Pt(111)</td>
<td>100</td>
</tr>
<tr>
<td><strong>6 C-N COUPLING REACTION OF ETHYLENE ON N-COVERED PT(111)</strong></td>
<td>111</td>
</tr>
<tr>
<td>6.1 Background</td>
<td>111</td>
</tr>
<tr>
<td>6.2 Experimental</td>
<td>114</td>
</tr>
<tr>
<td>6.3 Results and discussion</td>
<td>115</td>
</tr>
<tr>
<td>6.3.1 TPRS study</td>
<td>115</td>
</tr>
<tr>
<td>6.3.2 RAIRS study</td>
<td>117</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

CHAPTER

CITED LITERATURE ........................................... 125
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td>97</td>
</tr>
<tr>
<td>III</td>
<td>107</td>
</tr>
</tbody>
</table>

I. STRATEGIES FOR REDUCING NO$_X$ EMISSIONS FROM DIESEL ENGINES. 
II. FITTING RESULTS OF C$_2$D$_2$ ON PT(111) 
III. FITTING RESULTS OF C$_2$D$_4$ ON PT(111)
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Sources of NO\textsubscript{x} (EPA, 2002).</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>NH\textsubscript{3}-SCR in a stationary source.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>NH\textsubscript{3}-SCR in mobile source.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>The direct NO decomposition mechanism.</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>The indirect NO reaction mechanism via hydrocarbon intermediates.</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>Schematic cartoon of the high pressure chamber.</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>28</td>
</tr>
<tr>
<td>The sliding seal.</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>28</td>
</tr>
<tr>
<td>Pumping scheme for the high pressure system.</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>30</td>
</tr>
<tr>
<td>The quadrupole mass spectrometer system.</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>LEED optics.</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>36</td>
</tr>
<tr>
<td>The Universal curve describe the relationship between the kinetic energy of an electron and its mean free path in a solid.</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>39</td>
</tr>
<tr>
<td>Schematic of the Auger process.</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>40</td>
</tr>
<tr>
<td>Geometry of the CMA Auger spectrometer.</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>42</td>
</tr>
<tr>
<td>Schematic diagram of a Michelson interferometer.</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>52</td>
</tr>
<tr>
<td>AES spectra of the Ni(110) surface, demonstrating the cleaning process.</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>53</td>
</tr>
<tr>
<td>IR spectra of nitrogen adsorption on the Ni(110) surface at 120 K.</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>56</td>
</tr>
<tr>
<td>The NO baking effect, expose nitrogen to the chamber, and monitor changes of various mass signals (m/z= 28, 2, 14, 12 ) before and after a NO bake out.</td>
<td></td>
</tr>
<tr>
<td>FIGURE</td>
<td>TEXT</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>18</td>
<td>IR spectra of nitrogen adsorption on the Ni(110) surface at 176 K after a NO bake out. .................................................. 57</td>
</tr>
<tr>
<td>19</td>
<td>IR spectra of nitrogen adsorption on the Ni(110) surface at 193 K after an NO bake out. .................................................. 59</td>
</tr>
<tr>
<td>20</td>
<td>AES spectra of the Pt(111) surface, demonstrating the cleaning process to obtain clean surface. ........................................ 62</td>
</tr>
<tr>
<td>21</td>
<td>AES spectra vs O\textsubscript{2} exposure to Pt(111) at room temperature. ........ 63</td>
</tr>
<tr>
<td>22</td>
<td>LEED pattern of the (2 x 2) O\textsubscript{2} on Pt(111). .......................... 64</td>
</tr>
<tr>
<td>23</td>
<td>AES spectra of N layer on Pt(111), following preparation of the N layer on Pt(111). .................................................. 66</td>
</tr>
<tr>
<td>24</td>
<td>IR spectra of hydrogenation of N layer on Pt(111) at room temperature at elevated pressure. ........................................... 67</td>
</tr>
<tr>
<td>25</td>
<td>IR spectra of N hydrogenation on Pt(111) at room temperature at torr level pressure. .................................................. 69</td>
</tr>
<tr>
<td>26</td>
<td>TPD results for m/z = 14 and m/z = 28 of nitrogen layer on Pt(111). . 75</td>
</tr>
<tr>
<td>27</td>
<td>LEED pattern obtained after preparing P(2 x 2)-N/Pt(111). .............. 76</td>
</tr>
<tr>
<td>28</td>
<td>LEED pattern obtained after annealing the P(2 x 2)-N/Pt(111)surface to 420 K. .................................................. 77</td>
</tr>
<tr>
<td>29</td>
<td>LEED pattern obtained after annealing the P(2 x 2)-N/Pt(111)surface to 450 K. .................................................. 78</td>
</tr>
<tr>
<td>30</td>
<td>AES spectra of nitrogen layer on Pt(111). ................................... 79</td>
</tr>
<tr>
<td>31</td>
<td>TPD spectra of 0.8 L of ethylene from clean Pt(111) and from 0.25 ML of nitrogen on Pt(111). .................................................. 80</td>
</tr>
<tr>
<td>32</td>
<td>RAIR spectra following exposure of 0.8 L of ethylene to 0.25 ML of nitrogen on Pt(111). .................................................. 83</td>
</tr>
<tr>
<td>33</td>
<td>PDOS for clean Pt(111) and for Pt(111) covered with 0.25 ML of N... 84</td>
</tr>
<tr>
<td>FIGURE</td>
<td>DESCRIPTION</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>34</td>
<td>RAIR spectra of different ethylene exposures to the p(2 x 2)-N/Pt(111) surface at 90 K, followed by annealing to different temperatures. (a) 0, (b) 0.4, (c) 0.8, and (d) 1.6 L. 85</td>
</tr>
<tr>
<td>35</td>
<td>Cartoon schematic of adsorption site switching of C$_2$H$_4$ on Pt(111) vs. N/Pt(111). 87</td>
</tr>
<tr>
<td>36</td>
<td>ND$_3$ desorption following exposure 0.8 L C$_2$D$_2$ to N covered Pt(111). 94</td>
</tr>
<tr>
<td>37</td>
<td>D$_2$ thermal desorption results following exposure of 0.8 L C$_2$D$_2$ to the Pt(111) surface. 96</td>
</tr>
<tr>
<td>38</td>
<td>D$_2$ thermal desorption results following exposure of 0.8 L C$_2$D$_2$ to the N/Pt(111) surface. 96</td>
</tr>
<tr>
<td>39</td>
<td>TPD results for m/z = 14 following ethylene exposure to Pt(111) and N/Pt(111). 98</td>
</tr>
<tr>
<td>40</td>
<td>TPD results for m/z = 20 (ND$_3$) following 10 L D$_2$ vs 0.8 L C$_2$D$_2$ on N/Pt(111). 101</td>
</tr>
<tr>
<td>41</td>
<td>TPD results for m/z = 4 D$_2$ following 10 L D$_2$ vs 0.8 L C$_2$D$_2$ on N/Pt(111). 101</td>
</tr>
<tr>
<td>42</td>
<td>TPD results for m/z = 20 (ND$_3$) after a 0.8 L ethylene exposure on N/Pt(111) at 350 K, and subsequent exposing 10 L D$_2$ at 90 K vs exposing 0.8 L C$_2$D$_2$ on N/Pt(111). 102</td>
</tr>
<tr>
<td>43</td>
<td>TPD results for m/z = 20 (ND$_3$) desorption after exposing 0.8 L C$_2$D$_4$ to N/Pt(111). 106</td>
</tr>
<tr>
<td>44</td>
<td>TPD results for m/z = 2 (H$_2$) desorption after exposing 0.8 L C$_2$H$_4$ to Pt(111) and N/Pt(111). 106</td>
</tr>
<tr>
<td>45</td>
<td>TPD results for m/z = 20 (ND$_3$) desorption followed by different ethylene exposure on N/Pt(111) 109</td>
</tr>
<tr>
<td>46</td>
<td>TPD results for m/z = 20 (ND$_3$) followed by exposing of 0.8 L acetylene at different temperatures on N/Pt(111) 110</td>
</tr>
<tr>
<td>47</td>
<td>TPD results of HCN desorption followed by exposing 0.8L C$_2$H$_4$ to N covered Pt(111). 116</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>48</td>
<td>TPD results of HCN desorption followed by exposing different amount C\textsubscript{2}H\textsubscript{4} to N covered Pt(111).</td>
</tr>
<tr>
<td>49</td>
<td>TPD results for m/z = 52 (C\textsubscript{2}N\textsubscript{2}) desorption followed by different C\textsubscript{2}H\textsubscript{4} exposure to N covered Pt(111).</td>
</tr>
<tr>
<td>50</td>
<td>TPD results for m/z = 52 (C\textsubscript{2}N\textsubscript{2}) desorption followed exposing 0.8 L C\textsubscript{2}H\textsubscript{4} vs 0.8 L C\textsubscript{2}D\textsubscript{4} to N covered Pt(111).</td>
</tr>
<tr>
<td>51</td>
<td>RAIR spectra followed by exposing 0.8 L C\textsubscript{2}H\textsubscript{4} to N covered Pt(111).</td>
</tr>
<tr>
<td>52</td>
<td>RAIR spectra followed by exposing 0.8 L C\textsubscript{2}H\textsubscript{4} to N covered Pt(111) and annealing to 560 K.</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>ALS</td>
<td>Advanced light source</td>
</tr>
<tr>
<td>APPS</td>
<td>Ambient pressure photoelectron spectroscopy</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental protection agency</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>IRAS</td>
<td>Infrared reflection absorption spectroscopy</td>
</tr>
<tr>
<td>L</td>
<td>Langmuir</td>
</tr>
<tr>
<td>LNC</td>
<td>Lean NO\textsubscript{x} catalyst</td>
</tr>
<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
</tr>
<tr>
<td>MCT</td>
<td>Mercury cadmium telluride</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>NAAQS</td>
<td>National ambient air quality standards</td>
</tr>
</tbody>
</table>

xii
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSR</td>
<td>NO$_2$ storage-reduction</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>RAIRS</td>
<td>Reflection absorption infrared spectroscopy</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SEM</td>
<td>Secondary electron multiplier</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>TAP</td>
<td>Temporal analysis of product</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TPRS</td>
<td>Temperature programmed reaction spectroscopy</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadruple mass spectrometry</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh vacuum</td>
</tr>
<tr>
<td>XAFS</td>
<td>X-ray absorption fine structure</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
</tbody>
</table>
SUMMARY

The selective catalytic reduction (SCR) of NO\textsubscript{x} by hydrocarbons on noble metals is critically important to the implementation of leaner-burning, more fuel-efficient combustion engines in order to handle the increased amount of NO\textsubscript{x} that is produced. Understanding the reaction mechanisms and pathways is essential for designing an effective catalytic system for exhaust treatment. As one small part of this effort, we focus on the interaction of nitrogen atoms and simple unsaturated hydrocarbons such as ethylene and acetylene on the Pt(111) surface under ultra high vacuum conditions to understand the potential intermediates in NO\textsubscript{x} reduction.

In this study, we employ a variety of surface techniques, including temperature programmed desorption (TPD), and reflection absorption infrared spectroscopy (RAIRS) in an attempt to identify reaction pathways in hydrocarbon SCR. Three interesting observations have been made. First, we observed the presence of $\pi$-bonded ethylene below 220 K, indicating a switch in the preferred binding site for ethylene on N-Pt(111) as compared to the clean surface. This result suggests that nitrogen could potentially serve as a promoter in metal catalyzed hydrogenation reactions. Second, the formation of ammonia is observed through ND\textsubscript{3} desorption by using isotopically labeled ethylene or acetylene at 500 K. Because direct reaction between nitrogen atoms and hydrogen does not proceed to form ammonia, the appearance of ammonia is believed to be the result of a reaction between N atoms with coadsorbed ethynyl (CCH). This route to ammonia synthesis has not been previously observed under UHV conditions. Third, above 560 K, CN coupling occurs as indicated by the desorption of HCN and the identification of CNH\textsubscript{2}.
SUMMARY (Continued)

with RAIRS. In addition, a new dual UHV/“high-pressure” chamber has been constructed and tested through two proof of principle experiments. First, nitrogen adsorption on Ni(110) has been examined at pressures ranging up to the torr level. Second, we have studied the hydrogenation of a nitrogen layer on Pt(111) at room temperature to determine the effects of pressure on the ability to achieve a higher coverage of NH than what can be achieved under UHV conditions. A detailed discussion about the system limitations are provided and possible improvements are suggested.
CHAPTER 1

INTRODUCTION

1.1 NO\textsubscript{x} emission and regulations

Nitrogen oxides, also known as NO\textsubscript{x}, are harmful gases that are normally produced as a deleterious byproduct of air-based combustion processes at high temperature. NO\textsubscript{x} has huge negative environmental impacts. For example, NO\textsubscript{x} is a contributor to air pollution (photochemical smog), acid rain and affects human health, especially the respiratory system. Therefore, its emission is rigorously controlled by the Environmental Protection Agency (EPA) in the United States [1].

EPA first set standards for NO\textsubscript{x} in 1971, with 0.053 parts per million (53 ppb) annually. In 1990, the Clean Air Act Amendment required the EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment. The EPA set standards for six “criteria” pollutants, including NO\textsubscript{x}, along with ozone, particulate matter, carbon monoxide, sulfur dioxide and lead. In January 2010, EPA strengthened its NAAQS for nitrogen oxides, adding a one hour NO\textsubscript{x} standard at 100 parts per billion (ppb), primarily near major roads and also updated the monitoring network [2]. The new emission standard for NO\textsubscript{x} control is applied to all major diesel ships, nonroad diesel equipment, locomotives, aircraft and power plants. Figure 1 shows the source of NO\textsubscript{x} emissions, based on
the 2002 national emission inventory data from the EPA [2, 3]. The majority (58%) of NO\textsubscript{x} emissions come from mobile sources, including on road and off road vehicles and equipment.

![Figure 1. Sources of NO\textsubscript{x} (EPA, 2002).](image)

1.2 NO\textsubscript{x} removal in stationary sources

In order to meet the new emission standards, retrofit technologies have been proposed. For most power plants, selective catalytic reduction using ammonia (NH\textsubscript{3}-SCR) as a reductant has been widely used to convert NO\textsubscript{x}. NH\textsubscript{3}-SCR is a well established technology in stationary sources [4], such as industrial boilers, thermal power plants, and cogeneration units.
As shown in Figure 2, in NH$_3$-SCR, ammonia is fed into the flue gas containing with NO$_x$, the gas mixture flows over the catalyst elements, and NO$_x$ is reduced to nitrogen via equation 1.1.

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O$$  \hspace{1cm} (1.1)$$

In addition, this SCR technology can be also combined to remove of SO$_x$ and CO, which makes it a very powerful deNO$_x$ technology. This reaction occurs at temperature between 250 and 450°C, depending on the choice of catalyst. Precious metal catalysts typically activate NO$_x$ reduction at low temperature, while metal oxides require higher temperatures to be active [5,6].

The first SCR systems were installed in Japan in the late 1970s, and then it spread to Europe.
during the 80s, now these systems account for more than 90% of deNO$_x$ gas treatments in Europe.

1.3 **NO$_x$ removal in mobile sources**

1.3.1 **Background**

NO$_x$ removal from mobile sources is more challenging. Normal gasoline engines run at an air to fuel ratio of 14.7, whereas for lean-burn diesel engines, which operate under air-rich conditions, the air to fuel ratio can reach as high as 25:1. High air to fuel ratios improve fuel efficiency and reduce CO$_2$ production but necessarily result in an increase in NO$_x$ production [6–9]. Therefore, to expand the use of more fuel efficient engines, it’s necessary to substantially improve NO$_x$ abatement under increasingly more challenging conditions.

1.3.2 **Technology review**

Technological improvements, such as engine modifications, exhaust gas recirculation, and catalytic after-treatments, have all resulted in significant emission reduction. Table 1 shows the latest “retrofit technologies” for diesel engines. The major technology-based strategies including lean NO$_x$ traps, exhaust gas recirculation, and selective catalytic and non-catalytic reduction.

1.3.2.1 **Lean NO$_x$ trap**

Lean NO$_x$ catalysis (LNC) is a relatively new technology, and it’s capable of achieving NO$_x$ reduction in the range of 10 to 25% [9]. The new technology that’s capable of reducing NO$_x$ in excess oxygen, is also called NO$_x$ storage-reduction (NSR) catalyst [10–12]. The NO$_x$ storage medium is often a Ba salt. During the lean-burn stage, NO$_x$ is oxidized by oxygen and stored in the form of nitrate (NO$_3^-$) in the storage material. In the rich condition, a pulse of a reductant
such as hydrogen or a hydrocarbon is introduced to react with \((\text{NO}_3^-)\) and reduces it into nitrogen, water and carbon dioxide. The first NSR catalysts were developed and put onto the market by Toyota in 1994. The catalyst of choice has been Pt-Ba/Al\(_2\)O\(_3\). One of the biggest problems with this technology is deactivation caused by sulfur and thermal deterioration due to the reaction of storage material with compounds in the wash-coat. Reviews of NSR technology can be found in the literature [10,13].

1.3.2.2 Exhaust gas recirculation

Exhaust gas recirculation (EGR) reduces NO\(_x\) emission by recirculating a portion of the engine’s exhaust and then introducing it to the upstream of the engine in order to dilute the oxygen content of the air entering the engine’s combustion chamber. EGR is able to reduce NO\(_x\) up to 40% or more [9]. The first EGR valves appeared in 1973 on GM cars, bolted to the intake manifold next to the carburetor. Today’s major challenge of the EGR systems is the precision control of the recirculated exhaust flow.
1.3.2.3 **Selective Catalytic Reduction**

Selective Catalytic Reduction (SCR) is a rather mature NO\textsubscript{x} reduction technology used in stationary sources. This catalyst-based strategy can reduce NO\textsubscript{x} up to 90\%, which is the most efficient technology currently available. The primary disadvantage of SCR is the necessity to have ammonia, usually in the form of urea [14]. Although urea is colorless, odorless, nontoxic and biologically harmless, the presence of a urea tank in mobile sources presents an explosion hazard [15]. In addition, the potential risk of ammonia slip requires precise dosing of the reductant and therefore adds complexity and extra costs for monitoring and warning systems, which must be included as a part of the SCR urea injection system. Therefore the installation and maintenance of these systems become difficult to achieve because of these reason.
1.4 Hydrocarbon SCR catalysts

Selective Catalytic Reduction using hydrocarbons is the most promising and stable NO\textsubscript{x} reduction technology. For stationary sources without catalysts, the reduction reaction can occur in the range of 925 to 1125\textdegree C, which is also called “Thermal deNO\textsubscript{x}”. To lower the reaction temperature and achieve kinetic control, catalysts must be employed. In stationary sources, catalyst choice is often dictated by the economics of material costs. Therefore, metal oxides such as chromium, copper, iron and vanadium supported on alumina, silica, and titania are used (though zeolites have drawn a lot of attention in recent years). The most popular catalyst right now is V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} \cite{16}.

The catalyst morphology and pore size distribution are also very critical. A good catalyst should have a nice balance between diffusion of reagents and products and should sustain the reaction by providing high geometric surface areas, as well as possess very good mechanical properties.

For mobile sources, the catalyst has to be active at very low temperature, where the exhaust temperature can be as low as 125\textdegree C. The advantage of noble metal catalysts (specifically platinum group metals), is their ability to be active at low temperatures. For example, Tokota and coworkers reported that Pt catalysts display NO\textsubscript{x} reduction activity even at 373 K \cite{17,18}. However, these catalysts are very expensive, and combustion of the reducing agent dominates at high temperatures, restricting their use to a narrow window with respect to operating temperature and with a relatively lower selectivity towards nitrogen as considerable N\textsubscript{2}O is formed. Traditional three-way catalysts composed of Rh, Pt, Pd that are used for exhaust remediation
of gasoline-powered vehicles are also not very effective under initial startup conditions in diesel engine applications because in the oxygen-rich environment of diesel exhaust, it’s difficult to chemically reduce the NO$_x$ to nitrogen. Therefore, improvement of selective NO$_x$ reduction catalysts under the variable conditions of a mobile emission source remains a long standing goal of the automotive industry [8, 19].

1.5 **Reaction mechanism**

Determining the reaction pathway and identifying the reaction intermediates are important in designing an effective catalytic system. In the past twenty years, numerous experiments have been conducted in studying various catalytic systems under lean-burn conditions, and several reaction mechanisms have been proposed [20–24]. To date, considerable uncertainty surrounds the real reaction mechanism and no single mechanism alone can fully explain all the experimental results.

1.5.1 **Decomposition mechanism**

The most widely accepted mechanism in earlier days was the NO decomposition mechanism, proposed by Burch [20]. In this scheme, NO completely dissociates on the metal surface and N$_2$ or N$_2$O is formed subsequently. Burch’s proposed mechanism suggested that the primary role of the hydrocarbon is to keep the metal surface clean (i.e. not poisoned by oxygen) in order to allow the active adsorption and dissociation site of NO$_x$ [25].

However, subsequent studies challenged this mechanism in several aspects [26, 27]:

1. Fritz and coworkers demonstrated the overall reduction reaction also takes place over a fully oxidized Pt surface (PtO surface), even when using propane as the reductant (which is known
to be unable to reduce PtO.) [27].

2. The discovery that various materials, including zeolites, which do not catalyze direct NO decomposition, can serve as catalysts for NO\(_x\) reduction also indicates that the direct NO decomposition may not be the key to the NO\(_x\) reaction [28,29].

### 1.5.2 Reaction intermediates

Another competing mechanism relies on the idea that nitrogen is formed via a short lived reaction intermediate as a result of interactions between nitrogen containing species and hydrocarbons. In this scheme, hydrocarbons activate NO as opposed to the requirement that NO must be dissociated by the catalyst [22-24,26,30-34]. In summary, four types of organic species have been detected on supported metal catalysts, and have been argued as possible reaction intermediates. They include:

1. Isocyanates (R-NCO)
2. Nitriles (R-CN) or isonitriles (R-NC)

3. Nitro (R-NO₂), nitrite (R-ONO) or nitrato (R-ONO₂) compounds

4. Oximes (R-CH=NOH), amines (R-NH₂) or NH₃

However, absorption of these species does not imply direct involvement in the primary reaction pathway for NOₓ reduction and therefore a deeper understanding is required.

1.6 **Elementary steps-microscopic level**

1.6.1 **NO adsorption on Pt surfaces**

Regardless of the reaction mechanism, NO adsorption on the metal surface is believed to be the first step in the NOₓ reduction reaction [8]. Low energy electron diffraction (LEED) measurements of NO saturation on Pt(111) under ultra high vacuum conditions show a p(2x2) pattern [35], suggesting a 0.25 ML coverage. LEED-IV data is well fit by a model with NO molecules in fcc 3-fold hollow sites. Subsequent density functional theory (DFT) calculations from King [22, 36] support this conclusion that the fcc site is most stable, while the atop
site is the least stable. NO adsorbs in an upright geometry on Pt(111) with the molecular axis perpendicular to the surface in an N-down configuration. Early IRAS (infrared reflection absorption spectroscopy) and EELS (electron energy loss spectroscopy) showed two different vibrational modes on the surface [37,38]. A low frequency mode in the range from 1476 to 1498 cm\(^{-1}\) is seen at a low coverage (around 0.12 ML) of NO. Originally this result was interpreted as due to NO at bridge sites, but this work has now been reinterpreted and these features have been reassigned to three fold sites. At higher coverage of NO (larger than 0.13 ML), a second higher frequency mode in the range from 1700 to 1725 cm\(^{-1}\) appears and is assigned to an atop site.

1.6.2 NO dissociation on Pt surfaces

The dissociation energy of NO (630 kJ mol\(^{-1}\)) is relatively low compared to CO (1076 kJ mol\(^{-1}\)) [37,39], implying that noble metals are able to dissociate NO. The formation of N\(_2\)O on Pt surfaces suggests that indeed NO dissociates and forms N adatoms on the surface even below 300 K. However, NO dissociation can only occur on a clean metal surface that is neither completely oxidized nor blocked by carbon species [40,41]. It is now generally believed that NO dissociation mainly takes place on the steps of the Pt surface [42,43]. The stepped Pt surface, (e.g., the 410) surface, is much more active for NO decomposition than the (111) surface.

1.6.3 NO\(_2\) and oxygenate hydrocarbon species

The discovery that the introduction of O\(_2\) in the reaction stream enhances NO\(_x\) conversion indicates oxygen plays an important role [38,44]. There are two possible routes for oxygen in
the reduction process, oxidation of NO to form NO₂, and reaction with hydrocarbons to form oxygenates. The two pathways are illustrated as follows:

\[ \text{NO} + O_2 \xrightarrow{\text{Pt}} NO_2 + C_nH_{2n} \rightarrow R - ONO_{\text{ads}}, R - NO_{2\text{ads}} \xrightarrow{\text{Pt}} N_2 + N_2O + CO_2 + H_2O \] (1.2)

\[ O_2 + C_nH_{2n} \xrightarrow{\text{Pt}} R - CHO, R - COOH + NO \xrightarrow{\text{Pt}} N_2 + N_2O + CO_2 + H_2O \] (1.3)

For the first pathway, temporal analysis of product (TAP) and reflection-absorption IR spectroscopy (RAIRS) experiments have shown that NO₂ will be subsequently quickly reduced by hydrocarbons [45]. In Tanaka [32] and coworkers’ IR experiments, NO, C₃H₆, and oxygen were exposed to Pt/SiO₂ catalysts and three peaks were observed at 1565, 1655 and 1740 cm⁻¹, respectively. The first two peaks shifted with ¹⁵N isotopic substitution, suggesting that they are nitrogen containing species, such as nitromethane (CH₃NO₂) or nitrite species (R-ONO) and have been assigned as RNO₂_ads or R-ONO_ads. The peak at 1740 cm⁻¹ did not shift and was therefore believed to be a carbonyl species. Following introduction of NO₂ at 393 K, the peak at 1740 cm⁻¹ decreases as nitrogen and nitrous oxide evolve simultaneously, while the peaks assigned to nitromethane (CH₃NO₂) and nitrite species (R-ONO) did not change. This result implies that the carbonyl species is involved in the key steps of NOₓ reduction. However, N₂O also appears in this wave number region, so its presence may offset the depletion of the proposed intermediates and therefore their involvement in NOₓ reduction cannot be completely ruled out.
The second scheme involves the activation of hydrocarbons. Alkenes have been found to adsorb strongly in competition with oxygen, giving a reduced catalytic surface that contains a high concentration of carbonaceous species. The oxygen may help C-H activation [23, 32].

Captain [23] and coworkers studied NO reduction by propylene over Pt/SiO$_2$, using *insitu* FTIR experiment where NO/He [1.0% NO] was passed over a Pt/SiO$_2$ sample that was pre-exposed to C$_3$H$_6$. After a period of 4 min, a weakly bond surface cyanide species was observed at 2090 cm$^{-1}$ as well as nitrous oxide. Nitrous oxide is believed to be produced by CN+NO in this case. This results indicate that the cyanide species may be formed by the reaction between carbonaceous species and NO. With the addition of oxygen, the surface cyanide peak grows; indicate the promoting effect of O$_2$. In this case, surface isocyanate (NCO) is believed to be the critical reaction intermediate.

Lacombe et al. [46] used a TAP reactor to investigate NO reduction by butane on Pt catalysts, and found that the amount of N$_2$ produced from NO pulses over Pt is much less than for Pt pre-exposed to butane, leading to the conclusion that differences in nitrogen appearance may result from different pathways for nitrogen evolution, which are faster when carbonaceous species are present on the surface. In this case R-CNO could be a possible reaction intermediate and it is refer to as the “carbon-assisted” mechanism [47, 48].

Catalytic reduction of NO with H$_2$ on Pt surfaces also exhibits a number of interesting properties such as surface explosions, kinetic oscillatory behavior, and surface wave propagation. Mechanisms that have been proposed include a reversible surface reconstruction, interaction in the adsorbed layer, or an autocatalytic increase in the formation of vacant sites during reaction,
as key steps of the oscillation cycle [49, 50]. In Madden’s TPD experiment of coadsorbed NO and H₂ on the Pt(100) surface, the two species react to form extremely narrow product peaks. Besides N₂ and H₂O, NH₃ was also found as a reaction product [51, 52]. NH₃ is thought to be produced from hydrogenation of N_{ads} that has resulted from NO dissociation on Pt defects upon thermal activation, which can also served as a subsequent reductant for NO reduction at high temperature.

Granger [53] and coworkers reported kinetic investigation of the NO + H₂ reaction on supported Pt and Pd surfaces. It was found for both surfaces that the rate determining step is the dissociation of chemisorbed NO molecules. The rate enhancement observed for NO + H₂ has primarily been related to the involvement of a dissociation step of chemisorbed NO molecules assisted by adjacent chemisorbed H atoms. A maximum in the formation of NH₃ is observed in the temperature range of 473 - 573 K on Pt/Al₂O₃ catalysts, above these temperature, successive reactions involving NH₃ take place. Interestingly, the formation of NH₃ is inhibited on Rh/Al₂O₃ surfaces, although NO molecules are known to be easily dissociated on Rh surfaces [54].

1.6.4 Summary

Although the rather complicated catalytic reaction system makes it hard to determine the reaction mechanism, there are some important findings that have been established in the literature, which are summarized as follows: [18, 30, 34, 39, 53, 55]
1. NO, not NO₂, is the critical species in NOₓ reduction. Not only does NO account for 95% of NOₓ, it has also been observed that even in the presence of oxygen, NO₂ is readily reduced to NO above 100°C [27].

2. Oxygen is important for creation of possible reaction intermediates. In the presence of O₂, NO conversion begins at a lower temperature as compared to in the absence of oxygen and conversion increases with the concentration of oxygen to some degree. Even on the fully oxidized Pt surface, the NO oxidation reaction still proceeds [41].

3. It is almost certain that O₂ and NO participate in the formation of reaction intermediates to some degree, and the reaction intermediates should also involve carbonaceous species formed from hydrocarbon; therefore, compared to nitrile (R-CN), nitro (R-NO₂), nitrite (R-ONO), and nitrato (R-ONO₂) species, isocyanates (R-NCO), appear to be the most likely of the potential candidates [56, 57]. Of course, other intermediates that only exist on a millisecond time scale, and which are therefore impossible to be detected using conventional experimental methods, could be present. In fact, the observation of species with IR is often an indication that the observed species do not participate directly in the main reaction mechanism as these species are merely highly stable intermediates that cover the surface. The rapid ability of NCO to hydrolyze under wet conditions leads to the suspicion that amines (R-NH₂) may be reaction intermediates too, as water is always present under real working conditions.

4. As demonstrated by XPS results, NO dissociates only on the reduced Pt surface, forming nitrogen and N₂O. On a fully oxidized Pt surface, NO does not dissociate [27].
5. Major products of these catalytic reactions include N\textsubscript{2}O, N\textsubscript{2} and NH\textsubscript{3}; Possible minor products include: C\textsubscript{x}H\textsubscript{y}O\textsubscript{z} species such as acetone, acid, alcohol; C\textsubscript{x}H\textsubscript{y}N\textsubscript{z} species such as acetonitrile; and C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}N\textsubscript{t} compounds such as alkynitrites and alkynitrates. Among these minor products, the most abundant species are acetone, ethylnitrite, and acetonitrile [24].

1.7 **Surface science: Unraveling reaction mechanisms through model systems**

1.7.1 **Motivation**

Surface science provides a set of powerful tools to understand reaction mechanisms in heterogeneous catalysts in great detail [58,59]. By probing interfaces at the molecular level scientists can break down complex catalytic reactions into elementary steps and investigate them at a microscopic level. The 2007 Nobel Prize in chemistry was awarded to Gerhard Ertl for his thorough studies of fundamental molecular processes at the gas-solid interface. His major contributions including understanding hydrogen adsorption on metal surfaces, CO oxidation on Pt surfaces and investigations of the reactions in the Haber-Bosch process which serve as a model of how sophisticated experimental methods can be used to study a phenomenon of utmost practical relevance.

1.7.2 **The recent development of surface science**

Traditional surface science involves studying reactions in an ultra high vacuum chamber, normally at a pressure in the lower 1 x 10\textsuperscript{-10} range. A well-characterized single crystal is used as a model catalyst. Experimental probes often involve electron spectroscopies and therefore require low pressure. In addition, low pressure allows the surface to be kept clean from unwanted background species. A detailed description of the different surface science techniques
employed in this thesis is discussed in Chapter 2. Two important gaps still exist between UHV single crystal experiments and high surface area heterogeneous catalysts as we attempt to add complexity and create more realistic model systems.

1. The pressure gap from low pressure to high pressure [60].

2. The materials gap from a signal metal crystal to nanoparticles supported on (metal oxide) surfaces [61, 62].

1.7.2.1 **Bridging the pressure gap**

The pressure gap refers to the 13 orders of magnitude difference in pressure between UHV based experiments and typical operating pressures inside a catalytic reactor.

A surface produced in a UHV environment does not necessary replicate the surface under reaction conditions [60, 61]. At elevated pressures new phases may form that do not exist at lower pressure for thermodynamic reasons. In addition, the structure of a catalyst will be largely determined by dynamic processes. The static ideal structures created in UHV at low temperature may not be relevant to the overall reaction. There have been many *insitu* methods developed to bridge the pressure gap and their use is greatly increasing. Among those the most popular are:

1. Sum-frequency generation vibrational spectroscopy (SFG): In this case, molecules which are located at a symmetry breaking plane (*i.e.* a surface) may be observed even at high pressure (or in aqueous environments). SFG measurements are now fairly common but interpretation of peak shapes is non-trivial [63–66].
2. In-situ X-ray photo emission spectroscopy (XPS): known as ambient pressure photoelectron spectroscopy (APPS), “High pressure” XPS operates at pressure above $10^{-5}$ torr. Only three of these systems are currently available worldwide. The first is at the Advanced Light Source (ALS) in Berkeley (California, USA) [67]. A second-generation instrument is now operating at the BESSY synchrotron (Berlin, Germany) [68]. The third one was also at the ALS with an improved design that makes it possible to increase the working pressure to $\approx 10$ torr.

3. In situ X-ray absorption fine structure (XAFS) [69,70], which is usually divided into two energy regions: 1) the edge region of the X-ray absorption near edge structure (XANES), and 2) the extended X-ray absorption fine structure (EXAFS), which provides detailed element-specific information regarding the chemical oxidation state and local geometry of materials. However, like most X-ray techniques, XAFS is not surface sensitive and provides average information rather than resolution of specific particles.

4. In-situ scanning tunneling microscopy (STM), which provides atomically resolved images of surfaces under high gas pressures and during catalytic reactions [71,72].

5. Polarization-modulation IR reflection absorption spectroscopy (PM-IRAS) [73,74], allows for an accurate subtraction of gas phase contributions to yield surface vibrational spectra. The application of infrared spectroscopy will be further discussed in the second chapter.

1.7.2.2 Bridging the material gap

The material gap refers to the fact that surface science studies typically focus on single crystal surfaces, and neglect the structural complexity of industrial heterogeneous catalysts, which are typically metal nanoparticles supported on porous oxides.
The use of single crystals, while successful, does not allow a direct interrogation of particle size effects, which have been shown to play an important role in catalytic activity and selectivity. In additions, support effects are not included. Finally the effect of alloy and promoters are not included [75, 76].

To bridge the material gap, and develop model catalysts that have more complexity, metal oxide single crystal substrates have been employed upon which metal nanoparticles can be evaporately deposited. However, many metal oxide possess bandgaps that preclude their use for electron spectroscopies (TiO$_2$ is a notable exception). In addition, recipes for the synthesis of different types of thin film metal oxides that allow for electron-tunneling have been developed in recent years, primarily by Freund’s group. The particle size and density can be varied by controlling evaporation flux. These studies have revealed significant insight into particle size effects [77–79].

1.8 Experimental Preview

There are two major parts for this thesis. The first part will include technology development, including the construction of the new high pressure reflection absorption infrared system, which is a current state of the art surface science technique that bridges the pressure gap of traditional surface science.

This system comprises a two-stage, an upper UHV chamber and a lower high pressure cell that allows experiments at millitorr pressures to be carried out. High pressure experiments are carried out in the lower chamber and after the reaction, the lower chamber is pumped down to the pressure of the upper chamber, where subsequent analysis can be carried out.
The sample probe can translate by 356 mm between the two stages. The pressure isolation of the two stages with the sample probe is achieved by a differentially pumped sliding seal that couples the two chambers, a detailed description of the system can be found in the second chapter. Two proof of principle experiments are performed to test the system, the N\textsubscript{2} absorption on Ni(110), and hydrogenation of a N layer on Pt(111) at room temperature.

The second part of the thesis is a study of the SCR reaction using a Pt(111) single crystal. Our experimental objective is to try to answer some unsolved questions regarding mechanisms for SCR reactions using surface science techniques. Hopefully, we can gain some insight into the determination of some facets of the overall mechanism and to examine the role of various reaction intermediates, specifically with regard to the reduction of NO by hydrocarbons.

Griffiths’ group [80–83] has investigated the interaction between NO and C\textsubscript{2}H\textsubscript{4} on Pt(332), with and without the presence of oxygen, using Fourier transform infrared reflection-absorption spectroscopy (FTIR-RAS) and thermal desorption spectroscopy (TDS). Their IR spectra didn’t show the presence of any intermediates formed from reaction between NO and ethylene and, therefore, they concluded that there is no direct chemical reaction between NO and C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{4}-derived hydrocarbons, which is related toward N\textsubscript{2} formation. The reaction is conceived to proceed through a mechanism of NO decomposition and subsequent oxygen removal by reaction with the hydrocarbon. The contribution of C\textsubscript{2}H\textsubscript{4} and its derivatives to the catalytic reduction of NO on the surface of Pt(332) is then summarized as:
1. C$_2$H$_4$ may promote NO dissociation through electron back-donating effects, as it’s known that like most hydrocarbons, C$_2$H$_4$ can donate electrons to metal atoms and NO serves as an electron acceptor to some degree.

2. C$_2$H$_4$ provides a source of reductants, *i.e.*, H, CH$_x$, C$_2$H$_x$, or even C, which removes the atomic O from NO dissociation or reacts directly with NO and leaves the surface with more vacant sites for further NO dissociation.

In the presence of oxygen, also, no intermediates such as NCO with $\nu_{\text{as}}$(NCO) at 2232 cm$^{-1}$ or CN with $\nu$(CN) at 2130-2162 cm$^{-1}$, were observed. The N$_2$ desorption, however, is assumed to come from facile NO dissociation on the stepped sites of the Pt surface, which is significantly enhanced by the co-adsorption of C$_2$H$_4$ molecules, leading to the desorption of nitrogen at rather low temperature (360-380 K). Griffiths and co-workers proposed two mechanisms to explain the experimental results: Oxygen helps activate reactants (through NO$_x$) and oxygen consumes carbon species through oxidation. They subsequently did experiments by oxidation of C$_2$H$_4$ with O$_2$ before NO exposure and oxidation of NO with O$_2$ before C$_2$H$_4$ exposure. They found that the presence of O$_2$ always leads to a decrease in N$_2$ production and, therefore, concluded that oxygen does not play the role of activating reactants. This is in direct contradiction to many previous results that confirmed O$_2$ did play an important role in promoting the reduction reaction of NO. However sequential dosing of reactants in a UHV environment may not allow for the production of intermediates critical to the reduction cycle. In their continued study of NO$_x$ reduction over Pt(332), Griffiths studied the coadsorption of NO with hydrocarbons such as C$_6$H$_6$ and C$_2$H$_5$OH. As in their results with C$_2$H$_4$, no evidence for unique intermediates
in NO\textsubscript{x} reduction were observed. However, it could be that the N-containing intermediates are not observed because NO dissociation has not proceeded simultaneously with hydrocarbon decomposition. In order to overcome this possible limitation, our strategy was to populate the surface with N atoms instead of NO for the examination of the chemistry of intermediates in NO\textsubscript{x} reduction. This will be discussed at length later in this thesis.

Our studies have begun with an examination of the interaction of ethylene with N atoms on Pt surfaces in an effort to understand formation routes to nitrile species that could serve as potential intermediates in NO\textsubscript{x} reduction. Three interesting observations have been made. First, we observed the presence of π-bonded ethylene below 220 K, indicating a switch in the preferred binding site for ethylene on N-Pt(111) as compared to the clean surface. Second, above 500 K, CN coupling occurs as indicated by the desorption of HCN and the identification of CNH\textsubscript{2} with RAIRS. Third, the formation of ammonia is observed through NH\textsubscript{3} desorption as well as by observation of the δ\textsubscript{s}(NH\textsubscript{3}) mode of NH\textsubscript{3} at 1170 cm\textsuperscript{-1} with RAIRS. The appearance of ammonia is believed to be the result of a reaction between N atoms (or NH) with coadsorbed ethynyl(CCH). This route to ammonia has not been previously observed under UHV conditions but real automotive exhaust tests have detected the formation of ammonia between unburnt hydrocarbons and NO\textsubscript{x} via previously unknown pathways.
CHAPTER 2

EXPERIMENTAL

2.1 Construction a UHV system with high pressure capabilities

2.1.1 Background

Through the years, a number of attempts have been made to construct UHV chambers with high pressure capabilities to bridge the pressure gap between surface science experiments and ambient pressure reactivity measurements [84–90].

In the early 70s, Somorjai proposed a design [86] that used a movable bellows-cup where a sample can be encased in a small volume located inside the larger UHV analytical chamber for the high pressure experiment. The high pressure reactor is isolated from the main chamber by a gold O-ring between two knife edges, one on the reactor cup and the other on the reactor flange. When performing high pressure experiments, the reactor cup is closed and isolated from the main chamber. After the high pressure experiment, the reactor is pumped out and the reactor cup is opened to the main UHV chamber. This is a compact design that does not require moving the sample. However, the biggest disadvantages in this design are the potential contamination of the UHV chamber and the limited access to the sample for the surface analytical techniques.

Another option for a dual stage chamber has been developed by Goodman and co-workers [84]. In this design, a UHV compatible high-pressure cell utilizing differentially pumped, spring loaded teflon seals is attached to a port on the bottom of a UHV analysis chamber. A long
travel manipulator with a highly polished shaft used to transfer the sample from the UHV section to the high pressure cell.

The most important factor in a successful design is to ensure that no appreciable pressure rise occurs in the UHV chamber when operating the high-pressure experiment in the high pressure cell. Therefore, it is critical that the spring loaded teflon seals clamp tightly to the manipulator shaft to maintain a pristine environment.
2.1.2 System description

Our new system uses a similar design as to Goodman’s. As shown in Figure 6, the upper chamber is a typical UHV analysis chamber (Nor-Cal) equipped with a quadrupole mass spectrometer, (Prisma QMS200 with a measurable mass range of 0-200 amu), Low Energy Electron Diffraction (LEED) and an Auger Electron Spectrometer (AES) system from LK technologies (Series RVL2000). A home made glass shield was designed and put on the ionizer of the mass spectrometer, with a 12 mm wide aperture to ensure that only the gases from the sample, not from the background, entered into the ion chamber and are detected by the mass spectrometer.

The glass shield is coated with tin oxide using tin tetrachloride. The coating process is first to heat the glass shield (made of quartz) using a bunsen burner to red hot, and then spray tin tetrachloride on the surface. The tin tetrachloride quickly reacts with air forming a hydrochloride fume and a tin oxide film is left on the surface. The thin tin oxide film changes the conductivity of the glass shield so that charge won’t accumulate on the shield during experiments. The advantage of using a glass shield verse a metal shield is that the glass shield will not outgas as much as a metal shield also that the shield is transparent so that we can tell the condition of the filament.

The LEED optics are retractable by about 66 mm, and the end of the optics is approximately 19 mm from the sample during operation. The AES uses a CMA2000 electron energy analyzer mounted on 2.75 inch conflat flange with 4 inch linear retraction mechanism. A port aligner from VG Scienta (ZPA070) was used to adjust the cylindrical mirror analyzer (CMA)’s angular position so that it can be positioned directly in front of the sample.
The high pressure cell is located underneath the upper UHV chamber. A fourier transform infrared spectrometer (FTIR) from ABB laboratory (FTLA2000-154) was used with a spectral range from 500 to 12000 cm\(^{-1}\). The collimated beam from the spectrometer was directed to the external port and reflected by a flat mirror and then focused onto the crystal surface at a grazing incident angle of about 86 degree from surface normal by an off-axis paraboloidal mirror. After reflecting off the sample, the IR beam is then focused onto a mercury-cadmium-telluride (MCT) detector by two off-axis paraboloidal mirrors. The IR beam enters and exits the UHV chamber through differentially pumped O-ring sealed KBr windows. The detector box is sealed for purging with dry air, which is produced by removing water and carbon dioxide from the air by passing it through desiccant chambers connected to a compressor (General Cable Co.). All the RAIR spectra were taken with a resolution of 4 cm\(^{-1}\) and were scanned 128 times with a scanning speed about 46 scans/minute.

The sample, usually a well polished metal single crystal, is attached to the sample holder via two 0.75 mm tungsten wires spotwelded to the sides of the crystal. These two tungsten wires are connected to a thermocouple feedthrough (Ceram Tec 3181-01-w) using a barrel connector. The thermocouple feedthrough is welded to a 25.4 mm OD mirror polished stainless tube which can be transferred up to 356 mm long and mounted onto a X,Y,Z Manipulator (Thermionics). A chromel-alumel thermocouple (0.075 mm diameter, type K) were also spotwelded to the top of the sample for measuring the temperature. The sample is heated resistively up to 1400 K by passing electrical current through the tungsten wires and cooled conductively down to 87
K by filling the stainless steel tube with liquid nitrogen. All the wiring, heating wires and thermocouple wires are inside the stainless tube.

The sealing between the two chambers is accomplished by differentially pumped Teflon spring seals from Sain-Gobain as shown in Figure 7. Three teflon spring seals are stacked together with two spacers with the same dimensions between each seal. The spacers are used here so that the sealing is not too tight when it’s differentially pumped so that the sample probe can transfer into the sliding seal easily back and forth. Small holes are drilled inside the seals and spacers to allow easy pumping. The seals and spacers are placed into a custom-made conflat flange that is placed under the small gate valve and above the IR cell. The seals and spacers are screwed tightly to the flange and a metal piece stopper is used at the bottom of the seal to prevent the seals and spacers from falling off when forces are applied by lifting the sample probe from the high pressure cell to the UHV chamber.

When performing high pressure experiments, the mirror polished stainless steel sample probe is inserted into the spring seal, which has two stages of pumping with a mechanical pump on the high pressure side and a turbo pump on the low pressure side. This sliding seal ensures that the upper UHV chamber remains at low pressure when doing high pressure experiment in the lower IR cell. Care must be taken when inserting the sample probe into the sliding seal, any longitudinale scratch on the sample probe will causing a leak from the high pressure side to the low pressure side. After finishing an experiment, the lower IR cell must be pumped by a turbo pump before the sample probe can be transferred back into the UHV chamber.
Figure 7. The sliding seal.

Figure 8. Pumping scheme for the high pressure system.
2.1.3 Pumping scheme

Figure 8 shows the pumping scheme for the whole system; the base pressure of the system remains at around $1.5 \cdot 10^{-10}$ torr. Two gate valves, a small 2.75” gate valve (MDC) between the upper chamber and the IR cell and a larger six inch gate valve (MDC) help to isolate the two chambers. When both gate valves are closed, the upper chamber and IR cell are completely isolated, and two pumps, a titanium sublimation pump (Duniway TSP-275-00) and an ion pump (Varian 9192641M001) are responsible for keeping the low pressure for the upper UHV chamber. However, those two pumps are not suitable for high pressures and high pumping volumes. Therefore a turbo pump (Pfeiffer PM P02825) is used to quickly pump down the upper UHV chamber and it is also used to pump down the IR cell after finishing a high pressure experiment. In addition, the turbo pump can be used to pump down the gas manifold lines to prevent cross contamination when gases are exposed to the chamber. A mechanical pump is used as a rough pump for evacuating the IR cell as well as to back up the turbo pump.

2.2 Experimental methods

2.2.1 Temperature Programmed Desorption

Temperature programmed desorption (TPD) experiments are performed in the UHV analytical chamber using the mass spectrometer. TPD gives information on kinetics of desorption processes, adsorbate interactions, adsorption sites and phase transitions. It allows us to calibrate the coverage of adsorbates. Experiments are carried out by ramping the sample at a linear rate while monitoring the gases that are evolving from the sample surface using the quadrupole mass spectrometer (QMS). A quadrupole mass spectrometer consists of an ion source, rod
Figure 9. The quadrupole mass spectrometer system.

The ion source consists of an electrically heated tungsten filament that generates free electrons by thermionic emission, which are then accelerated to an electron collector (anode). The emitted electron density depends upon the temperature as well as the work function of the filament material according to the Richardson-Dushman equation.

\[
J = C \exp\left(-\frac{\phi}{KT}\right) \tag{2.1}
\]

where \(J\) represents the current density of emitted electrons, \(C\) is a constant (independent of the filament material), \(T\) is the temperature and \(\phi\) is the work function of the filament material.
From the equation, the emission current clearly increases with the temperature and increases with the decreasing work function of the source.

The ions are subsequently generated by electron impact ionization. After passing the orifice, the ions are guided into the rod system where ions are selected according to their mass-to-charge ratio by the detector. The rod system consists of four cylindrical, precision-layout and ground rod electrodes. A variable radio-frequency voltage is applied to the rod system causing the ions to oscillate in the electrical field. Depending on the the amplitude, ions with a specific mass/charge ratio will reach the detector side, while others are filtered out.

The voltage applied to the two pairs of opposite rods can be expressed as

\[ V_1 = U + V \cdot \cos(\omega \cdot t) \] (2.2)

\[ V_2 = -U - V \cdot \cos(\omega \cdot t) \] (2.3)

with a constant component \( U \) and a radio-frequency component \( V \cdot \cos(\omega \cdot t) \). Only ions with certain values of \( U \) and \( V \) will pass through the rod assembly, other ions will strike the rod and lose their charge.

The faraday cup or second electron multiplier are used as detectors, and the subsequent signal is sent to the pre-amplifier and then to the PC.

To interpret TPD spectra, the Polanyi-Wigner equation is used.

\[ r_{des} = -\frac{d\theta}{dt} = \nu_n \cdot \exp\left(\frac{-\Delta E_{des}}{RT}\right) \cdot \theta^n \] (2.4)
where $\nu_n$ is the frequency factor, $\theta^n$ is the coverage factor, $n$ is the kinetic or desorption order, and $\Delta E_{des}$ is the activation energy. The activation parameters can also depend on the temperature itself and thus on the heating rate $\beta$ (k s$^{-1}$). Assuming the sample is heated in linear fashion, the temperature is given by

$$T(t) = T_0 + \frac{dT}{dt}t = T_0 + \beta t \quad (2.5)$$

Using

$$dt = (1/\beta) \cdot dT \quad (2.6)$$

and substituting into the above two equations, we obtain

$$\frac{d\theta}{dT} = \frac{1}{\beta} \cdot \nu_n \cdot \exp \left( - \frac{\Delta E_{des}}{RT} \right) \cdot \theta^n \quad (2.7)$$

For the maximum at $T = T_{max}$

$$\left. \frac{dr_{des}}{dT} \right|_{T_{max}} = 0 \quad (2.8)$$

must be fulfilled, thus

$$\left. \frac{d^2 \theta_{des}}{dT^2} \right|_{T_{max}} = n \theta^{n-1} \cdot \frac{d\theta}{dT} + \theta^n \cdot \frac{\Delta E_{des}}{RT_{max}^2} = 0 \quad (2.9)$$
solving for $\Delta E_{\text{des}}/RT$, yields

$$\frac{\Delta E_{\text{des}}}{RT_{\text{max}}^2} = -\frac{1}{\beta} \cdot \nu_1 \cdot n \exp\left(-\frac{\Delta E_{\text{des}}}{RT}\right) \cdot \theta^{n-1} \quad (2.10)$$

From the shape of the spectra, we can get the information about the kinetic order. Zero-order desorption from finite coverage leads to a series of peaks that all share the same leading edge, when the desorption order changes to $n > 0$, a peak is observed. The saturation coverage is reached when multilayer adsorbates start to form. Because the peak area is directly proportional to the adsorbate coverage, if we know the saturation coverage of a particular adsorbate on the sample (via LEED for example), by comparing the integrated spectral area, we can get the coverage with different exposures.

For the first order desorption, $n=1$, $T_{\text{max}}$ is independent of the coverage, but dependent on the heating rate. The above equation then changes to

$$\frac{\Delta E_{\text{des}}}{RT_{\text{max}}^2} = -\frac{1}{\beta} \cdot \nu_1 \cdot \exp\left(-\frac{\Delta E_{\text{des}}}{RT_{\text{max}}}ight) \quad (2.11)$$

Taking the logarithm of both sides, we obtain

$$\ln \frac{T_{\text{max}}^2}{\beta} = \frac{\Delta E_{\text{des}}}{RT_{\text{max}}} + \ln \frac{\Delta E_{\text{des}}}{\nu \cdot R} \quad (2.12)$$
If we observe a family of desorption curves as a function of coverage, and then plot out \( \ln\left(\frac{T_{\text{max}}^2}{\beta}\right) \) vs. \( \frac{1}{T_{\text{max}}} \), the \( \Delta E_{\text{des}} \) can be determined by the slope. Furthermore, the frequency factor \( \nu_1 \) can be determined from the intercept.

For second order desorption, we find

\[
\frac{\Delta E_{\text{des}}}{RT_{\text{max}}} = -\frac{2}{\beta} \cdot \nu_2 \cdot \theta(T_{\text{max}}) \cdot \exp\left(-\frac{\Delta E_{\text{des}}}{RT_{\text{max}}}\right) \tag{2.13}
\]

plotting \( \ln\left(\frac{T_{\text{max}}^2}{\beta}\right) \) vs. \( \frac{1}{T_{\text{max}}} \) the activation value as well as the frequency factor may be obtained if the coverage is known. TPD experiments are critical to our understanding of the surface chemistry of NO\(_x\) reduction as will be discussed in Chapters 4-6.

### 2.2.2 Low Energy Electron Diffraction

Low-energy electron diffraction (LEED) is a technique for the determination of the surface structure of crystalline materials and adsorbates on ordered surfaces. The positions of the bright spots in the diffraction pattern give information on the symmetry of the crystal surface and the size of the unit cell. The intensities of the spots can be analyzed to determine the complete surface structure, and reveal the positions of all the atoms within the unit cell.

The sample is bombarded with a mono-energetic, collimated beam of low energy electrons (usually 20-200 eV) that’s been produced by an electron gun. The diffracted electrons are observed as spots on a fluorescent screen, as illustrated in Figure 10. The sample itself must be a single crystal with a well-ordered structure in order to generate a back-scattered electron diffraction pattern. whereby only the elastically-scattered electrons contribute to the diffraction
pattern, as the lower energy (secondary) electrons are removed by energy-filtering grids placed in front of the fluorescent screen. Each grid plays an important part in producing the diffraction pattern. The LEED optics as showed in Figure 10 are, in reality, a momentum selector and not an energy selector, so it’s essential that no magnetic field is present that would cause the distortion of the pattern. Grid 1 (G1) is held at the same potential as the sample (usually ground) to produce a field free region around the sample so that electrons that scatter from the surface travel in straight line trajectories and Grid 1 shields the sample from electric fields.

Figure 10. LEED optics.
caused by the other grids in the optics. Grid 2 and Grid 3 act as energy selectors, as a suppress voltage is applied to these grids so that only electrons with energies higher than the setting are passed through the filter. Two grids are used to improve the energy resolution of the high pass filter. Grid 4 is grounded, and in this system it’s primarily used in the AES mode for screening.

The inelastic mean free path of electrons in a solid depends on the energy of electrons and does not depend on the chemical identity of the solid. The universal curve illustrated in Figure 11 shows that, for incident energies between 20 to 500 eV, electrons interact strongly with the sample and their mean free path is around 5 to 10 Å. Therefore, LEED is a highly surface sensitive technique, because only the 3-4 top layers of the sample contribute electrons to the scattering.

The beam of electrons can be viewed as a succession of electron waves incident on the sample.
due to their wave-particle duality. Thus the wavelength of the electrons is given according to the de Broglie relation:

\[ \lambda = \frac{h}{p} \tag{2.14} \]

where \( \lambda \) is the wavelength, \( h \) is Planck’s constant, and \( p \) is the electron momentum, which depends on the mass and velocity of the electron. According to Bragg’s diffraction equation, a one-dimensional lattice of periodicity \( a \) leads to constructive interference at angle \( \theta \):

\[ n \cdot \lambda = a \sin \theta \tag{2.15} \]

From the Bragg equation, it can be seen that the the diffraction angle is inversely proportional to the lattice constant \( a \) and inversely proportional to the electron energy. The observed LEED 2D pattern is a representation of the reciprocal space lattice of the real space structure. The relationship of the real vector \( a_i \) and the reciprocal vector \( a_j^* \) is represented by

\[ a_i \cdot a_j^* = 2 \cdot \pi \cdot \delta_{ij} \tag{2.16} \]

where \( \delta_{ij} = 0 \) if \( i \neq j \), and \( \delta_{ij} = 1 \) if \( i = j \). This implies that \( a_i^* \perp a_j \) for \( i \neq j \). If the angle between \( a_1 \) and \( a_1^* \) is defined as \( \gamma \) and \( \gamma^* \) is defined as the angle between \( a_2^* \) and \( a_2^* \), we obtain:

\[ a_1^* = \frac{1}{a_1 \cdot \sin \gamma} \tag{2.17} \]
Real and reciprocal space have an inverse relationship, so the long vector in the LEED pattern actually represents a short vector in real space. LEED spots are observed in the LEED pattern only if the surface is ordered in two dimension. Streaking or the broadening of the spots in one direction is indicative of the loss of order in that dimension. A disordered region results in a diffuse background. The use of LEED to determine surface coverages will be discussed in Chapter 4.

2.2.3 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is one of the most widely used analytical technique for obtaining the chemical composition of solid surfaces. The primary advantages of this technique are its high sensitivity for chemical analysis and its ability to detect all elements above helium. AES can identify the elements on surfaces of materials, and provides quantitative determination of elemental concentrations on the surface.

A typical KL$_1$L$_2$ Auger transition process can be described as follows (also shown in Figure 12): The sample is bombarded by electrons with energy, $E_p$, about 2.5-5 keV, ejecting an electron from the atomic core levels (for example the K level as shown in Figure 12) and a core or valence electron from L$_1$ subsequently fills the resulting hole, thereby releasing energy ($E_k$-$E_{L1}$) and leaves the atom in an excited state. The excited state energy is quenched by the ejection of a
second electron in the L\textsubscript{2} level, and this resulting “Auger electron” is detected with an electron spectrometer. The Auger electron will have energy given by:

\[ E = E_k - E_{L1} - E_{L2} \]  \hspace{1cm} (2.19)

The incident electrons entering a solid are scattered both elastically and inelastically. At the primary beam energy a sharp peak is observed caused by electrons that have been elastically scattered back out of the sample, whereas at lower energies there are smaller peaks due to
electrons that have undergone characteristic energy losses. On the lower energy side of the spectrum, there is a large peak corresponding to the inelastic scattered electrons. The intensity of the Auger electrons can be plotted as a function of energy, $N(E)$, but typically the derivative, $dN(E)/dE$ is plotted.

The geometry of the electron gun, sample and analyzer are shown in Figure 13. The electron gun and analyzer are $90^\circ$ apart, and the CMA is very close to the sample ($\approx 3$ mm). The CMA2000 is a compact double pass cylindrical mirror analyzer, which selects the electron energy by means of a potential difference between the concentric cylinders, with the inner cylinder held at ground potential while the outer cylinder is scanned at a voltage $V_0$. This
selects the kinetic energy of electrons that pass through the two stages of the CMA2000 and reach the detector. The pass energy is given as

\[ E = -C(eV_0) \] (2.20)

where C is about 1.7, and it’s adjustable. Electrons that pass the two stages enter the front end (cone) of the electron multiplier. The signal is then greatly amplified by applying a high voltage across the multiplier (bias voltage). Signal detection is facilitated by modulating the outer cylinder voltage at a frequency f and detecting the 2f component of the signal by means of a lock-in amplifier.

To analyze the Auger data quantitatively, we can use the measured relative sensitivity factors \( S_x \) found in the *handbook of Auger Electron Spectroscopy*, to find the fraction of A, \( X_A \) on a surface consisting of A and B by

\[ x_A = \frac{I_A/S_A}{I_A/S_A + I_B/S_B} \] (2.21)

where \( I_A \) and \( I_B \) are the intensities of the peaks associated with the adsorbate and the substrate respectively and \( S_A \) and \( S_B \) are the relative sensitivity factors. The intensity of the peak is often taken as the peak height, or the integration of the peak area. This analysis allows us to assess surface concentrations of species.
2.2.4 **Reflection Absorption Infrared Spectroscopy**

Reflection absorption infrared spectroscopy is a vibrational spectroscopy (RAIRS) technique that provides information about molecular adsorption and surface reactions without perturbing the chemisorbed surface state. In RAIRS, as a molecule sits on a surface, it will vibrate and such vibrations can be studied by shining infrared light onto the surface. A molecule having a dipole moment will absorb infrared light, but only at certain fixed frequencies corresponding to the energy differences between vibrational states. Hence, an infrared spectrum of light reflected
from the surface will show absorption peaks that are characteristic of the molecule and its method of bonding to the surface. In order to use RAIRS, several requirements have to be met. First, the substrate surface must be an extremely good reflector because the angle of the incidence of the IR radiation must be close to grazing. Second, the absorption cross-section of the adsorbed layer at the characteristic frequencies must be sufficiently larger such that the resultant signal-to-noise ratio is high enough to allow adequate energy resolution to be used. As mentioned above, one of the requirements that has to be fulfilled is that the incident light must be at a grazing angle with respect to the sample. As the grazing angle is decreased, the absorption intensity is enhanced simply because of an increase in the number of adsorbed species sampled due to an increase in the area irradiated.

The absorption intensity in RAIR spectra is described by the intensity of the reflected beam, i.e. by reflectivity. The change in reflectivity due to the adsorbed molecules is defined as:

\[
\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0}
\]  

(2.22)

where \( R \) and \( R_0 \) are the reflectivity of the surface with and without adsorbed molecules, respectively. Since changes in \( \frac{\Delta R}{R_0} \) are due to absorption of the IR light by the adsorbed molecules on the surface, RAIR spectra will be similar in appearance to the conventional gas phase absorption spectra but with the peaks pointing downward. On the other hand, RAIR spectra are significantly simpler than the gas phase spectra due to the interaction of the IR beam with the metal surface, which imposes the well known surface selection rule.
A Michelson interferometer is the heart of any FTIR spectrometer, as shown in Figure 14, and it is a device that converts infrared radiation to a time domain spectra. It splits a beam of radiation into two paths and then recombines them so that the changes in the radiant power of the exit beam are measured by a detector as a function of path difference. The time domain spectra are subsequently converted mathematically by a Fourier transform to the frequency domain spectra, and then displayed traditionally as a plot of IR intensity vs. wavenumber.

The simplest version of the interferometer consists of two plane mirrors, one of which can move in a direction perpendicular to the plane of the other, with a beam splitter between them. In practice, the movable mirror can be moved at a constant velocity (continuous-scan mode for conventional measurements) or held at equidistant points for fixed short time periods and rapidly stepped between these points (step-scan mode for time resolved studies). Under ideal conditions, the light entering the interferometer is split into two beams of equal intensities by the beam splitter. The light returning from the fixed mirror is transmitted and recombines with the light from the moving mirror. The two reunited beams will interfere constructively and destructively, depending on the relationship between path difference (or retardation), and wavelength of the light. The IR source is the sum of the flux of radiation, which has different wavelengths. Therefore the interferogram of polychromatic light is a sum of all the interferograms. When the movable and stationary mirrors are equidistant from the beam splitter (zero retardation), the distances the two beams travel are identical and are perfectly in-phase on recombination at the beam splitter. Under these conditions, all radiation entering the beam splitter after reflection interfere constructively to produce a maximum flux at the detector,
which is known as the center burst. As the movable mirror is displaced from this point, the
distances the two light beams travel differ. This difference in path causes destructive inter-
ference of monochromatic light, resulting in the rapid decrease of the IR beam intensity. The
interferogram created by an IR beam contains information about the entire spectral range from
the IR source and is converted by Fourier transformation into a typical spectrum of the form
of IR intensity vs. wavenumber. RAIRS will be used extensively as a tool to identify surface
intermediates in Chapters 3-6.
CHAPTER 3

PROOF OF PRINCIPLE EXPERIMENTS-HIGH PRESSURE STUDY

3.1 $\text{N}_2$ adsorption on Ni(110)-a high pressure study

3.1.1 Motivation

The $\text{N}_2$/Ni(110) system is chosen to be the first proof of principle test of the high pressure system for several reasons.

First of all, this system has been the subject of numerous studies employing a wide variety of experimental techniques, such as LEED, XPS, UPS, EELS, and RAIRS and therefore its behavior under UHV conditions is well understood [91–99]. This presents an interesting opportunity to study the system under high pressure to observe differences between UHV conditions and ambient conditions. Under UHV conditions the maximum achievable coverage for a given adsorbate on a given surface may differ substantially from the coverage observed at ambient conditions, leading to remarkable differences in the reaction mechanisms, etc. For example, Hendrik and coworkers [100] studied methanol oxidation on a copper catalyst using \textit{in situ} x-ray photoelectron spectroscopy under high pressure and showed that there was a linear correlation between the catalytic activity of the sample and the presence of a subsurface oxygen species that can only be observed \textit{in situ}. We chose to focus on nitrogen adsorption on Ni(110) as a test case for the instrument in order to observe how the system performs under high pressure and understand the limitations of the apparatus.

46
Another advantage of this system is its relative simplicity, no reactions are involved, only adsorption and desorption process. \( \text{N}_2 \) weakly chemisorbs on transition metal surfaces under UHV conditions. Of course there are also some potentially interesting phenomena such as island formation and phase transitions [101, 102].

In addition, nitrogen does not have a dipole moment in the gas phase, so we can easily discriminate the gas phase signal from the surface signal in the RAIRS experiment.

### 3.1.2 Background

On the Ni(110) surface, nitrogen atoms form a (2 x 1) pattern at 0.5 ML coverage. The (2 x 1) phase is the most thermodynamically stable and has a maximum heat of adsorption of 42±2 kJ/mol [92]. At saturation coverage, nitrogen on the nickel surface forms a c(1.4 x 2) pattern, which corresponds to a coverage of 0.72 ML. Angle-resolved photoemission indicates that the molecular axis is oriented perpendicular to the Ni(110) surface. This result is corroborated by IR experiments that show that the N-N stretching band indicating that the molecule is not oriented parallel to the surface.

The thermal desorption of nitrogen showed a single peak at 152 K for the lowest nitrogen coverage, the peak shifts to lower temperature with increasing coverage and a second peak at 126 K develops when coverage increased to more than half a monolayer. The RAIRS experiment shows that at low coverage, an asymmetric band at 2200 cm\(^{-1}\) appears, and that this peak shifts to lower frequency as the coverage increases; the shift is around 6-8 cm\(^{-1}\). This is in contrast to CO on the Ni(110) surface, which shows a shift in the C-O stretching frequency from 1960 to 2016 cm\(^{-1}\) as the CO exposure increases. The large increase in the C-O stretching frequency
with increasing coverage for CO on the Ni(110) surface is explained as the reduction of electron density in the $2\pi^*$ orbital of CO as the metal electron density is shared by more CO molecules. The explanation for the frequency shift of nitrogen on the Ni(110) surface is that the large increase in frequency due to dipole-dipole coupling is almost completely canceled by a downward shift due to purely chemical effects, which has been confirmed by later experiments [99]. The amount of dipole coupling depends on the difference in frequency between the oscillating dipoles, therefore, by studying the vibrational spectra of various isotopic mixtures at constant coverage, the frequency shift due to dipole coupling can be determined. In addition, the chemical shift is related to the electronic distribution between the metal and the adsorbed molecule. The difference between the frequency of the pure isotope at low coverage and the frequency for the same isotope at the dilution limit in the presence of a high coverage of the other isotope is a measure of the frequency shift due to chemical effects. Results showed that the dipole coupling shift is $+35 \text{ cm}^{-1}$ while the chemical shift is $-41 \text{ cm}^{-1}$, which explains the overall downshift of the frequency by $6 \text{ cm}^{-1}$ as coverage increases. A detailed discussion about the frequency shift can be found elsewhere [97].

The first “high pressure” study of $N_2$ adsorption was performed on the Ni(111) surface by Yoshinobu and coworkers [96]. Yoshinobu et al., studied the adsorption of $N_2$ at pressures up to $10^{-2}$ mbar using RAIRS, and LEED was used in complementary measurements to get information about the long-range order of the molecules.

A single stretching band at $2218 \text{ cm}^{-1}$ is assigned to singleton nitrogen species, terminally bound to a Ni atom and with increasing pressure, a second band appears at $2212 \text{ cm}^{-1}$. The
appearance of the second band is ascribed to island formation in the intermediate coverage region. Above $5 \times 10^{-5}$ mbar, these two bands disappear and a third band at $2198 \text{ cm}^{-1}$ appears, which is assigned to an in-phase collective vibration of an ordered and relatively homogeneous nitrogen adlayer. Yoshinobu et al., performed other studies of nitrogen adsorption on chemically modified Ni(111) surfaces such as H-predosed Ni(111), O/Ni(111), CO-predosed Ni(111) and observed that nitrogen stretching bands were observed at higher wave numbers. These modifiers also served to decrease the saturation IR intensity due to chemisorbed nitrogen.

### 3.1.3 Experimental

A full description of the apparatus used for these experiments can be found in the second chapter. The pressure of the two chambers are measured by two separate Bayard-Alpert nude ion gauges (Granville-Phillips).

The Ni(110) crystal (99.995% purity) was obtained as a 12.5 mm diameter disk 1.5 mm thick from Monocrystals, Inc in 1984. It was reoriented to within 0.5° of the (110) plane by x-ray diffraction with the Laue back reflection technique. It was polished to a mirror finish with increasingly finer diamond based polishing compounds down to a 0.25 µ grit size.

The commercial Fourier transform infrared spectrometer (FTIR) used here is a ABB (FTLA 2000-154). The scan rate is 46 scans per minute, and a mercury cadmium telluride (MCT) detector was used for all the experiments.

All IR spectra reported in this chapter were obtained in the following way: After cleaning the crystal, the sample is transferred into the IR cell while holding the crystal at 600 K with liquid nitrogen in the sample holder reservoir (to prevent CO contamination from background).
The crystal is then cooled back to 87 K (taking about ∼ 7 min), then 128 scans (taking ∼ 3 min) of the clean surface were recorded. Upon completion of the background scans, the crystal was exposed to the N\textsubscript{2} by backfilling the IR cell, and sample scans were taken while the IR cell is exposed to varying N\textsubscript{2} pressures. All the spectra are taken at 4 cm\textsuperscript{-1} resolution.

3.1.4 Results and discussion

3.1.4.1 Cleaning procedure

The primary contaminants of the Ni crystal are sulfur, carbon and oxygen. The sample is cleaned by cycles of Ar\textsuperscript{+} sputtering and subsequent annealing to 1400 K.

Figure 15 shows AES data. The first spectrum showed that the condition of Ni(110) prior to cleaning. The surface is covered by a large amount of carbon demonstrated by a large peak at 273 eV, and the Ni features are essentially unobservable. The second spectrum shows that after annealing the surface to 1000 °C, sulfur has been brought to the surface from the bulk as demonstrated by the peak at 151 eV. Sulfur contamination is a well known problem for Ni single crystals and it migrates to the surface after annealing. The crystal is then sputtered for 30 min to remove sulfur, although the sputtering duration time and beam voltage may vary as appropriate to the thickness of the contamination layer. However, long sputtering times and high beam voltages may roughen the surface, which then requires subsequent high temperature annealing to heal the surface which may induce segregation of S.

After sputtering, the sulfur peak disappears but the carbon peak may return, with the carbon peak partially attributed to the CO on the surface, which has adsorbed from the background. In addition some CO and hydrocarbons in the background are dissociated by the
electron beam and deposit carbon on the surface. Therefore its preferable to sputter the surface above the CO adsorption temperature.

CO can be removed by annealing the surface to above 600 K. and Figure 16 shows a RAIRS spectrum of the clean surface with only three Ni peaks at 716, 783 and 848 present and any contamination present is below the AES’s detection limit. A well ordered (1 x 1) structure was also observed with LEED.

### 3.1.4.2 RAIRS study of nitrogen adsorption on the Ni(110) surface

For IR experiments, when the pressure is lower than $1 \times 10^{-5}$, the ion gauge is used whereas for higher pressure readings, a convectron gauge (Duniway GP275-071) is used. The convectron gauge was calibrated with the ion gauge so that the two gauges display the same value at boundary pressure of $10^{-5}$ torr.

As shown in Figure 16, a peak at $2195 \text{ cm}^{-1}$ appears on Ni(110) at 120 K when $10^{-8}$ torr nitrogen is present in the IR cell. Since each scan takes about 167 seconds, it was estimated that 1.67 L of nitrogen was exposed to the surface. As we increased the pressure to $10^{-7}$ torr, the peak height did not increase. This result indicates that even at $10^{-8}$ torr the surface is saturated with nitrogen at 120 K. Based on the previous results of Brubaker et al., [92] the N-N stretch peak will shift from 2200 to 2194 cm$^{-1}$, the coverage is saturated under UHV conditions. We observe a frequency of $2195 \text{ cm}^{-1}$, in agreement with Brubaker et al.’s result. Upon increasing the pressure, the peak does not change until above $10^{-5}$ torr. At this point, the $N_2$ stretching peak starts to shift to higher frequency and decreases in amplitude, possibly
Figure 15. AES spectra of the Ni(110) surface, demonstrating the cleaning process.
Figure 16. IR spectra of nitrogen adsorption on the Ni(110) surface at 120 K.
indicating a decrease in N\textsubscript{2} coverage. A new peak at 1865 cm\textsuperscript{-1} now begins to appear at \(10^{-8}\) and continues to grow. The 1865 cm\textsuperscript{-1} feature is attributed to bridge bonded CO on the Ni(110) surface. A previous study of CO adsorption on Ni(110) suggested that CO bands in the frequency ranges from 2000-2060 cm\textsuperscript{-1} can be assigned to atop sites and peaks at 1880-1940 cm\textsuperscript{-1} are attributable to CO on bridge sites [103]. Thus the decrease of the nitrogen peak could be due to collision induced desorption by nitrogen atoms or the interaction with co-adsorbed CO.

Takaoka and coworkers used molecular beam techniques to study the collision induced chemistry of nitrogen on the Ni(100) surface. After creating a Ni(100)-c(2 x 2)-N\textsubscript{2} surface (N\textsubscript{2} coverage is 0.5 ML), the surface was exposed to a 1.07 eV Xe beam and the N\textsubscript{2} coverage change was monitored by FTIR. Takaoka et al. found that the decay of the nitrogen coverage is a function of xenon exposure. Since the CO peak increases with increasing pressure (of nitrogen) this suggests that once CO is bound to the surface it does not desorb readily, and because CO is bound more strongly than nitrogen, the calculated adsorption energy for CO on top sites of Ni(110) is 1.15 eV, and on bridge sites is 1.58 eV. Therefore, the presence of CO is not removed by the high pressure of nitrogen.

3.1.4.3 **NO baking of the stainless steel chamber**

The nitrogen gas source has a purity of 6N (99.9999%) and the gas manifold was thoroughly baked before the experiments so it seems unlikely that the CO contamination stems from the gas source. A more plausible explanation for the presence of CO is the high nitrogen pressure aids in the removal of some CO from the chamber walls and eventually found its way to the
crystal surface, which was held at 120 K.

In order to passivate the stainless steel chamber and reduce the CO contamination, a high temperature bake out (up to 200 °C) was performed using a strong oxidizer, nitrogen oxide. It’s well known that the presence of a surface oxide layer on the chamber walls appears to play an important role for lowering stainless steel out gassing [104]. The NO bake was performed after a regular bake out when the chamber was still warm (around 80-90 °C). NO was exposed into the chamber for 6 hours at 1 x 10⁻⁷ torr.

Figure 17 shows various mass signals vs $N_2$ pressure before and after baking with NO. In this experiment, nitrogen was exposed to the chamber and CO, $H_2$, $N_2$ are monitored by the mass spectrometer as the pressure is increased. The result shows that baking with NO is effective, as the CO and hydrogen peaks were greatly suppressed.

3.1.4.4 RAIRS study of nitrogen adsorption on the Ni(110) surface after a NO bake out

After bake out of the chamber using nitrogen oxide, additional FTIR experiments were performed with the sample at 176 K and 193 K as shown in Figure 18 and 19. Nitrogen desorbs from Ni(110) surface at 152 K under UHV conditions, whereas at higher pressures the surface will achieve saturation if the sample temperature is too low. At 176 K, no nitrogen peaks were seen under low pressure, while at $10^{-5}$ torr, a peak at 2208 cm⁻¹ appears. This peak is an indication of the start of a low coverage of nitrogen to develop at high pressure. Another peak at 1870 cm⁻¹ also appears, again indicating the presence of bridge bonded CO. The nitrogen peak increases as the pressure increases while the CO peak doesn’t change appreciably. The
Figure 17. The NO baking effect, expose nitrogen to the chamber, and monitor changes of various mass signals (m/z= 28, 2, 14, 12) before and after a NO bake out.
Figure 18. IR spectra of nitrogen adsorption on the Ni(110) surface at 176 K after a NO bake out.
results indicate that an NO bake out is effective but still not able to remove all of the CO in the chamber.

At 193 K, an N-N stretch peak was not seen until the N$_2$ pressure reached 10$^{-4}$ torr. The peak increases as we increase pressure to 10$^{-2}$ torr. Previously before NO baking, no nitrogen peak were seen at 193 K at high pressure, suggesting that CO is the major contaminant in the chamber that affect nitrogen adsorption, therefore, a very pristine chamber condition is the key to the success of these experiments and further steps must be taken.
Figure 19. IR spectra of nitrogen adsorption on the Ni(110) surface at 193 K after an NO bake out.
3.2 Hydrogenation of the N layer on Pt(111)

3.2.1 Background

Another proof of principle experiment we chose to study is hydrogenation of nitrogen atoms on Pt(111). The kinetics of formation and dissociation of the NH species on Pt(111) under UHV conditions has been studied experimentally with time-resolved reflection absorption infrared spectroscopy (RAIRS) and theoretically with density function theory (DFT) [105, 106]. The NH species has an intense and narrow peak at 3321 cm\(^{-1}\), and adsorbs at three-fold hollow sites with the NH axis aligned close to the surface normal. The N-H bond of NH breaks upon heating to 450 K, but the nitrogen atoms produced can be rehydrogenated by additional exposure to hydrogen.

Experimental results show that NH formation follows first-order kinetics with an activation energy of 0.23 eV. Time resolved IR experiments were performed at four different temperatures, 182 K, 188 K, 195 K and 201 K, and plots of \(\ln(1 - A(t)/A(t_c))\) vs time(s) showed a linear relationship, where \(A(t)\) is the NH IR peak area, and \(A(t_c)\) is the peak area at the time when the reaction is completed. A plot of \(\ln(K)\) vs 1/T gives an activation energy of 0.23 eV and a pre-exponential factor of \(1.5 \times 10^3\) s\(^{-1}\). In contrast, DFT calculations predict a barrier of 0.62 eV with a pre-exponential of \(1.1 \times 10^{13}\) s\(^{-1}\). Interestingly, the rate predicted by DFT matches well to the experimental rate, implying that if the pre-exponential were artificially adjusted to \(10^{13}\) s\(^{-1}\), the resulting barrier nearly matches the DFT result. This implies that a compensation effect exists whereby the pre-exponential and activation barrier are correlated so that an assumption of a constant activation energy could lead to a poor estimation from the
Arrhenius plot. This compensation effect is likely due to an increase in the activation barrier for NH formation with increasing NH coverage. The dissociation reaction is found to follow the second-order kinetics with an activation energy of 1.10 eV from experiments. Since NH is more stable on the surface than N and H, the dissociation rate is limited by the recombinative desorption of hydrogen, which accounts for the observed reaction order.

3.2.2 Results and discussion

The Pt(111) surface was cleaned by cycles of Ar⁺ bombardment and then heated in 1x10⁻⁷ torr of O₂ at 825 K for 1 hour. AES spectra in Figure 20 indicates that the Pt surface is easily poisoned by CO, which can be removed by annealing the surface to above 600 K. However, the carbon layer has to be removed by oxidation, and then subsequently annealing the surface to 850 °C to generate a clean, well ordered Pt surface. The absence of impurities was verified by AES before each experiment. All experiments that are described in this section are performed at room temperature. The N layer was prepared by oxidation of ammonia on Pt(111). An oxygen layer was prepared on the surface first, then ammonia was exposed to the chamber and subsequently annealed to 400 K. The saturation oxygen coverage on Pt(111) is 0.25 ML, which can be prepared by exposing 2 L of oxygen at 90 K on Pt(111) and subsequently annealing to 300 K. The recipe for the O layer preparation on Pt(111) must be modified because the sticking coefficient at room temperature is very low, (≈ 0.05) compared to at 90 K (unity). Oxygen peaks (at 503 eV) were not seen in the AES spectra below a 20 L exposure. Instead, a saturation oxygen layer on Pt(111) at room temperature can be prepared by exposing 5x10⁻⁸ torr oxygen into the chamber for about 10 min. The AES results can be found in Figure 21.
Figure 20. AES spectra of the Pt(111) surface, demonstrating the cleaning process to obtain clean surface.
Figure 21. AES spectra vs $O_2$ exposure to Pt(111) at room temperature.
The high oxygen exposure raises the chamber background pressure, which then contributes more carbon to the surface from CO which can be removed by simply annealing the surface to 600 K before dosing ammonia into the chamber. Due to the slow pumping of the system, the major background gases are CO, CO$_2$ and H$_2$. We carefully checked the desorption temperature of CO, CO$_2$ and H$_2$ on Pt(111), and found that CO desorbs from the surface below 480 K, CO$_2$ and H$_2$ desorb below 350 K and 400 K while atomic oxygen stays till 680 K. Therefore, its possible just by annealing the surface above 500 K, we can remove all the other impurities from the surface without losing the layer of atomic oxygen.

![Figure 22. LEED pattern of the (2 x 2) O$_2$ on Pt(111).](image)
After significant testing of the recipe of preparation of the oxygen layer, it was determined that dosing for relatively long periods at lower pressure gives a better result than short doses at high pressure. The LEED results in Figure 22 showed that a p(2 x 2) oxygen layer has been prepared on the surface at room temperature using the method described above.

18 L of ammonia was then exposed to the chamber and the sample was annealed to 400 K to create the N layer as confirmed by AES as showed in Figure 23. Because the N peak is overlaps with part of a Pt peak at 390 eV, the amount of N was calculated by taking the ratio of the 390 eV peak to the 237 eV peak, which is the major peak for Pt. For bare Pt, the ratio 390/237 stays constant; therefore, the higher the N content, the higher the ratio. After preparing the first N layer on the surface, we then expose another 30 L oxygen and 12 L ammonia, anneal to 400 K giving an even higher N peak this time, indicating that the N coverage is increased. A third exposure of ammonia and oxygen saturates the N peak. We then annealed the surface to different temperatures for an hour and calculated the peak ratio again, and observed that the N layer can remain up to 400 K without losing significant intensity. After we successfully prepared the N layer on the surface, we then held the sample at 400 K and transferred it to the high pressure IR cell for hydrogenation experiments. The experimental results are shown in Figure 24.

The N-H peak at 3320 cm$^{-1}$ appears when the IR cell is under 10$^{-8}$ torr hydrogen pressure. A second peak at 2070 cm$^{-1}$ is also visible, which is attributed to atop CO on Pt(111). The N-H feature fully disappears when bridge CO begins to populate the surface as observed by appearance of a peak at 1843 cm$^{-1}$ above 10$^{-6}$ torr. When further increasing the hydrogen
Figure 23. AES spectra of N layer on Pt(111), following preparation of the N layer on Pt(111).
Figure 24. IR spectra of hydrogenation of N layer on Pt(111) at room temperature at elevated pressure.
pressure, the N-H peak is observed to be positive, indicating that some of the N atoms had been hydrogenated by background hydrogen during the transfer process before the hydrogen exposure experiments. Bridge bonded CO has removed all the N-H features on the surface. Further increasing the hydrogen pressure to above 1 torr, as shown in Figure 25, results in depletion of all the CO features, indicating that the hydrogen displaces the background CO from the surface above this pressure.

Unfortunately once again background CO prevents a detailed kinetic analysis of the reaction. Further steps to prevent contamination must be taken.
Figure 25. IR spectra of N hydrogenation on Pt(111) at room temperature at torr level pressure.
CHAPTER 4

FORMATION OF $\pi$ BONDED ETHYLENE

4.1 Summary

The formation of $\pi$-bonded ethylene on a nitrogen-covered Pt(111) surface has been studied by reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD). The observation of a RAIRS peak at 975 cm$^{-1}$ due to the $=\text{CH}_2$ wagging (out of plane) mode is a clear indication of the presence of $\pi$-bonded ethylene on the surface. This form of ethylene desorbs from the surface at 216 K, a temperature much lower than ethylene desorption from the clean surface. Density functional theory calculations confirm that $\pi$-bonded C$_2$H$_4$ becomes thermoneutral compared with di-$\sigma$C$_2$H$_4$ when 0.25 ML of N atoms are coadsorbed on the Pt(111) surface.

4.2 Background

The adsorption and hydrogenation of ethylene on Pt surfaces have been extensively studied as model systems for alkene hydrogenation. [56,107–110] Under ultrahigh vacuum (UHV) conditions below 240 K, ethylene is known to adsorb on Pt(111) via two $\sigma$ bonds to the metal surface. The di-$\sigma$ bonded ethylene then dehydrogenates to the ethylidyne CCH$_3$ species upon annealing. Although ethylidene CHCH$_3$ and surface ethyl species have been argued as relevant hydrogenation reaction intermediates in RAIRS and kinetic studies, it is now generally appreciated that $\pi$-bonded ethylene is the critical species for the ethylene hydrogenation reaction. [56,63,110,111]
Cremer and coworkers studied ethylene hydrogenation on the Pt(111) surface using sum frequency generation (SFG) under reaction conditions and determined that $\pi$-bonded ethylene is the dominant reaction intermediate that leads to the formation of ethane [63]. Whereas varying the concentration of di-$\sigma$ bonded ethylene did not affect the hydrogenation rate at 295 K, the coverage of ethylidyne was directly proportional to the presence of di-$\sigma$ bonded ethylene, indicating that both ethylidyne and di-$\sigma$ bonded ethylene are spectator species [112–114]. In contrast, the $\pi$-bonded ethylene peak was unchanged by the coverage of ethylidyne. However, in Cremer’s experiment, the features ascribed to $\pi$-bonded ethylene are weak, indicating that it is present as a minority species on the surface.

Further study has revealed that two types of $\pi$-bonded ethylene may potentially exist on the Pt(111) surface: physisorbed and chemisorbed species. Physisorbed $\pi$-bonded ethylene can be observed on the clean Pt(111) surface at low temperature, but above 52 K, it begins to convert to di-$\sigma$ bonded ethylene [115]. Chemisorbed $\pi$-bonded ethylene has been reported to form on Pt(111) surfaces modified with such coadsorbates as oxygen [116] and potassium or cesium [115, 117, 118]. These studies have typically relied on indirect methods such as Ultraviolet Photoelectron Spectroscopy (UPS) for determining the presence of $\pi$-bonded ethylene. In addition, Kubota / et al. have used RAIRS to detect $\pi$-bonded ethylene on Pt(111) at 112 K in the presence of $10^{-3}$ Torr of ethylene [119]. The $\pi$-bonded ethylene was observed to disappear as soon as the gas-phase ethylene was pumped away and UHV was restored. To this point, there is no RAIRS evidence of chemisorbed $\pi$-bonded ethylene on Pt(111) under UHV conditions. Here we demonstrate that N atoms on the Pt(111) surface can stabilize $\pi$-bonded ethylene relative
to di-σ bonded ethylene, a result supported by density functional theory (DFT) calculations. In promoting the stability of the form of ethylene that is reactive toward hydrogenation on Pt(111), nitrogen is revealed to have the desirable ability to alter the chemical properties of a catalyst surface subtly while not being a reactant itself.
4.3 **Experimental**

The experiments were performed in two separate UHV chambers using two different Pt(111) crystals. The TPD results were obtained in a chamber (chamber 1) with a base pressure of $1 \times 10^{-10}$ Torr. Detailed description of the system can been found elsewhere [120]. In brief, the system is equipped with low-energy electron diffraction (LEED), an XPS system, and a quadrupole mass spectrometer (QMS) (UTI 100C) for TPD. The heating rate in the TPD experiment was 2 K/s. The data were smoothed using the Savitzky-Golay method. The RAIRS experiments were performed in a second chamber (chamber 2) with a base pressure of $2 \times 10^{-10}$ Torr. A detailed description of this system can be found elsewhere. [92] In brief, this UHV chamber is equipped for AES, LEED, and RAIRS using a commercial Fourier transform infrared (FTIR) spectrometer (Bruker IFS 66v/S). The IR beam enters and exits the UHV chamber through differentially pumped O-ring-sealed KBr windows and passes through a polarizer before reaching the infrared detector. An MCT (HgCdTe) detector and a SiC IR source were used. In cases where the sample was annealed to a temperature $> 90$ K, the sample was cooled back to 90 K before a spectrum was acquired. The background reference spectrum was also taken at 90 K. The resolution for the spectra is 4 cm$^{-1}$. The Pt(111) surfaces were cleaned and judged free of impurities by a standard procedure previously described [121]. Ammonia (99.9992%), oxygen (99.998%), and ethylene (99.8%) were purchased from Matheson Trigas and used without further purification.
4.4 **Computational Methodology**

The DFT calculations in this work are performed using the Vienna ab initio simulation package (VASP) [122,123]. A plane-wave basis set with a cutoff energy of 400 eV and ultrasoft Vanderbilt pseudopotentials (US-PP) were employed [124]. Calculations were performed using the Perdew-Wang (PW-91) form of the exchange-correlation functional [125] for thermodynamics of \( \text{C}_2\text{H}_4 \) adsorption. The (2 x 2) unit cell representing the system is four layers thick, in which the two uppermost metal layers were allowed to relax and approximately five layers of vacuum were used to separate the slabs. The Brillouin zone is sampled with a uniform 7 x 7 x 1 k-point grid (Monkhorst-Pack), as determined by convergence tests [126]. In general, the geometries of the structures were optimized within a convergence tolerance of \( 10^{-3} \) eV.

4.5 **Results and discussion**

The preparation of a well-ordered p(2 x 2)-N/Pt(111) surface has been discussed previously in detail [106]. In brief, the 0.25 monolayer (ML) N-Pt(111) surface was created by the oxidative dehydrogenation of ammonia. Ammonia and oxygen are coadsorbed at 85 K, followed by annealing the sample to 400 K, generating water (which desorbs) and leaving behind a p(2 x 2)-N/Pt(111) surface with a nitrogen coverage of 0.25 ML.

Figure 26 shows the TPRS spectra of the nitrogen layer on the Pt(111) surface. The desorption peaks of m/z = 14 and 28 peak indicate that the nitrogen layer on the surface desorbs at 464 K. The LEED pattern was obtained after the Pt(111) surface was exposed to 2.0 L of oxygen and 0.4 L ammonia at 85 K, and then annealed to 400 K for 60 s. A sharp p(2 x 2) pattern is observed that implies an absolute nitrogen coverage of 0.25 ML as showed in
Figure 26. TPD results for m/z = 14 and m/z = 28 of nitrogen layer on Pt(111).
Figure 27. Annealing the surface to 420 K led to a decrease in intensity of the p(2 x 2) spots due to desorption of nitrogen as showed in Figure 28. After annealing the surface to 450 K, the 1 x 1 pattern was restored, indicating that most of the nitrogen has desorbed before this temperature. However, since the LEED pattern requires long range periodicity of the surface structure for it to be observed, it’s still believed that, even at this temperature, some nitrogen atoms still form patches on the surface.

![LEED pattern obtained after preparing P(2 x 2)-N/Pt(111).](image)

The AES spectra in Figure 30 confirmed that a nitrogen overlayer on Pt(111) can be prepared free of oxygen and other contaminants. The spectra were obtained with an incident beam current of 10 \( \mu \) A and an energy of 2.5 kV. Upon adsorption of oxygen at 85 K on the
clean Pt(111) surface, the oxygen KLL peak at 508 eV is observed. Although the Auger peak corresponding to surface nitrogen overlaps with one of the platinum transitions at 390 eV, the changes in this peak upon ammonia exposure clearly reveal the presence of surface nitrogen.

Figure 31 shows the TPD results for m/z = 28 and 27 after exposing 0.8 L of ethylene to both clean and nitrogen-covered Pt(111). On clean Pt(111), the saturation coverage of ethylene gives only a single peak around 300 K in agreement with previous work. Simultaneous to ethylene desorption, some di-σ bonded ethylene is converted to ethylidyne. When C_2H_4 is exposed to a surface precovered by 0.25 ML of nitrogen atoms, two peaks are seen at 216 and 300 K which we assigned to π-bonded ethylene and di-σ bonded ethylene. Additional features for m/z = 28 are observed above 400 K (but not for m/z = 27), which are ascribed to N_2 desorption. Subsequent to these results, however, we obtained spectra using a different quadrupole mass spectrometer (prisma 200) in a different chamber, indicated the π-bonded ethylene actually only
contribute to a small shoulder in the low temperature range. We suspected that the separate low temperature peak for $\pi$-bonded ethylene we obtained using UTI quadrupole mass spectrometer is a misleading result and it might due to that ions were trapped into the ionization chamber for a longer time before pumping out, those ions bounce back and force and contribute to a separate peak, with UTI mass spectrometer we used a metal shield, and it’s outgas much larger than what we have on the prisma 200 with a glass shield.

Figure 32 shows RAIRS spectra following exposure of 0.8 L of $C_2H_4$ to the p(2x2)-N/Pt(111) surface at 90 K. The most characteristic and intense peak due to $\pi$-bonded ethylene [119,127], is the $=CH_2$ wagging (out-of-plane) mode, which appears at 975 cm$^{-1}$ in this figure. The peak at 2920 cm$^{-1}$ is assigned to the $CH_2$ symmetric stretching mode of di-$\sigma$ bonded ethylene. The peak at 2964 cm$^{-1}$ follows the same changes with coverage and temperature as the 975 cm$^{-1}$ peak and is therefore assigned to a CH stretching mode of $\pi$-bonded ethylene. The high
Figure 30. AES spectra of nitrogen layer on Pt(111).
Figure 31. TPD spectra of 0.8 L of ethylene from clean Pt(111) and from 0.25 ML of nitrogen on Pt(111).
frequency of the CH stretch peak at 3083 cm\(^{-1}\) indicates that it is also due to a form of \(\pi\) bonded ethylene. The fact that this peak disappears with annealing to only 130 K, whereas the 975 and 2964 cm\(^{-1}\) peaks persists to 210 K, indicates that the 3083 cm\(^{-1}\) peak is due to a form of \(\pi\) bonded ethylene that is less stabilized by the presence of N atoms on the surface. The \(\pi\) bonded ethylene species disappears upon annealing to 210 K, whereas di-\(\sigma\) bonded ethylene remains on the surface before ultimately converting to ethylidyne at 310 K. Therefore, we assign the ethylene desorption peak at 216 K in TPD to the \(\pi\) bonded ethylene species because the \(=\text{CH}_2\) wagging mode of \(\pi\)-bonded ethylene is diminished at the same temperature.

Previous DFT calculations suggest that \(\pi\) bonded ethylene occupies an atop site on Pt(111) [128], in analogous fashion to its bonding in organometallic clusters [129]. Therefore, one possible explanation for the observation of \(\pi\)-bonded ethylene at low ethylene coverages on the p(2 x 2)-N/Pt(111) surface is that N atoms block the preferred adsorption sites for di-\(\sigma\) bonded ethylene. However, our DFT calculations indicate that nitrogen atoms occupy fcc three-fold hollow sites [105] whereas di-\(\sigma\) bonded ethylene bonds atop/atop to the Pt(111) surface in agreement with earlier experiments [130,131], allowing coadsorption of 0.25 ML C\(_2\)H\(_4\) on the N-Pt(111) surface. This implies that a simple site blocking mechanism is not likely to control the adsorption of C\(_2\)H\(_4\). The calculations also confirm that whereas adsorption of di-\(\sigma\) C\(_2\)H\(_4\) on clean Pt(111) in an atop/atop arrangement is favored by 0.44 eV over \(\pi\)-C\(_2\)H\(_4\) at a C\(_2\)H\(_4\) coverage of 0.25 ML, the situation changes dramatically in the presence of coadsorbed nitrogen atoms.

On the N-Pt(111) surface, the favored site for di-\(\sigma\) bonded ethylene switches from atop/atop
to atop/bridge where the molecule is centered over the fcc site. In addition, \( \pi \)-C\(_2\)H\(_4\) and di-\( \sigma \) C\(_2\)H\(_4\) are essentially thermoneutral (di-\( \sigma \) C\(_2\)H\(_4\) is favored by only 0.01 eV), indicating that both species should exist on the surface depending upon variations in local coverages. As depicted in Figure 33, density of states calculations of the nitrogen-covered surface reveal a shift in the d-band center of the metal away from the Fermi edge (from -1.94 to -2.52 eV on the 0.25 ML N surface). Following the d-band model of Norskov and Hammer, this shift in the d-band center readily explains a reduction in the reactivity of the surface toward adsorbates when N atoms are coadsorbed. Indeed, the adsorption energy of di-\( \sigma \) C\(_2\)H\(_4\) reduces from -1.13 eV on Pt(111) to -0.48 eV on the nitrogen-covered surface [132]. As indicated above, the extent to which the bonding of \( \pi \)-C\(_2\)H\(_4\) is weakened is much less than that of di-\( \sigma \) C\(_2\)H\(_4\). This can be explained by the lower coordination of \( \pi \)-C\(_2\)H\(_4\) ethylene to the surface.
Figure 32. RAIR spectra following exposure of 0.8 L of ethylene to 0.25 ML of nitrogen on Pt(111).
In an effort to better understand the results, further experiments varying the coverage of C₂H₄ were performed. As shown in Figure 34, the presence of π-bonded C₂H₄ is maximized at an exposure of 0.8 L of C₂H₄ to the nitrogen-precovered surface. TPD data mirror that of the IR data, although it should be noted that the peak ascribed to π-bonded C₂H₄ shrinks and narrows as the coverage of C₂H₄ increases. At higher exposure, more di-σ bonded ethylene is formed, which subsequently converts to ethylidyne when the surface is heated to higher temperatures. The reduced formation of π-bonded ethylene at high ethylene coverages suggests that the favored bonding mode for C₂H₄ on the N-Pt(111) surface may switch again back to di-
Figure 34. RAIR spectra of different ethylene exposures to the p(2 x 2)-N/Pt(111) surface at 90 K, followed by annealing to different temperatures. (a) 0, (b) 0.4, (c) 0.8, and (d) 1.6 L.
atop/ atop in an analogous way to which the favored adsorption site switches on the Pt(111) surface from di-σ to π-bonded as coverage increases.

DFT calculations could not, however, locate favorable adsorption configurations for higher C₂H₄ coverages. It is well known that halides and alkali metals may serve as promoters in metallic heterogeneous catalysts for many important reactions such as ethylene epoxidation [133] and Fischer-Tropsch synthesis [134]. Our work suggests that nitrogen atoms may be an effective promoter for the selective hydrogenation of alkenes as the bonding of alkenes to metal surfaces shifts from a spectator state to one that can easily be hydrogenated. By altering the nitrogen coverage, one may tune the electronic structure of the metal and potentially shift the selectivity dramatically. Furthermore, nitrogen atoms do not react with the molecular species and therefore present an intriguing option for promotion and selectivity control in other systems.

4.6 Conclusion

The formation of π-bonded ethylene on p(2x2)-N/Pt(111) has been observed by a combination of RAIRS and TPD. DFT calculations find that π-bonded C₂H₄ is thermoneutral compared with di-σ C₂H₄ when 0.25 ML of C₂H₄ is adsorbed on p(2 x 2)-N/Pt(111). However, changing the coverage of ethylene changes the relative portions of π-bonded C₂H₄ and di-σ C₂H₄ because of the repulsive interactions between ethylene and N atoms. Our results suggest that N may serve as a promoter for hydrogenation of alkenes.
Figure 35. Cartoon schematic of adsorption site switching of C$_2$H$_4$ on Pt(111) vs. N/Pt(111).
CHAPTER 5

AMMONIA FORMATION BY HYDROGENATION OF N ATOMS ON PT(111)

5.1 Background

Selective catalytic reduction of NO\(_x\) remains a challenging problem as mobile sources move toward higher air to fuel ratios resulting in improved efficiency but larger NO\(_x\) production. Pt-based catalysts have received attention because of their activity at relatively low temperature and because they are hydro-thermal resistant at working conditions [57,135,136]. Ammonia has been used effectively in selective catalytic NO\(_x\) reduction, particularly in stationary sources. However, ammonia injection technology for NO\(_x\) reduction by automotive catalysts is still problematic because of inherent safety issues in the handling of ammonia (or urea) and the possibility of ammonia slip. Alternatively, hydrocarbon SCR (selective catalytic reduction) of NO\(_x\) may be better suited to mobile source NO\(_x\) reduction but activity must be improved so that NO\(_x\) can be removed from exhaust over a wide range of conditions. Noble metal catalysts (specifically platinum group metals) are known to be active at low temperatures [137]. For example, Tanaka and coworkers reported that Pt catalysts display NO\(_x\) reduction activity even at 373 K [17]. However, at higher temperatures, the combustion of the reducing agent dominates [8], restricting use to a narrow range of operating temperatures and resulting in a relatively lower selectivity towards nitrogen as considerable NO\(_x\) is formed [18]. Therefore, improvement
of selective NO\textsubscript{2} reduction catalysts that could be used under the variable conditions of a mobile emission source remains a long standing goal of the automotive industry.

To date, considerable uncertainty surrounds the reaction mechanism and no single mechanism alone can fully explain all the experimental results. Previously the most widely accepted mechanism was a direct NO decomposition, proposed by Burch [20, 25]. In this scheme, NO completely dissociates on the metal surface and N\textsubscript{2} or N\textsubscript{2}O is formed subsequently. However, competing mechanisms rely on the idea that nitrogen is formed via a short lived reaction intermediate as a result of interactions between nitrogen-containing species and hydrocarbons [22–24, 26, 30–33, 33, 34]. In this scheme, hydrocarbons activate NO as opposed to the requirement that NO must dissociate on the catalyst surface.

In an effort to reduce the complexity of these systems and gain insight into the reaction mechanism, the Griffiths group has undertaken a series of surface science studies of the interaction of NO and ethylene on Pt (322) [80–82]. Although the presence of the co-adsorbed hydrocarbon led to the production of N\textsubscript{2} H\textsubscript{2}O and CO\textsubscript{2}, no reaction intermediates were observed. However, it appears that NO served as an oxygen source to activate ethylene and the presence of ethylene also facilitates NO bond cleavage.

Following the example of Griffiths et al., we have studied the interaction of N atoms and C\textsubscript{2}H\textsubscript{4} on the Pt(111) surface to determine how N-containing hydrocarbon species, which are widely reported in the literature, may be formed. In our study, we bypass the NO dissociation step, which is usually believed to occur on the step sites of a Pt surface [42,138]. By creating a well ordered nitrogen layer on the Pt(111) surface, we are able to probe the reaction between
ethylene and nitrogen atoms. As will be discussed in this chapter, we have observed ammonia formation via temperature programmed reaction, demonstrating that traditional hydrocarbon SCR may lead to ammonia formation via reaction of hydrocarbons with N atoms. Although, ammonia formation has been observed previously [139], NH$_3$ formation under UHV conditions has not been observed in any similar studies which may subsequently reduce NO$_x$.

The chemistry of ammonia on Pt(111) has been studied extensively by DFT calculation [140] and experimental methods such as EELS, TPD, UPS, and RAIRS [105, 141–144]. Previous work has found that there are two types of ammonia on the surface, namely $\alpha$ ammonia and $\beta$ ammonia. $\alpha$ ammonia chemisorbed on the surface via the N atom, with an inverted umbrella configuration has a calculated adsorption energy of 68 KJ mol$^{-1}$. As coverage increases, $\beta$ ammonia starts to form in a second layer that is hydrogen bonded to $\alpha$ ammonia. N atoms on Pt(111) occupy three hollow sites, and migrate to atop sites via bridge sites upon hydrogenation. The computational results showed that for N atoms, imide-species(NH), amide-species(NH$_2$), and (NH$_3$), the most stable positions are fcc, fcc, bridge and atop sites, respectively. Michaelides and coworkers calculated the reaction barrier ($E_{act}$) for nitrogen hydrogenation on Pt(111) [145] and found that the biggest barrier is the hydrogenation of NH to form (NH$_2$), with an $E_{act}$ that is as high as 1.31 eV, while the barrier for NH and NH$_3$ formation are 0.94 and 0.74 eV respectively, this result is also in agreement with more recent calculations by Novell [146] and Offerman [140]. The calculated energy barriers for ammonia dissociation reactions, on the other hand, are generally higher than the hydrogenation reactions as the dehydrogenation barriers for NH$_3$, NH$_2$ and NH are 1.02, 1.10 and 0.97 eV respectively. We have recently examined this
issue as well and find that the barriers to hydrogenation are highly sensitive to the coverages of N and NH, but not to the coverage of H [105]. For example, as the coverage of N increases from 0.11 ML to 0.77 ML, the barrier for hydrogenation decreases from 0.82 to 0.54 eV. On the p(2 x 2) layer the barrier was estimated to be 0.67 eV for the hydrogenation reaction, whereas the NH dissociation reaction has a barrier of 1.31 eV. Furthermore, while the hydrogenation reaction was found to obey first order kinetics, the dehydrogenation reaction was observed to follow second order kinetics. The authors explain this apparent contradiction by noting that the dissociation reaction is limited by the desorption of hydrogen (which is second order). The hydrogenation reaction order is suggested to be due to the relatively high mobility of hydrogen with respect to nitrogen. Herceg and coworkers studied NH$_x$ on Pt(111) using RAIRS and TPD but found that NH$_2$ is not detected by RAIRS. The authors suggest that the hydrogenation reaction does not proceed beyond NH to form NH$_2$ and NH$_3$ on Pt(111) because NH dissociation is favored over NH$_2$ formation. This is in agreement with Mudiyanselage’s theoretical study that found NH$_2$ formation was thermoneutral over the nitrogen p(2 x 2) Pt(111) surface with a rather large barrier (0.95 eV). Under conditions where NH$_2$ formation could occur, hydrogen already begins to desorb at a high rate and therefore NH$_3$ is not observed.

5.2 Experimental

The experiments were performed in two separate UHV chambers using two different Pt(111) crystals. The TPD results were obtained in the new system described in Chapter 2 (denoted as chamber 1). The RAIRS experiments were performed in a second chamber (denoted as chamber 2) with a base pressure of 2 x 10$^{-10}$ torr. A detailed description of this system
can be found elsewhere [147]. In brief, this UHV chamber is equipped for RAIRS, AES, and LEED experiments. The chamber is coupled to a commercial Fourier transform infrared (FTIR) spectrometer, a Bruker IFS 66v/S. The IR beam enters and exits the UHV chamber through differentially pumped O-ring sealed KBr windows and passes through a polarizer before reaching the infrared detector. The detector we used here is a MCT (HgCdTe) detector with a SiC source. In cases where the sample was annealed to a temperature above 90 K, it was cooled back to 90 K before the spectrum was acquired. The background reference spectrum was also taken at 90 K. The resolution for the spectra was 4 cm$^{-1}$. The Pt (111) surfaces were cleaned and judged free of impurities by a standard procedure described earlier [92]. Ammonia (99.9992%), oxygen (99.998%), and ethylene (99.8%) were purchased from Matheson Tri-gas and used without further purification. Acetylene (99.6%) was purchased from BOC Gases. Deuterated ethylene ($C_2D_4$, 98%) deuterated acetylene ($C_2D_2$, 99%D) and isotopically labeled ammonia ($^{15}NH_3$ 98%) were purchased from Cambridge Isotope Laboratories and used without further purification.

5.3 Results and discussion

5.3.1 Ammonia formation from the reaction of acetylene with nitrogen covered Pt(111)

A p(2 x 2)-N layer was formed by exposing to 2 L of oxygen and 0.4 L of ammonia to the surface at 90 K and then annealing to 400 K for 60 s following the experimental procedure reported by Herceg et al. [106] An intense and sharp p(2 x 2)(0.25ML) LEED pattern due to the presence of an atomic nitrogen layer was observed.
We have previously found that \( \pi \)-bonded ethylene species were formed after exposing ethylene on the nitrogen covered Pt surface at 90 K, suggesting that a more reactive form of \( \text{C}_2\text{H}_4 \) is available for NO reduction. \[148\] By exposing 0.8 L deuterated acetylene \( (\text{C}_2\text{D}_2) \) to the 0.25 ML nitrogen covered Pt(111) surface, we see the ammonia coming off from the surface with a peak at 504 K as shown in Figure 36. The shape of the desorption curve can be fit very well by a lorentzian function curve showed underneath. This result suggested that the deuterated hydrogen from acetylene can hydrogenate nitrogen on Pt(111) to make ammonia. Comparison of our result on the nitrogen covered surface with the signal from an ammonia TPD experiment on the clean Pt surface, suggests that only about one tenth of the nitrogen from the \( \text{p}(2 \times 2) \) layer has been completely hydrogenated to form ammonia. The remaining unreacted nitrogen atoms (or \( \text{NH}_x \) species) ultimately recombine (or dehydrogenate before recombination) to form molecular nitrogen, which then desorbs from the surface. Ammonia desorbs from the Pt surface below 400 K \[149–152\]. Therefore, the fact that ammonia is formed at 504 K implies that ammonia must be a reaction limited product. Furthermore, the presence of acetylene appears to help stabilize nitrogen atoms on the Pt surface and prevents recombination.

As the \( \text{p}(2 \times 2) \)-N layer is created from oxidation of \( \text{NH}_3 \), it is not surprising that some residual ammonia may be present in the chamber, which readsorbs on the surface as the crystal cools down. However, since the desorption temperature has shifted more than 100 K, it seems unlikely that the presence of ammonia is related to reabsorption. In order to confirm our experimental results, not only did we use isotopically labeled \( \text{C}_2\text{D}_2 \) and monitored \( \text{ND}_3 \) species, a pair of control experiments were also performed. The first readsorption elimination experiment
Figure 36. ND$_3$ desorption following exposure 0.8 L C$_2$D$_2$ to N covered Pt(111).
was done by holding the crystal at 390 K after preparing the N layer. The sample was warmed up using dry air to blow out the liquid nitrogen in the sample reservoir while waiting for 90 min for the residual ammonia to be pumped away. Our prior results indicate that the majority of the N layer remains on the surface up to 400 K but ammonia desorbs from the surface below 390 K. Therefore, background ammonia should be pumped out during the waiting period without contaminating the sample. Afterwards we expose the same amount of C<sub>2</sub>D<sub>2</sub> into the chamber and the peak intensity of ND<sub>3</sub> didn’t change from the original temperature programmed reaction experiment. If the ND<sub>3</sub> seen before came from the result of deuterium exchange of C<sub>2</sub>D<sub>2</sub> with background ammonia that had readorsbed, we would except to see significantly less ND<sub>3</sub> desorption in this control experiment. A second control experiment was performed by mixing a 1:1 ratio of C<sub>2</sub>D<sub>2</sub> and NH<sub>3</sub> in the gasline and then exposing the mixture into the chamber. The absence of m/z=20 suggested that H-D exchange between C<sub>2</sub>D<sub>2</sub> and NH<sub>3</sub> in the gasline or on the stainless steel chamber did not occur.

Figures 37 and 38 depict the desorption of hydrogen from C<sub>2</sub>D<sub>2</sub> on Pt(111) and on N covered Pt(111). Hydrogen (deuterium) desorbs following C<sub>2</sub>D<sub>2</sub> adsorption on the surface can be fitted into four Gaussian peaks (denoted as peak 1 to 4) at 510 K, 554 K, 626 K and 702 K respectively. Detailed information on the fitted curve can be found in the following table.

The ratio of the four integrated peak area at different desorption temperatures is around 2:1:1:1, suggesting that step wise dehydrogenation of acetylene on Pt(111). It’s well known that acetylene adsorbed at low temperatures converts to ethylidyne (CCH<sub>3</sub>) upon warming above room temperature on Pt(111) [110,153]. Experimental results also suggest that vinyl (CHCH<sub>2</sub>)
Figure 37. $\text{D}_2$ thermal desorption results following exposure of 0.8 L $\text{C}_2\text{D}_2$ to the Pt(111) surface.

Figure 38. $\text{D}_2$ thermal desorption results following exposure of 0.8 L $\text{C}_2\text{D}_2$ to the N/Pt(111) surface.

may be a stable intermediate in the formation of ethylidyne from acetylene on Pt(111). The dehydrogenation is believed to proceed through vinylidene ($\text{CCH}_2$) and CCH. Hydrogen desorption from $\text{C}_2\text{D}_2$ on the nitrogen covered Pt(111) surface can also be fitted into four gaussian peaks at 510 K, 554 K, 629 K and 711 K, respectively. The desorption of hydrogen is largely suppressed in this case, the integrated peak area indicated that for peaks 1, 2 and 3, the peak areas are only 41%, 65%, and 53% of the peak area for hydrogen desorption of $\text{C}_2\text{D}_2$ on bare Pt(111). This result also suggests that nitrogen is hydrogenated stepwise in a equal manner at these three different desorption temperatures, analogous to the dehydrogenation events of the hydrocarbon. The suppression of hydrogen desorption from $\text{C}_2\text{D}_2$ on nitrogen covered Pt(111) is also an indication that the hydrogen that comes from acetylene is consumed by hydrogenation.
of the nitrogen atoms.

Figure 39 shows the temperature programmed reaction of 0.8 L ethylene on Pt(111) and N/Pt(111) while monitoring m/z=14 species, which could be a fragment of ethylene \( \text{CH}_2^+ \), doubly charged ethylene \( \text{C}_2\text{H}_4^{++} \) or \( \text{N}^+ \) from nitrogen containing species. The low temperature peak around 310 K is attributed to ethylene fragments. The peak broadens and forms a small shoulder at lower temperature after exposing ethylene to N/Pt(111). As discussed in Chapter 4, this feature can be explained by the formation of \( \pi \)-bonded ethylene on the surface. At high temperature, a small peak evolved that is absent on the bare surface suggesting that nitrogen containing species (ammonia) are formed. The desorption temperature agrees with the ND\(_3\) desorption.

5.3.2 Hydrogenation of N layer by deuterium

As mentioned in Chapter 3, there have been several previous studies of hydrogenation of N atoms on Pt(111) [105, 143]. It was discovered that exposing hydrogen to a nitrogen

| TABLE II |
| FITTING RESULTS OF C\(_2\)D\(_2\) ON PT(111) |
| Peak | 0 | 1 | 2 | 3 |
| Location | 510 K | 554 K | 626 K | 702 K |
| Height | 3.8 | 1.5 | 1.3 | 1.0 |
| Area | 1.9 | 1.0 | 1.2 | 1.0 |
| FWHM | 1.0 | 1.4 | 1.9 | 2.0 |
Figure 39. TPD results for m/z = 14 following ethylene exposure to Pt(111) and N/Pt(111).
covered Pt surface at 300 K and annealing to 380 K will form NH species which can be easily detected by RAIRS. Approximately 60\% of surface N atoms can be converted to NH and the NH formation follows first-order kinetics with an apparent activation energy of 0.23 eV, whereas the dissociation reaction follows second-order kinetics with an activation energy of 1.1 eV. As mentioned at the beginning of this chapter, DFT calculations predict a somewhat higher barrier (0.66 eV). These results are rationalized by noting that fitting the rate data to a linearized Arrhenius expression results in a lower apparent activation energy since the activation energy is not constant with varying temperature (due to coverage effects). However, the hydrogenation reaction does not proceed beyond NH to form NH$_2$ or NH$_3$ under UHV conditions. The NH peak intensity in the RAIRS spectrum increases as the hydrogen exposure increases from 10 L to 80 L, but it doesn’t further increase for higher exposures (i.e. 160 L). In this case, we performed similar experiments by exposing 10 L D$_2$ to N/Pt(111) and monitoring ND$_3$ (m/z = 20) species. The absence of a m/z = 20 peak agrees with previous studies that assert that direct hydrogenation of the N layer on Pt(111) cannot produce ammonia as shown in Figure 40. The majority of deuterium desorbs from the surface below 300 K without reacting with N atoms, as shown in Figure 41. Instead, although it’s believed that some of the deuterium produced ND on the surface, ND should dissociate before it can be completely hydrogenated. The D$_2$ recombinative desorption peak at high temperature after the N-D bond breaks was negligible but this might be due to considerable D-H exchange in the chamber as hydrogen is always present in the background.
Our results suggest that the hydrogen source to form ammonia is ethylidyne (CCH$_3$) or ethynyl (CCH), whereas large doses of hydrogen on the surface do not produce ammonia. Considering our DFT results that show that the second hydrogenation process has the highest reaction barrier, the role of hydrocarbon might be that the C-H bond helps to hold hydrogen on the surface to higher temperature. Therefore, at high temperature, the barriers to hydrogenation can be overcome to transfer hydrogen from the hydrocarbon to NH$_x$ to form ammonia. In a effort to better understand the reaction mechanism and determine whether ethylidyne (CCH$_3$) or ethynyl (CCH) merely provide a crowded surface that induces reaction between H and N, a N/Pt(111) surface that had been previously exposed to 0.8 L acetylene at 350 K was dosed with hydrogen. At 350 K acetylene has completely converted to ethylidyne on Pt(111), and the surface is now crowded as in our previous experiment. When we cool down the crystal and expose to 10 L D$_2$ at 90 K, no ammonia is observed in the subsequent TPD spectra. This result as shown in Figure 42 suggests that the hydrogen source is direct transfer from ethylidyne (CCH$_3$) or ethynyl (CCH) of acetylene. The rising baseline is due to the background increase which usually occurs when large amount of gases are delivered into the chamber.

5.3.3 Ammonia formation from ethylene reaction with nitrogen covered Pt(111)

The presence of ammonia in exhaust streams is deleterious. However, provided one could control ammonia formation from NO$_x$ and hydrocarbons, it may be possible to generate ammonia “in-situ” from hydrocarbon sources to effectively pair hydrocarbon SCR with ammonia SCR. Therefore, one would like to understand what hydrocarbon sources will make for the
Figure 40. TPD results for m/z = 20 (ND$_3$) following 10 L D$_2$ vs 0.8 L C$_2$D$_2$ on N/Pt(111).

Figure 41. TPD results for m/z = 4 D$_2$ following 10 L D$_2$ vs 0.8 L C$_2$D$_2$ on N/Pt(111).
Figure 42. TPD results for m/z = 20 (ND₃) after a 0.8 L ethylene exposure on N/Pt(111) at 350 K, and subsequent exposing 10 L D₂ at 90 K vs exposing 0.8 L C₂D₂ on N/Pt(111).
optimal conversion to ammonia. To further improve our understanding of the ammonia formation reaction mechanism between N atoms and hydrocarbons, we have also examined the reaction of ethylene and nitrogen on Pt(111) for comparison with our results using acetylene. The ammonia desorption after exposing 0.8 L C$_2$D$_4$ to N covered Pt(111) can be fitted by three peaks centered at 335, 504 and 549 K as shown in Figure 43. The peak heights and peak areas, however, are much smaller compared to C$_2$D$_2$, which is only 30%. The peak at 335 K is very weak and suggests incomplete removal of adsorbed NH$_3$ from N-layer creation. Although ethylene dehydrogenates forming ethylidyne and releases considerable amounts of hydrogen at around 300 K, our previous results with NH formation suggest that we cannot form ammonia at such low temperature. Therefore, we believe that the low temperature feature is the desorption of ammonia that has readSORBED on the sample and the signal for m/z = 20 is related to the exchange reactions that occur with deuterium that desorbs as C$_2$D$_4$ dehydrogenates either on the sample surface or in the ionization chamber of QMS.

The desorption of hydrogen as seen with TPRS also shows important differences between ethylene adsorption and decomposition on the clean surface versus the nitrogen-covered surface as shown in Figure 44. Ethylene decomposition on the clean surface gives two hydrogen desorption peaks around 300 and 500 K, which is in good agreement with the literature [43,110,154]. The low temperature feature is ascribed to the dehydrogenation and isomerization of ethylene to form ethylidyne. The higher temperature peak is associated with the further dehydrogenation of ethylidyne to form CCH. On the nitrogen-covered surface, the high temperature peak is greatly diminished with a small broad peak centered around 520 K remaining. This indicates
that in the second stage of ethylene dehydrogenation, hydrogen didn’t recombine, but may instead react with nitrogen to form ammonia. Similar experiments were carried out previously by Herceg [143, 155], in which the Pt(111) surface was exposed to 0.1 L of ethylene and 0.2 L of ammonia at 85 K followed by 100 eV electrons bombardment. In Herceg et al.’s experiment, the hydrogen TPRS data appears the same as the case of ethylene on the clean surface, with two peaks centered around 300 K and 470 K, with a small additional tail at 516 K, which is thought to be associated with the formation of HCN. The electron bombardment of ammonia generates N atoms and NH$_x$ species on the surface. However, there was no evidence indicating that nitrogen atoms generated by electron bombardment of ammonia underwent complete rehydrogenation to produce ammonia. The formation of ammonia has been previously discovered in the reaction of NO and hydrogen by Satsuma et al. who studied the SCR reaction of NO and hydrogen under oxygen rich conditions over supported Pt catalysts [156,157]. The reaction pathway for the ammonia formation of the SCR reaction can be summarized as follows. NO dissociates on the surface into N$_{(ad)}$ and O$_{(ad)}$, O$_{(ad)}$ reacts with hydrogen atoms from dihydrogen or hydrocarbons to produce water. N$_{(ad)}$ can potentially react with H$_{(ad)}$ to form NH$_x$, ultimately generating ammonia [24].

However, if the ammonia is formed by the sequential addition of H atoms to adsorbed nitrogen atoms, then NH$_3$ should have been observed in the experiment of Herceg, et al. Instead, the hydrogenation stopped at the NH species. This result can be explained as follows: First, the hydrogenation process may be structure sensitive (although this seems unlikely given that the reaction is a bond-making rather than bond-breaking reaction), and can only be realized for
certain geometric arrangements of the reactants on the surface. Further DFT studies by Ricart and coworkers showed that the ammonia dehydrogenation reaction is structure sensitive [146]. In addition, while Mudiyanselage, et al. showed that while nitrogen atoms on Pt(111) can be rehydrogenated to form NH, further hydrogenation to NH$_2$ or NH$_3$ is not favorable under UHV conditions. However, in contrast, hydrogenation of NO on the Pt(100)-(1 x 1) surface resulted in the formation of NH$_2$$_{ads}$ through hydrogenation of N$_{ads}$ produced by NO$_{ads}$, which dissociated on the surface at 300 K [150], so Satsuma’s results may be linked to small particles that have a variety of geometries, which ultimately favor NH$_3$ formation.
Varying amounts of ethylene were exposed to the N/Pt(111) surface in an effort to understand coverage effects in this system as shown in figure 45. While increasing ethylene exposure from 0.4 to 0.8 L resulted in an increase in the ammonia desorption peak, further increasing the exposure from 0.8 to 1.6 L didn’t produce additional ammonia. Apparently, additional exposure of after exposing 0.8 L C\textsubscript{2}H\textsubscript{4} does not result in surface geometries favorable for hydrogen
TABLE III
FITTING RESULTS OF C₂D₄ ON PT(111)

<table>
<thead>
<tr>
<th>Peak</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting curve</td>
<td>Lorentzian</td>
<td>Gauss</td>
<td>Lorentzian</td>
</tr>
<tr>
<td>Location</td>
<td>335 K</td>
<td>504 K</td>
<td>549 K</td>
</tr>
<tr>
<td>Height</td>
<td>1.0</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Area</td>
<td>1.0</td>
<td>3.2</td>
<td>2.1</td>
</tr>
<tr>
<td>FWHM</td>
<td>1.6</td>
<td>2.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

transfer from the hydrocarbon to N atoms. The fact that the same exposure of acetylene generates much more ammonia is slightly counterintuitive since ethylene possesses twice as much hydrogen as acetylene. In addition, more ethylidyne is produced by ethylene and therefore if decomposition of this species is responsible for ammonia formation, ammonia production should be higher when using ethylene as the hydrocarbon source. Therefore, these observations suggest that CCH is the hydrogen source for ammonia formation. In order to confirm this hypothesis, we exposed 0.8 L of C₂D₂ to nitrogen covered Pt(111) at 480 K and at 400 K as depicted in figure 46. Previous RAIRS data showed that at 400 K, C₂D₂ converts partially to CCD₃ on the surface but at 480 K, most C₂D₂ converts to CCD [158]. The ammonia desorption peak is about 46% when C₂D₂ is exposed to nitrogen covered Pt(111) at 480 K as compared to at 400 K. However, considering that by 480 K some nitrogen atoms start to desorb from the surface, which likely contributes to the decrease of the ammonia desorption peak. As a further test, the nitrogen layer was annealed to 480 K and then C₂D₂ was exposed at 400 K, which resulted
in an ammonia peak intensity comparable to that found by exposing to C$_2$D$_2$ at 480 K. This results suggests that CCH is the primary source for hydrogen that leads to ammonia formation.
Figure 45. TPD results for m/z=20 (ND₃) desorption followed by different ethylene exposure on N/Pt(111)
Figure 46. TPD results for m/z=20 (ND₃) followed by exposing of 0.8 L acetylene at different temperatures on N/Pt(111)
CHAPTER 6

C-N COUPLING REACTION OF ETHYLENE ON N-COVERED PT(111)

6.1 Background

Reduction of NO using hydrocarbons by Pt catalysts is of great interest in automotive exhaust catalysis. Nitrile and C-N containing species, such as isocyanic acid (HNCO), have been detected on the surface by various surface spectroscopy techniques and are argued to be key reaction intermediates. However, direct evidence of the identity of the possible reaction intermediates is still lacking. Therefore the C-N coupling reaction on the Pt(111) surface is of potential interest and importance to an understanding of deNO\textsubscript{x} chemistry.

Previously, DeLouise and Winograd reported formation of surface CN species as a product of reaction between NO with carbidic carbon prepared by decomposition of ethylene on Rh(331) surface [159]. Hardeveld and co-workers reported HCN formation in the reaction of NO with ethylene (C\textsubscript{2}H\textsubscript{4}) on the Rh(111) surface and they also reported the formation of HCN and C\textsubscript{2}N\textsubscript{2} in the reaction of atomic N with ethylene using TPRS and secondary ion mass spectrometry (SIMS). Nitrogen atoms are prepared by thermal dissociation of NO on Rh surfaces and subsequent removal of oxygen by exposing hydrogen at 375 K. In contrast, Griffith et al. had undertaken a series of surface science studies of the interaction of NO and ethylene on Pt (322) [80–82]. Although the presence of the co-adsorbed hydrocarbon led to the production of N\textsubscript{2}, no HCN or any other species associated with the C-N coupling reaction were observed.
Unlike Pt, Rh is known to be particularly effective for NO$_x$ reduction with CO and hydrogen as it can dissociate NO much more readily than Pt, which is essential for the C-N coupling reaction to occur. Thus, examination of the interaction between nitrogen atoms and hydrocarbons is much more challenging on Pt surfaces than on Rh surfaces.

The C-N coupling has been reported recently on the Pt(111) surface after exposure of the surface to NH$_3$ and various hydrocarbons such as methyl iodide and C$_2$ produced from acetylene dehydrogenation [143,155,160]. Herceg and co-workers created C atoms and N atoms on Pt(111) by electron bombardment of methyl iodide and ammonia on Pt(111) under ultrahigh vacuum (UHV) conditions. The CN coupling reaction was studied as a means of examination of the HCN formation mechanism. The relevant industrial synthesis of HCN is from CH$_4$ and NH$_3$ over Pt gauze catalysts at near atmospheric pressures and at temperatures in the range of 1100-1300 °C. Their study showed that the coupling reaction occurs only between carbon atoms and nitrogen atoms and not any other CH$_x$ or NH$_x$ species. After annealing the surface to 480 K, all the CH$_x$ and NH species have undergone complete dehydrogenation as shown in the hydrogen desorption spectra. However, HCN is seen to desorb at around 500 K. Their study also showed that there is no significant C-N coupling reaction at temperatures above 500 K, at which temperature much fewer N atoms are available on the surface [143]. In another study of the interaction of NH$_3$ and dicarbon, which was prepared by decomposition of acetylene on Pt(111) by heating to 750 K, the C-N coupling reaction was also detected. XPS and RAIRS data indicate that the coupling step takes place at temperatures as low as 200 K, but the RAIRS spectrum of the C-N species is rather weak. Deng et al. suggested that the
C-N coupling involves formation of an HCCNH$_2$ surface intermediate.

Ternary and co-workers have discovered a very effective way of preparing a well-ordered, clean nitrogen-covered Pt surface by oxygenation of ammonia on the surface and subsequent removal of water by annealing the surface to 400 K. A detailed procedure can be found in Herceg et al. [106]. LEED data indicated the nitrogen coverage on the surface is 0.25 ML. This provides us with a good foundation to study the reaction between nitrogen atoms and hydrocarbons on Pt(111).

Two main issues are probed in the current work. First, we wish to investigate the reaction of hydrocarbon species (specifically C$_2$H$_4$ as a model compound) on N-covered Pt(111), in the absence of oxygen to improve our understanding of the mechanisms in SCR of NO by hydrocarbons and to determine how C-N coupling may play a role in deNO$_x$. Second, in this system, we wish to explore the potential addition of N atoms to C=C bonds, in a manner analogous to ethylene epoxidation on Ag [161] and styrene oxidation on oxygen-covered Au(111) [162]. The Friend group has studied addition of N and NH to C=C double bonds on Ag(110) and Au(111) [163,164]. Temperature programmed desorption experiments of styrene on N and NH covered Ag (110) and Au (111) and suggested that cycloaddition of N to the alkene to form aziridine occurred at 450 K. Friend et al. proposed that N atoms are also responsible for the production of benzonitrile and HCN, where the C=C double bond breaks. However, it is not clear how general this chemistry is or if aziridine can form on the Pt(111) surface as Pt(111) may hold one or both of the reactants more strongly than Au or Ag. In particular, Pt is more
reactive than Ag or Au for dehydrogenation of olefinic bonds, leading to decomposition of the hydrocarbon before insertion can occur.

6.2 Experimental

The experiments were performed in two separate UHV chambers using two different Pt (111) crystals. The TPD results were obtained in the new system described in the second chapter (denoted as chamber 1). The RAIRS experiments were performed in a second chamber (denoted as chamber 2) with a base pressure of $2 \times 10^{-10}$ torr. A detailed description of this system can be found elsewhere [147]. In brief, this UHV chamber is equipped for RAIRS, AES, and LEED experiments. The chamber is coupled to a commercial Fourier transform infrared (FTIR) spectrometer, a Bruker IFS 66v/S. The IR beam enters and exits the UHV chamber through differentially pumped O-ring sealed KBr windows and passes through a polarizer before reaching the infrared detector. We used a MCT (HgCdTe) detector and a SiC source. In cases where the sample was annealed to a temperature above 90 K, it was cooled back to 90 K before the spectrum was acquired. The background reference spectrum was also taken at 90 K. A resolution of 4 cm$^{-1}$ was used for all spectra. The Pt(111) surfaces were cleaned and judged free of impurities by a standard procedure described earlier [147]. Ammonia (99.9992%), oxygen (99.998%), and ethylene (99.8%) were purchased from Matheson Tri-gas and used without further purification.
6.3 Results and discussion

6.3.1 TPRS study

A p(2 x 2)-N layer was formed by exposing the surface to 2 L of oxygen and 0.4 L of ammonia to the surface at 90 K and then annealing to 400 K for 60 s following the experimental procedure reported by Herceg et al. [106]. An intense and sharp p(2 x 2)(0.25ML) LEED pattern due to the presence of an atomic nitrogen layer was observed.

The results of a TPRS study following exposure of 0.8 L ethylene to clean Pt(111) and on nitrogen covered Pt(111) is shown in Figure 47. m/z = 27 can be ascribed to either HCN or a fragment of ethylene. The low temperature peak around 300 K is the desorption of ethylene from the surface, on N covered Pt(111), π bonded ethylene as well as di-σ bonded ethylene formed on the surface contribute to a small shoulder at lower temperature besides the major peak compared to on the clean surface. A detailed discussion of the formation of π bonded ethylene can be found elsewhere [148]. The high temperature peak around 580 K is the desorption of HCN, indicating C-N coupling reaction occurs below this temperature and CN is subsequently hydrogenated before desorption as HCN. Previous TPRS results show that the CN desorbs as HCN in the presence of coadsorbed H and as C$_2$N$_2$ in the absence of hydrogen.

Figure 48 shows that, as the ethylene exposure increases from 0.4 to 1.6 L, the low temperature peak increases as well, but the high temperature peak does not follow this trend. In fact, the smallest amount of HCN desorption occurred with a 0.8 L ethylene exposure. Recalling that ethylene may also hydrogenate the nitrogen atoms to produce ammonia at slightly lower temperature, with a maximum in the amount of NH$_3$, at a 0.8 L ethylene exposure, we speculate
Figure 47. TPD results of HCN desorption followed by exposing 0.8L C_2H_4 to N covered Pt(111).
that the ammonia formation occurs before the C-N coupling reaction occurs at this exposure and therefore consumes a large fraction of the nitrogen, thus resulting in a smaller amount of CN. It’s also concluded from these results that the C-N coupling is related to the availability of both the carbon source and nitrogen atoms on the surface.

We also monitored m/z = 52 as a measure of cyanogen (C$_2$N$_2$) desorption with varying ethylene exposure as showed in Figures 49 and 50. The signal for cyanogen desorption is small compared with HCN desorption. The desorption of cyanogen is due to the recombinative desorption of CN from the surface [165]. The smallest cyanogen desorption peak is found with 0.8 L ethylene exposure, in agreement with what we found for the HCN desorption result. Because the signal for C$_2$N$_2$ is very weak, we used isotopic ammonia $^{15}$NH$_3$ to help verify our result. Exposing ethylene on $^{15}$N layer on the surface, the m/z of cyanogen C$_2$N$_2$ also shifted to 54 with an intensity similar to the same condition using$^{14}$N, and there is no desorption peak at m/z = 52.

6.3.2 RAIRS study

RAIRS data obtained after exposing 0.8 L of ethylene to the 0.25 ML nitrogen covered Pt surface at 90 K and subsequent heating to the indicated temperatures are shown in the Figure 51.

As mentioned in Chapter 4 the peaks at 3083 and 975 cm$^{-1}$ are assigned to π-bonded ethylene and the peak at 1341 cm$^{-1}$ is assigned to the CH$_3$ symmetric deformation of ethylidyne. It is also readily apparent that a large peak is present that shifts from 1151 to 1191 cm$^{-1}$ as the surface is heated from 130 to 310 K, which is consistent with the symmetric deformation mode
Figure 48. TPD results of HCN desorption followed by exposing different amount C$_2$H$_4$ to N covered Pt(111).
Figure 49. TPD results for m/z = 52 (C\textsubscript{2}N\textsubscript{2}) desorption followed by different C\textsubscript{2}H\textsubscript{4} exposure to N covered Pt(111).
Figure 50. TPD results for m/z = 52 (C$_2$N$_2$) desorption followed exposing 0.8 L C$_2$H$_4$ vs 0.8 L C$_2$D$_4$ to N covered Pt(111).
of NH$_3$. The ammonia peak increases upon annealing and shifts to higher frequencies. After annealing to 250 K, a new peak appears at 3320 cm$^{-1}$, due to the NH species, which grows until 410 K. It’s known that less than 3% of ammonia will be dissociated on Pt(111) [141]. Therefore, the NH peak at 410 K may be partly due to the dissociation of readsorbed ammonia on the surface and partly due to the hydrogenation of N atoms on the surface. Upon annealing above 500 K, the NH peak decreases significantly, consistent with previous results showing that NH dissociates on Pt(111) at 450 K [105]. While ammonia normally desorbs without dissociation from Pt(111) below 400 K, the spectra from this experiment shows that ammonia remains on the surface as indicated by the observation of the NH$_3$ deformation peak up to 560 K. The presence of the NH peak at 560 K indicates that there are small amount of NH$_x$ species remaining on the surface at this temperature.

Previously Trenary and co-workers demonstrated that although surface CN cannot be directly detected by RAIRS, CN is readily hydrogenated at room temperature to aminocarbyne (CNH$_2$) which has a strong characteristic vibrational spectrum [121, 166]. Figure 52 shows RAIRS spectra for an exposure of 0.8 L ethylene to the 0.25 ML nitrogen covered Pt surface at 90 K, followed by annealing to 560 K, and then exposure to 10 L hydrogen at room temperature. Peaks at 1333, 1344, 1565, 3372 cm$^{-1}$ are assigned to the CN stretch, $\nu$(CN), the CH$_3$ bending mode of CCH$_3$, $\delta$ (CH$_3$), the NH$_2$ bending mode, $\delta$(NH$_2$) and the NH stretch, $\nu$(NH), respectively. The results are in agreement with the literature [166] and some of the peaks can therefore be assigned to aminocarbyne: CN, $\delta$(NH$_2$) and $\nu$(NH). The peak at 3320 cm$^{-1}$ is assigned to the NH stretch, $\nu$(NH) of surface NH formed by hydrogenation of the excess N$_{ads}$
atoms that remain on the surface. Annealing to temperatures lower than 560 K didn’t yield aminocarbyne in the RAIRS peaks.

This result differs slightly from the previous study carried out by Herceg and coworkers where they found that the C-N coupling reaction occurred between the thermal decomposition product of methyl iodide and the electron bombardment product of ammonia on the Pt(111) surface and detected CN species (HCN, H$_2$CN) by annealing to 500 K followed by hydrogenation. The fact that the temperature for the C-N coupling reaction occurs at higher temperature in the current experiment implies that ethylene didn’t undergo C-C bond cleavage before 560 K. In another RAIRS study of ethylene on Pt(111) [110], it was found that even after annealing to 500 K, C-H stretch bands were still present at 3037 and 2964 cm$^{-1}$, which were assigned to the C-H stretch of ethynyl (CCH). We already established that ethynyl (CCH) is an important hydrogen source for nitrogen hydrogenation to form ammonia, and it’s then suggested that C-N coupling occurs after the ammonia formation. Secondly, the observation of the CH$_3$ bending mode of CCH$_3$, δ(CH$_3$), at 1344 cm$^{-1}$ suggests that some C-C bonds remain intact on the surface at this temperature and the C$_2$ species can be rehydrogenated to form CCH$_3$. Our previous study showed that in the presence of nitrogen atoms, the density of states of Pt(111) shift away from the Fermi level and make the Pt surface less reactive. Under such circumstances, C-C bond cleavage is reduced. Finally, the intensity of the aminocarbyne peaks observed here is twice as intense as observed in previous study of Herceg et al., indicating a much stronger coupling reaction with this method, possibly due to the presence of the ordered p(2 x 2) layer as opposed to Herceg et al.’s method for generation of N atoms.
Figure 51. RAIR spectra followed by exposing 0.8 L C$_2$H$_4$ to N covered Pt(111).
Figure 52. RAIR spectra followed by exposing 0.8 L C₂H₄ to N covered Pt(111) and annealing to 560 K.


VITA

NAME: Jun Yin

EDUCATION: Ph.D., Chemical Engineering, University of Illinois at Chicago, Illinois, 2011
M.S., Central South University, Changsha, China, 2006
B.A., Central South University, Changsha, China, 2003

PRESENTATIONS: UIC Research Forum, Chicago, IL, 2010
Annual Chicago Catalysis Club Symposium, Chicago, IL, 2010
Physical Electronic Conference, Milwaukee, WI, 2010
Gordon Conference on Catalysis, New London, NH, 2010
American Vacuum Society, Albuquerque, NW, 2010
American Institute of Chemical Engineering, Salt Lake, UT, 2010

PROFESSIONAL MEMBERSHIP: American institute of chemical engineers (AICHE)

MEMBERSHIP: American vacuum society (AVS)
Chicago catalysis club (CCC)

J.Yin, H.Q.Ye,: Preparation of flaky titanium dioxide, China powder science and technology, 6, 9-11, 2005