ABSTRACT

CHIN, PAUL. Preferential Oxidation of Carbon Monoxide on Structured Supports. (Under the direction of Drs. George W. Roberts and James J. Spivey)

Hydrocarbon fuels must be reformed in a series of steps to provide hydrogen for use in proton exchange membrane fuel cells (PEMFCs). Preferential oxidation (PROX) is one method to reduce the CO concentration to < 10 ppm in the presence of ~40% H₂, CO₂, and steam. This will prevent CO poisoning of the PEMFC anode. The PROX reaction requires an active, selective, and stable catalyst. Structured supports, such as ceramic monoliths, can be used for the PROX reaction. Metal foams offer advantages over the traditional ceramic monolith: higher thermal conductivity, radial mixing and heat transport, and a durable, low density, high strength structure.

Reaction studies were conducted on catalyzed structured supports using a fixed bed adiabatic reactor with an online non-dispersive IR gas analyzer. A study on ceramic monoliths showed that higher Fe loadings promoted on 5 wt% Pt / γ-Al₂O₃ increased CO and O₂ conversions and decreased CO selectivity. A study on metal foams showed that lower cell density and higher pores per inch foams exhibited higher CO conversions and selectivity. Under most operating conditions, the CO conversion and selectivity of the best 5 wt% Pt / 0.5 wt% Fe metal foam were comparable to the ceramic monolith. Comparison tests showed lower CO conversion and selectivity for the ceramic foam and the metal monolith compared to the metal foam and ceramic monolith.
Two important effects limit the PROX reaction: the reverse water-gas-shift (r-WGS) reaction, and transport resistances. Under adiabatic conditions, the r-WGS reaction made it impossible to achieve low outlet CO concentrations. The metal foam showed less r-WGS activity compared to the ceramic monolith. The effects of space velocity and linear velocity were studied independently using various catalyst lengths and flow rates. The CO conversion increased at higher linear velocities, which suggested mass transfer resistance between the bulk gas and the catalyst surface.

Carbon monoxide pulse chemisorption and temperature programmed desorption (TPD) were used to determine the number of active metal sites. Pulse chemisorption and TPD experiments on the blank reactor and the blank metal foam wrapped with glass wool insulation showed no CO adsorption. No CO adsorption was observed from pulse chemisorption tests on the ceramic fiber insulation, however, considerable CO desorption was observed from TPD tests. On catalyzed supports, an elongated tail in the pulse chemisorption tests was attributed to CO adsorption on either the $\gamma$-Al$_2$O$_3$ washcoat or on surface impurities. The pulse chemisorption and TPD results did not describe the catalyst performance results. Higher values of the number of CO adsorbed on the catalyst surface did not correspond to higher CO conversions from the PROX reaction.
Preferential Oxidation of Carbon Monoxide on Structured Supports

by

Paul Chin

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the requirements
for the Degree of Masters of Science

Department of Chemical Engineering

Raleigh, North Carolina
June 2004

Approved By:

Dr. H. Henry Lamb
Chemical Engineering

Dr. George W. Roberts
Chemical Engineering
Chair of Advisory Committee

Dr. James J. Spivey
Chemical Engineering
Co-Chair of Advisory Committee
To my grandmother, Gum Fung Yee, who passed away in 1994 at age 82. She took care of me when I was young, and I didn’t appreciate what she gave me and how much she loved me until after she passed away. Thank you for raising me as a child and making sure I wasn’t a troublemaker (too little, too late).
PERSONAL BIOGRAPHY

Paul Chin was born on November 30th, 1979 (Roman calendar) in Hong Kong en route to the United States. One month later he transitioned to the United States of America with his mother. He spent the first nine years of his life in Flushing, NY, and the latter nine years of his childhood in Burlington, MA. He is a Red Sox and a NY Mets/Yankees fan, making him the ultimate baseball paradox. Paul was a part-time Chinese restaurant front desk worker, part-time hospital volunteer, part-time actor in crazy high school videos, but a full-time wise-cracking New Englander.

After graduating with his high school diploma in 1997 from Burlington High School, he attended Cornell University for his undergraduate degree in Ithaca, NY. He volunteered substantially in his fraternity, Alpha Phi Omega, was active in the AIChE student chapter, and co-oped at Air Products and Chemical, Inc. He graduated with his Bachelors of Science in Chemical Engineering in May 2001, where he will be forever indebted to (both intellectually and financially).

In August 2001, he joined the rank of graduate student at North Carolina State University in Raleigh, NC, for his graduate degree in chemical engineering. His research focused on structured catalytic supports for fuel cell applications using kinetics, catalysis, and reaction engineering. He was co-advised by Drs. George W. Roberts and James J. Spivey.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisors Drs. George W. Roberts and James J. Spivey for their endless dedication, direction, and discussion. Without them I would not have achieved my goals for this thesis. Both of them have always been there, especially late in the evenings, when I needed help the most. I would also like to thank the Department of Energy for the research funds, and the chemical engineering department at North Carolina State University for taking a chance on me.

Secondly, I would like to thank Dr. Xiaolei Sun who worked with me as a post-doctorate when I started. Without her, I would have struggled to get my research off the ground. Thank you to Christopher J. Kloxin who composed the initial Matlab program for the pulse chemisorption and TPD analysis. Thank you to Kyle M. Bishop, a summer REU student who helped me model the r-WGS reaction equilibrium.

Thirdly, I would like to thank fellow graduate students Esther M. Wilcox and Susan M. Sigmon. Esther, thank you for putting up with me and teaching me the difference between a male and female fitting. Susan, thank you for teaching me about mammal anatomy using a Dr. Seuss book (Horton Hatches The Egg). I would also like to thank Apostolos (Tolis) A. Nikolopoulos for sharing all of his technical knowledge and expertise with me.
Fourthly, I would like to thank the wonderful employees at the NC State Machine Shop. Even though I could see their inner groans and sad faces every time I walked into the shop with my reactor, they were always helpful, fixed my problems, and welded on flanges to prevent more trips to the physical therapist from trying to open my old reactor.

Fifthly, I would like to thank Joan D. Patterson, Angelica M. Sanchez, and Brian G. Prevo, for making my three years here wonderful. We had a small incoming class, and without their support and understanding in my life I would not have made it past the first year. Also I would like to thank my exceptionally close high school friends, Emily K. Cheung, Chad A. Parmet, Calvin Ho, and Kenneth Eaton, all who have helped me in one form or another through tough times in various stages of my life.

Sixthly, I would like to thank Christopher A. Post, whom without his full love and support these past two and a half years, I would not have realized my full potential. Thank you so much.

Last, but not least, I would like to thank my family members, especially my parents, my brother Benjamin, and my sister-in-law Urvi. Without them I would have never made it this far in life. They have been there for me every step of the way, have always loved me unconditionally, and have supported me through all of my tough decisions. Were it not for them, I would not be the thoroughly neurotic, obsessive-compulsive (just kidding!) person I am today.
# TABLE OF CONTENTS

| LIST OF TABLES | ..............................................................................................................................x |
| LIST OF FIGURES | ..........................................................................................................................xii |
| LIST OF EQUATIONS | .......................................................................................................................xvii |
| LIST OF REACTIONS | ......................................................................................................................xviii |
| LIST OF SYMBOLS AND ABBREVIATIONS | .............................................................................................xix |

## CHAPTER 1 INTRODUCTION

1.1 CO Preferential Oxidation .............................................................................................................1

1.2 Metal Foam Supports ..................................................................................................................3

1.3 Objective .....................................................................................................................................5

1.4 References ..................................................................................................................................7

## CHAPTER 2 LITERATURE REVIEW

2.1 Fuel Cells ....................................................................................................................................11

2.1.1 Proton Exchange Membrane Fuel Cell .................................................................................12

2.1.2 Reformer Technology .............................................................................................................15

2.1.3 Other Types of Fuel Cells .....................................................................................................17

2.2 CO Preferential Oxidation ..........................................................................................................18

2.2.1 Different Types of Metals ......................................................................................................18

2.2.1.1 Platinum, Palladium, Ruthenium, and Rhodium Catalysts ..............................................19

2.2.1.2 Gold Catalysts ..................................................................................................................22

2.2.1.3 Bimetallic and Metal Oxide Promoted Catalysts ...............................................................25

2.2.2 Kinetics ..................................................................................................................................28

2.2.3 The Reverse Water-Gas-Shift Reaction ...............................................................................31

2.2.4 Catalyst Characterization .....................................................................................................35
2.3 Structured Supports ................................................................. 39
   2.3.1 Ceramic Monoliths ............................................................. 39
   2.3.2 Metal Foams ................................................................. 41

2.4 Other CO Reduction Methods .................................................. 44
   2.4.1 Methanation .................................................................. 44
   2.4.2 Pressure-Swing Adsorption ............................................ 45
   2.4.3 Selective Membranes .................................................... 46

2.5 References ............................................................................. 47

CHAPTER 3  PREFERENTIAL OXIDATION STUDY ......................... 54

3.1 Experimental Design ............................................................... 54
   3.1.1 Catalyst Preparation Procedure ........................................ 56
   3.1.2 Equipment and Measurement .......................................... 58
   3.1.3 Reactor Design ............................................................. 61
   3.1.4 Process Design ............................................................ 63

3.2 Data Analysis ........................................................................ 65

3.3 Ceramic Monoliths Results and Discussion ............................. 68
   3.3.1 Low Pt / Fe catalyst loading ............................................ 69
   3.3.2 5 wt% Pt / Varying Fe weight loading study ..................... 70

3.4 Metal Foam Results and Discussion ........................................ 73
   3.4.1 No Catalyst Pretreatment ............................................... 73
   3.4.2 Catalyst Pretreatment .................................................... 75

3.5 Metal Monolith and Ceramic Foam Results and Discussion ........ 77

3.6 References ............................................................................. 80

CHAPTER 4  PROX CATALYST SUPPORT COMPARISON ............ 82

4.1 Significance of the Reverse Water-Gas-Shift Reaction .............. 82

4.2 Metal Foam / Ceramic Monolith Comparison .......................... 89
   4.2.1 Reverse water-gas-shift activity ...................................... 89
   4.2.2 PROX reaction comparison (No Pretreatment) ................. 91
   4.2.3 Transient study ............................................................ 93
   4.2.4 $O_2/CO$ ratio study ...................................................... 95
4.3 Transport Effects Results and Discussion ............................................................97
  4.3.1 Linear Velocity (Constant GHSV) Study ......................................................103
  4.3.2 Space Velocity (Constant Linear Velocity) Study ....................................104
  4.3.3 “Identical” Pieces Similarity Study ..........................................................110

4.4 References .........................................................................................................113

CHAPTER 5 CATALYST SUPPORT CHARACTERIZATION ...............115
5.1 Experimental Design ..........................................................................................115
  5.1.1 Equipment & Process Design ..................................................................115
  5.1.2 Reactor Design ......................................................................................116

5.2 CO Pulse Chemisorption ...................................................................................118
  5.2.1 Theory ....................................................................................................118
  5.2.2 Data Analysis .......................................................................................119
  5.2.3 Experimental Procedure .......................................................................122
  5.2.4 Background Study ................................................................................122
  5.2.5 Initial Results .......................................................................................124

5.3 CO Temperature-Programmed Desorption (TPD) .........................................128
  5.3.1 Theory ....................................................................................................128
  5.3.2 Data Analysis .......................................................................................130
  5.3.3 Experimental Procedure .......................................................................132
  5.3.4 Background Study ................................................................................133
  5.3.5 Initial Results .......................................................................................136

5.4 Washcoating ICP / BET Results .....................................................................140
  5.4.1 NC State Wet Impregnation Procedure .................................................141
  5.4.2 ICP Results and Discussion ..................................................................142
  5.4.3 BET Results and Discussion ................................................................143

5.5 References .........................................................................................................145

CHAPTER 6 CONCLUSIONS ..............................................................................148
6.1 Conclusions .......................................................................................................148

6.2 Recommendations ............................................................................................151

6.3 References .......................................................................................................154
<table>
<thead>
<tr>
<th>APPENDICES</th>
<th>APPENDIX A METAL FOAM PICTURES</th>
<th>APPENDIX B REACTOR AND PROCESS DIAGRAMS</th>
<th>APPENDIX C PREFERENTIAL OXIDATION REACTION DATA</th>
<th>APPENDIX D PROX CATALYST SUPPORT COMPARISON DATA</th>
<th>APPENDIX E CATALYST CHARACTERIZATION DATA</th>
<th>APPENDIX F MATLAB CODE FOR CHARACTERIZATION ANALYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>156</td>
<td>157</td>
<td>158</td>
<td>163</td>
<td>166</td>
<td>177</td>
</tr>
</tbody>
</table>

ix
LIST OF TABLES

Page Number

Table 2.1 The fuel requirements for the principal types of fuel cells (reproduced from Larminie, J. and A. Dicks, Fuel Cell Systems Explained. 2000. Table 7.6) ................................................................. 18

Table 3.1 NDIR Components and Ranges .............................................................. 60

Table 3.2 $\Delta T_{ad}$ calculations for various CO inlet concentrations and $O_2/CO$ ratios .................................................................................................................... 67

Table 3.3 Effect of CO concentration on the monolith promoted Pt catalyst performance (GHSV=20,000 hr$^{-1}$, 2000 ppm CO inlet concentration, from Korotkikh and Farrauto, Catalysis Today, 2000. 62(2-3): p. 249-254, Table 2) .............................................................. 72

Table 5.1 Obtainable results from pulse chemisorption and TPD ......................... 115

Table 5.2 Pulse chemisorption results on a background study of the blank reactor, ceramic fibers, uncatalyzed, unwashcoated blank metal foam, and glass wool ........................................................................................................ 123

Table 5.3 CO pulse chemisorption results on the initial set of catalysts .............. 125

Table 5.4 TPD results on a background study of the blank reactor, ceramic fibers, uncatalyzed, unwashcoated blank metal foam, and glass wool with ramp rates of $\sim$ 5-15°C/min ............................................................... 133

Table 5.5 Low temperature peak CO TPD results on the initial set of four catalyst supports with ramp rates $\sim$ 8-11°C/min ................................................................. 136

Table 5.6 High temperature peak CO TPD results on the initial set of four catalyst supports with ramp rates $\sim$ 8-11°C/min ................................................................. 139

Table 5.7 Average BET surface areas for pure Pt, Pt/Fe, and Pt/Ni catalysts washcoated on $\gamma$-Al$_2$O$_3$ made in-house or by Environex .......................... 144

Table C.1 Effect of pretreatment on a 5 wt% Pt / 0.5 wt% Fe / $\gamma$-Al$_2$O$_3$ ceramic monolith and metal foam .............................................................................. 163

Table C.2 Comparison of Catalyst Performance for the Ceramic Foam, Metal Monolith, Metal Foam and Ceramic Monolith ............................................. 165
Table D.1  Comparison of catalyst activity and selectivity for three “identical” 40 ppi, 4% ρ metal foams (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 1.0, 150°C inlet temperature, GHSV=30,000 hr⁻¹).................................................................................................175

Table D.2  Comparison of catalyst activity and selectivity for three “identical” 400 cpsi ceramic straight-channel monoliths (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 1.0, 150°C inlet temperature, GHSV=30,000 hr⁻¹).................................................................................................175

Table E.1  ICP Analysis of Pt, Pt/Fe, and Pt/Ni catalysts washcoated on γ-Al₂O₃ made in-house or by Environex .................................................................179

Table E.2  BET surface area results for pure Pt, Pt/Fe, and Pt/Ni catalysts washcoated on γ-Al₂O₃ made in-house or by Environex ........................180
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Open cell structure of a foam</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>The “Hindenburg Disaster” of May 6(^{th}), 1937, which gave ( \text{H}_2 ) a bad reputation. (reproduced from the Hydrogen Now! website, <a href="http://www.hydrogennow.org/">http://www.hydrogennow.org/</a>, 2002)</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>Elementary steps for CO oxidation according to Langmuir-Hinshelwood reaction mechanism (reproduced from Farrauto, R.J. and C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, 1997.)</td>
<td>28</td>
</tr>
<tr>
<td>2.4</td>
<td>Generalized L-H schematic of the CO oxidation reaction rate as a function of CO partial pressure ( (P_{CO}) ) at a constant ( \text{O}<em>2 ) partial pressure ( (P</em>{O2}) )</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Examples of CO-Pt configurations in a (a) linear bond and (b) bridged bond</td>
<td>36</td>
</tr>
<tr>
<td>3.1</td>
<td>Catalyst support length and diameter</td>
<td>54</td>
</tr>
<tr>
<td>3.2</td>
<td>Sample pictures of a (a) 40 ppi, 4% ( \rho ) metal foam, (b) 400 cps( \iota ) ceramic straight-channel monolith, and (c) 400 cps( \iota ) equivalent metal monolith</td>
<td>56</td>
</tr>
<tr>
<td>3.3</td>
<td>Reaction reactor design schematic</td>
<td>62</td>
</tr>
<tr>
<td>3.4</td>
<td>Effect of Fe weight loading on 400 cps( \iota ), 5 wt% Pt / ( \gamma )-( \text{Al}_2\text{O}_3 ) ceramic straight-channel monoliths at inlet gas temperatures of (a) 100°C and (b) 170°C (1% CO inlet concentration, ( \text{O}_2/\text{CO} ) ratio = 1.0, GHSV = 30,000 hr(^{-1}))</td>
<td>71</td>
</tr>
</tbody>
</table>
Figure 3.5  (a) CO conversion and (b) CO selectivity for four different metal foams as a function of inlet gas temperature (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ catalysts, 1% CO inlet concentration, O₂/CO ratio = 1.0, GHSV = 30,000 hr⁻¹). ................................................................................... 74

Figure 3.6  Effect of pretreatment on (a) CO conversion and (b) CO selectivity as a function of inlet temperature for the 20 ppi, 12% ρ metal foam (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ catalyst, 1% CO inlet concentration, O₂/CO ratio = 1.0, GHSV = 30,000 hr⁻¹) .................................................... 76

Figure 3.7  400 cpsi equivalent metal monolith, 20 ppi, 11% ρ ceramic foam, and 40 ppi, 4% ρ “newer” metal foam comparison of (a) CO conversion and (b) CO selectivity as a function of inlet temperature (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 0.098 g/cm³ washcoat loading, 1% CO inlet concentration, O₂/CO ratio = 0.5, GHSV=30,000 hr⁻¹)............................... 79

Figure 4.1  CO formed by the r-WGS reaction on 5 wt% Pt / 0.1 wt% Fe / γ-Al₂O₃ ceramic straight-channel monoliths as a function of (a) the measured outlet temperature and (b) the adiabatic reaction outlet temperature (no CO in the feed, varying O₂ concentration and/or inlet temperature, GHSV=30,000 hr⁻¹)................................................................. 84

Figure 4.2  Illustration of the r-WGS reaction re-equilibrating at a lower temperature when the “hot spot” is located towards the inlet region........ 86

Figure 4.3  CO formed by the r-WGS reaction on the 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ ceramic straight-channel monolith (no CO in the feed, 0-1% O₂ inlet concentration, 170°C inlet temperature, GHSV=30,000 hr⁻¹) ...... 87

Figure 4.4  CO formed by the r-WGS reaction on the 5 wt% Pt / 0.1 wt% Fe / γ-Al₂O₃ ceramic straight-channel monolith (no CO in the feed, 0.1-1.0% O₂ inlet concentration, 170°C inlet temperature, GHSV=30,000 hr⁻¹).............................................................................................................. 89

Figure 4.5  CO formed by the r-WGS reaction on the 40 ppi, 4% ρ metal foam and 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, no CO in the feed, 0.1-1.0% O₂ inlet concentration, 100-170°C inlet temperatures, GHSV = 30,000 hr⁻¹)................................. 90

Figure 4.6  Comparison of CO (a) conversion and (b) selectivity on a 40 ppi, 4% ρ metal foam and a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1.0% CO inlet concentration, O₂/CO ratio = 1.0, GHSV=30,000 hr⁻¹, varying inlet temperatures)................................. 92
Figure 4.7  Transient effects on the (a) outlet temperature and (b) outlet CO concentration for the 400 cpsi ceramic straight-channel monolith and 20 ppi, 12% ρ metal foam after pretreatment (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 1.0, inlet temperature = 109°C, GHSV=30,000 hr⁻¹) .........................................................94

Figure 4.8  Effect of O₂/CO ratio on a (a) 40 ppi, 4% ρ metal foam and (b) 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, 0.25-1.0 O₂/CO ratio, 80°C inlet temperature, GHSV=30,000 hr⁻¹) ................................................................96

Figure 4.9  GHSV and linear velocity comparison between the 40 ppi, 4% ρ metal foam and 400 cpsi ceramic monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 10,000-45,000 hr⁻¹ GHSV) .................................................................................98

Figure 4.10  Effects of GHSV & linear velocity on the 40 ppi, 4% ρ metal foam (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 10,000 and 15,000 hr⁻¹ GHSV) ...........................................................................103

Figure 4.11  Schematic of possible heat and mass transport resistances under CO PROX conditions between the bulk inlet gas stream and the catalyst surface. .................................................................................................102

Figure 4.12  Effect of linear velocity at a constant GHSV on a 40 ppi, 4% ρ metal foam (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 10,000 and 15,000 hr⁻¹ GHSV) ......................................................................................................................103

Figure 4.13  Effect of GHSV at a constant linear velocity on a 40 ppi, 4% ρ metal foam (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 5,000-45,000 hr⁻¹ GHSV) ....105

Figure 4.14  Schematic drawing of Figure 4.13, linear velocity of 21.3 cm/sec (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 40 ppi, 4% ρ metal foam, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 5,000 and 15,000 hr⁻¹ GHSV) ........................................................................................................107

Figure 4.15  Schematic drawing of Figure 4.13, linear velocity of 64.0 cm/sec (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 40 ppi, 4% ρ metal foam, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 15,000 and 45,000 hr⁻¹ GHSV) ............................................................................................................109
Figure 4.16 (a) CO conversion and (b) CO selectivity of the three separate 40 ppi, 4% ρ metal foams (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, 0.25-1.0 O₂/CO ratio, 150°C inlet temperature, GHSV=30,000 hr⁻¹)........................................................................111

Figure 5.1 Characterization reactor design schematic.................................................117

Figure 5.2 Graphical representation of a theoretical pulse chemisorption test..........119

Figure 5.3 Graphical representation of a pulse chemisorption test with elongated tails .........................................................................................................................127

Figure 5.4 Typical graphical representation of TPD data: reactor inlet temperature and CO concentration as a function of time .........................130

Figure A.1 Different shapes of metal foams.................................................................157

Figure A.2 Metal foams inserted with metal tubes......................................................157

Figure B.1 Threaded reactor design dimensions......................................................158

Figure B.2 Characterization reactor design dimensions............................................159

Figure B.3 Flange and Gasket dimensions .............................................................160

Figure B.4 Process Flow Diagram .........................................................................161

Figure C.1 Effect of pretreatment on (a) CO conversion and (b) CO selectivity as a function of inlet temperature for the 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 400 cpsi ceramic straight-channel monolith (1% CO inlet concentration, O₂/CO ratio = 1.0, GHSV = 30,000 hr⁻¹)..................................................164

Figure D.1 Transient effects on the outlet concentrations of (a) CO (enlarged) and (b) O₂ for the 400 cpsi ceramic straight-channel monolith and 20 ppi, 12% ρ metal foam after pretreatment (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 1.0, inlet temperature = 109°C, GHSV=30,000 hr⁻¹)..................................................166

Figure D.2 Transient effects on the outlet temperature at an O₂/CO ratio = 0.5 for the 400 cpsi ceramic straight-channel monolith and 20 ppi, 12% ρ metal foam after pretreatment (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, 109°C inlet temperature, GHSV=30,000 hr⁻¹)....167
Figure D.3  O$_2$/CO ratio comparison between the 40 ppi, 4% ρ metal foam and 400 cpsi ceramic monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$, 1% CO inlet concentration, 0.25-1.0 O$_2$/CO ratios, 80°C inlet temperature, GHSV=30,000 hr$^{-1}$)..............................................................168

Figure D.4  First-Order CO Isothermal Kinetic Calculations ........................................169

Figure D.5  Effects of GHSV & linear velocity on a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$, 1% CO inlet concentration, O$_2$/CO ratio = 0.5, 80°C inlet temperature, 10,000-45,000 hr$^{-1}$ GHSV) ..............................................................................................170

Figure D.6  Effect of linear velocity at constant GHSV on a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$, 1% CO inlet concentration, O$_2$/CO ratio = 0.5, 80°C inlet temperature, 10,000 and 15,000 hr$^{-1}$ GHSV) ......................................................................................171

Figure D.7  Effect of GHSV at constant linear velocity on a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$, 1% CO inlet concentration, O$_2$/CO ratio = 0.5, 80°C inlet temperature, 5,000-45,000 hr$^{-1}$ GHSV) ..............................................................................................172

Figure D.8  Schematic drawing of Figure D.7, linear velocity of 21.3 cm/sec (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$ 400 cpsi ceramic monolith, 1% CO inlet concentration, O$_2$/CO ratio = 0.5, 80°C inlet temperature, 5,000 and 15,000 hr$^{-1}$ GHSV) ......................................................................................173

Figure D.9  Schematic drawing of Figure D.7, linear velocity of 64.0 cm/sec (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$ 400 cpsi ceramic monolith, 1% CO inlet concentration, O$_2$/CO ratio = 0.5, 80°C inlet temperature, 15,000 and 45,000 hr$^{-1}$ GHSV) ......................................................................................174

Figure D.10 (a) CO conversion and (b) CO selectivity comparison of the three separate 400 cpsi ceramic straight-channel monoliths (5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$, 1% CO inlet concentration, 0.25-1.0 O$_2$/CO ratios, GHSV = 30,000 hr$^{-1}$, 150°C or 170°C inlet temperature).........................176

Figure E.1  An example of a CO pulse on an uncatalyzed, unwashcoated “blank” metal foam. ...........................................................................................................177

Figure E.2  An example of an elongated pulse chemisorption data...............................178
<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>Langmuir-Hinshelwood kinetic rate equation for CO oxidation on platinum using a single-site mechanism</td>
<td>29</td>
</tr>
<tr>
<td>E2</td>
<td>Carbon monoxide conversion</td>
<td>65</td>
</tr>
<tr>
<td>E3</td>
<td>Carbon monoxide selectivity</td>
<td>65</td>
</tr>
<tr>
<td>E4</td>
<td>Diatomic oxygen conversion</td>
<td>65</td>
</tr>
<tr>
<td>E5</td>
<td>Gas hourly space velocity</td>
<td>66, 102</td>
</tr>
<tr>
<td>E6</td>
<td>Volumetric flow rate of the inlet gas stream</td>
<td>66, 102</td>
</tr>
<tr>
<td>E7</td>
<td>Theoretical adiabatic temperature rise</td>
<td>67</td>
</tr>
<tr>
<td>E8</td>
<td>Langmuir-Hinshelwood kinetic rate equation for CO oxidation on platinum and iron using a dual-site mechanism</td>
<td>100</td>
</tr>
<tr>
<td>E9</td>
<td>Molar value of CO adsorbed by the catalyst from each pulse</td>
<td>118</td>
</tr>
<tr>
<td>E10</td>
<td>Molar value of CO in the switching valve sample loop</td>
<td>120</td>
</tr>
<tr>
<td>E11</td>
<td>Molar value of CO detected by the NDIR gas analyzer</td>
<td>120</td>
</tr>
<tr>
<td>E12</td>
<td>Molar value of active metal sites</td>
<td>120</td>
</tr>
<tr>
<td>E13</td>
<td>Metal dispersion</td>
<td>122</td>
</tr>
<tr>
<td>E14</td>
<td>Percent error between the molar value of CO detected by the NDIR and the molar value of CO in the switching valve sample loop</td>
<td>123</td>
</tr>
<tr>
<td>E15</td>
<td>Calculated average metal crystallite size using a spherical model</td>
<td>132</td>
</tr>
<tr>
<td>E16</td>
<td>Surface area calculation based on BET surface area theory</td>
<td>144</td>
</tr>
</tbody>
</table>
## LIST OF REACTIONS

<table>
<thead>
<tr>
<th>Reaction R1</th>
<th>Carbon monoxide oxidation reaction ........................................................... 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction R2</td>
<td>Hydrogen oxidation reaction ........................................................................ 2</td>
</tr>
<tr>
<td>Reaction R3</td>
<td>Reverse water-gas-shift reaction ................................................................... 2, 32, 83</td>
</tr>
<tr>
<td>Reaction R4</td>
<td>Methanol reforming reaction ........................................................................... 16</td>
</tr>
<tr>
<td>Reaction R5</td>
<td>Carbon monoxide hydrogenation reaction (methanation) ..................................... 44</td>
</tr>
<tr>
<td>Reaction R6</td>
<td>Carbon dioxide hydrogenation reaction (methanation) ....................................... 44</td>
</tr>
<tr>
<td>Symbol</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>----------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>$X_{CO}$</td>
<td>Carbon monoxide conversion (%)</td>
</tr>
<tr>
<td>$S_{CO}$</td>
<td>Carbon monoxide selectivity (%)</td>
</tr>
<tr>
<td>$X_{O2}$</td>
<td>Oxygen conversion (%)</td>
</tr>
<tr>
<td>$\Delta G_{rxn,298K}$</td>
<td>Gibbs free energy of reaction at 298K (25°C)</td>
</tr>
<tr>
<td>$\Delta H_{rxn,298K}$</td>
<td>Heat of reaction at 298K (25°C)</td>
</tr>
<tr>
<td>$\Delta T_{ad}$</td>
<td>Adiabatic reaction temperature rise (°C)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Cell density (opposite of void volume)</td>
</tr>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline fuel cells</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BPR</td>
<td>Back pressure regulator</td>
</tr>
<tr>
<td>cpsi</td>
<td>Cells per square inch</td>
</tr>
<tr>
<td>$d_{metal}$</td>
<td>Average metal crystallite size</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>FeCrAlY</td>
<td>Iron-chromium-aluminum-yttrium</td>
</tr>
<tr>
<td>FSB</td>
<td>Fluidized sand bath</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity (hr$^{-1}$)</td>
</tr>
<tr>
<td>HEL</td>
<td>Higher explosive limit</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>HTP</td>
<td>High temperature peak</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal combustion engine</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>$k$</td>
<td>Kinetic reaction rate constant</td>
</tr>
<tr>
<td>L-H</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>LEED</td>
<td>Low-energy electron diffraction</td>
</tr>
<tr>
<td>LEL</td>
<td>Lower explosive limit</td>
</tr>
<tr>
<td>LTP</td>
<td>Low temperature peak</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate fuel cell</td>
</tr>
<tr>
<td>$n_{CO}$</td>
<td>Molar amount of carbon monoxide</td>
</tr>
<tr>
<td>$n_{metal}$</td>
<td>Molar amount of metal</td>
</tr>
<tr>
<td>NDIR</td>
<td>Nondispersive infrared</td>
</tr>
<tr>
<td>OD</td>
<td>Outer diameter</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid fuel cell</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>ppi</td>
<td>Pores per inch</td>
</tr>
<tr>
<td>PROX</td>
<td>Preferential oxidation</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure-swing adsorption</td>
</tr>
<tr>
<td>r-WGS</td>
<td>Reverse water-gas-shift reaction</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimeter per minute (cm$^3$/min)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>$T_{\text{des}}$</td>
<td>The desorption temperature (in TPD analysis)</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOS</td>
<td>Time-on-stream</td>
</tr>
<tr>
<td>TOF</td>
<td>Turnover frequency</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>WGS</td>
<td>Water-gas-shift reaction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
CHAPTER 1 INTRODUCTION

1.1 CO Preferential Oxidation

The study of carbon monoxide removal in the presence of a hydrogen-rich gas stream is well-established, especially for ammonia synthesis from steam reforming [1]. Traditional methods use CO hydrogenation or pressure-swing adsorption to remove the undesired CO. An alternative method for CO removal is oxidation. In the presence of oxygen, the catalyst must actively and selectively oxidize CO instead of H₂.

The development of practical fuel cell power for both automotive transportation and stationary applications requires the manufacture of fuel processors that convert liquid fuels into H₂ and carbon dioxide [2-4]. Fuel processors must be compact, mechanically durable, quick-starting, responsive to transient demands, and inexpensive. Proton-exchange membrane fuel cells (PEMFCs) have been specifically targeted for automotive applications because of their high power density and low operating temperatures [2-7]. The inlet gas feed for the PEMFC must have very low CO concentrations to avoid poisoning the Pt electrodes [2-10].

The final oxidation step prior to the PEMFC requires an active catalyst for CO oxidation (reaction R1) to reduce the CO concentration from ~1% to less than 10 ppm in the presence of high H₂, CO₂, and steam concentrations, using a minimum weight and volume of catalyst. However, the catalyst must not oxidize a significant quantity of H₂.
(reaction R2) since it is the fuel used in the PEMFC anode. Any \( \text{H}_2 \) consumed by reaction R2 during the selective oxidation step must be replaced, increasing both the size of, and the rate of feed to, the fuel processor. Therefore, the catalyst must be highly active and selective for \( \text{CO} \) oxidation over \( \text{H}_2 \). This process is known as “preferential oxidation” in the fuel cell community, and is referred to as the acronym “PROX.”

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad (\Delta H_{\text{rxn},298\text{K}} = -283 \text{ kJ/mol}) \quad \text{R1}
\]

\[
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad (\Delta H_{\text{rxn},298\text{K}} = -242 \text{ kJ/mol}) \quad \text{R2}
\]

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad (\Delta H_{\text{rxn},298\text{K}} = +41.2 \text{ kJ/mol}) \quad \text{R3}
\]

Thermodynamically, \( \text{CO} \) oxidation is more favorable than \( \text{H}_2 \) oxidation (\( \Delta G_{\text{rxn},298\text{K}} = -257 \text{ kJ/mol} \) versus \( -229 \text{ kJ/mol} \), respectively), and evolves more heat, as seen in the \( \Delta H_{\text{rxn},298\text{K}} \) for reactions R1 and R2. Based on the exothermic nature of these two reactions, some commercial designs for this element of the fuel processor use two fixed-bed adiabatic reactors in series, with an intermediate cooling step [11]. Adiabatic reactors may not be the ideal reactor design because the reverse water-gas-shift (r-WGS, reaction R3) reaction is favored by higher temperatures (\( \Delta G_{\text{rxn},298\text{K}} = +28.6 \text{ kJ/mol} \)). This side reaction can prevent the PROX reactor from reaching low \( \text{CO} \) concentrations [12-16], as discussed in Chapter 4, section 4.1.

Many different metal catalysts have been studied for the PROX reaction, from base metals like Cu and Mn [10], to the noble metals such as Au [17-23], Pd [13, 16, 24, 25],
Pt [10, 11, 13-15, 24-29], Ru [13, 16, 25, 27], and Rh [13, 24]. Additionally, bimetallic catalysts like Pt-Sn [30, 31] and promoted catalysts [12, 26, 32] have been investigated. On a Pt catalyst, both CO and \( \text{H}_2 \) oxidation occur by the Langmuir-Hinshelwood reaction mechanism [1, 12, 33, 34]. Both reactants must adsorb on the catalyst surface for the reaction to occur. Carbon monoxide strongly adsorbs on the Pt surface [6, 12, 14, 15, 26, 33, 35], inhibiting \( \text{O}_2 \) adsorption. One way to overcome this obstacle is to promote the Pt catalyst with another metal to form a metal oxide. For this study, the promoted metal used is iron [26, 35]. The role of Fe is to provide an alternative site for \( \text{O}_2 \) adsorption because Fe does not adsorb CO as extensively as \( \text{O}_2 \) [32, 35, 36]. The Fe will be in intimate contact with Pt, facilitating CO oxidation because it creates a non-competitive dual site reaction mechanism instead of the typical competitive dual site reaction mechanism observed on unpromoted Pt catalysts [37].

1.2 Metal Foam Supports

Uses for structured supports, such as ceramic monoliths, are well established. One of the most prominent examples is the Pt/Pd/Rh catalyst washcoated on a ceramic monolith in the catalytic converter of gasoline-powered automobiles. Instead of using traditional ceramic monoliths, metal foams can be used as the structured support for PROX reactions. Foams consist of irregular, open cells shaped in the form of a rigid matrix, seen in Figure 1.1. The catalytic material is added to the metal foam via a washcoating process, described in Chapter 3, section 3.1.1. Foams have been used as catalytic supports in several applications, such as exhaust fumes of power plants [38], and
automotive engines [39]. Among the different metals that can be used to create the foam, Fecralloy® metal foams are used in this research study. The composition of Fecralloy® is 72.8% Fe / 22% Cr / 5% Al / 0.1% Y / 0.1% Zr.

Metal foam supports have several potential advantages for fuel processors:

- The porosity of the metal foam can be very high, which minimizes the pressure drop and results in a low heat capacity, providing a rapid response to transients and to changes in the operating conditions;

- The cellular nature of the metal foam permits both radial and axial flow, and radial mixing of the fluid. This mixing alleviates problems associated with maldistribution of the fluid entering the reactor. The reticulated structure offers high surface areas, providing more surface for catalyst deposition;

- The range of possible cell densities for metal foams is larger compared to metal monoliths. Specifically, metal foams can be constructed with densities as low as 3% of the theoretical volume (i.e. 97% void volume). Low cell densities optimize the trade-off between pressure drop and mass transfer rates over the wide range of flow rates required in an automotive fuel processor;
• The metal foams can be formed in shapes other than right cylinders or square blocks, as seen in Figure A.1 in Appendix A. Fuel processors may require non-linear flow paths, and metal foams can be constructed to conform to these constraints, allowing them to fit the demanding size and space requirements;

• The metal foams can be metallurgically bonded to reactor shells, forming lightweight, durable, rugged reactors that are more stable, reliable, and tolerable under abrasive conditions versus their ceramic counterparts. The metals used have a high thermal conductivity, allowing for heat transfer and minimizing the potential of localized hot-spots in the reactor caused by the exothermic PROX reaction;

• Metal tubes can be mechanically inserted into the foam structure during the manufacturing process, as shown in Figure A.2 in Appendix A. These tubes can be exploited for heat removal from the PROX reactor. This heat transfer could eliminate the need for a two-stage PROX unit, save space and cost, and minimize the undesired H₂ oxidation and r-WGS reactions.

1.3 Objective

The objective of this research is to study the PROX of CO using different types of catalyzed structured supports. The gas compositions of a fuel processor stream entering the PROX reactor are replicated to try to simulate actual conversions and selectivities. This thesis aims to answer three main questions:

i. How do metal foams compare to conventional ceramic straight-channel monoliths for CO PROX under reformate gas stream conditions?

ii. How do side reactions and transport effects influence the CO PROX reaction? How do they limit the operating conditions and the ability to achieve low outlet CO concentrations?
iii. What are the characteristics of these catalyzed structured supports?

Chapter 2 of this thesis presents a literature review, providing a background for this research. Chapter 3 focuses on a study of different structured supports, such as metal foams and ceramic straight-channel monoliths, along with ceramic foams and corrugated metal monoliths. Chapter 4 concentrates on the r-WGS reaction and transport effects that need to be considered, in addition to a comparison of the ceramic monolith and metal foam. Chapter 5 employs different characterization techniques to describe the catalysts. Chapter 6 summarizes the conclusions inferred from this study.
1.4 References


33. Bourane, A. and D. Bianchi, *Oxidation of CO on a Pt/Al2O3 catalyst: From the surface elementary steps to lighting-off tests - II. Kinetic study of the oxidation of*


2.1 Fuel Cells

A fuel cell consists of a porous anode and cathode, with an electrolyte membrane bonded to the two electrodes. A generic schematic is shown in Figure 2.1 [1]. The principle of a fuel cell was first conceived by Sir William R. Grove in 1839. He used H\textsubscript{2} and O\textsubscript{2} as fuels catalyzed on Pt electrodes [2]. Hydrogen passes through the anode, where the H\textsubscript{2} splits into a proton and electron. The electron passes through the electric circuit and generates a current, while the proton (H\textsuperscript{+}) diffuses through the electrolyte. The electrolyte must be extremely selective for protons and not electrons [3]. The proton and electron rejoin in the cathode, and O\textsubscript{2} flows through to form only H\textsubscript{2}O in the exhaust.

Figure 2.1: A generic fuel cell schematic [1]

A fuel cell consists of a porous anode and cathode, with an electrolyte membrane bonded to the two electrodes. A generic schematic is shown in Figure 2.1 [1]. The principle of a fuel cell was first conceived by Sir William R. Grove in 1839. He used H\textsubscript{2} and O\textsubscript{2} as fuels catalyzed on Pt electrodes [2]. Hydrogen passes through the anode, where the H\textsubscript{2} splits into a proton and electron. The electron passes through the electric circuit and generates a current, while the proton (H\textsuperscript{+}) diffuses through the electrolyte. The electrolyte must be extremely selective for protons and not electrons [3]. The proton and electron rejoin in the cathode, and O\textsubscript{2} flows through to form only H\textsubscript{2}O in the exhaust.
which is a distinct advantage to the internal combustion (IC) engine for automotive applications.

2.1.1 Proton Exchange Membrane Fuel Cell

The proton exchange membrane fuel cell (PEMFC) was first developed in the 1960s by General Electric for NASA’s manned space vehicles. The PEMFC uses a proton-transporting polymer, such as sulphonated fluoropolymers, e.g., Nafion™. The best anode and cathode catalyst is Pt or Pt/Ru on a C support [2-6]. Hydrogen dissociatively chemisorbs on the Pt, followed by electroxidation into protons and electrons [5]. There are several advantages to the PEMFC:

1) the polymer electrolytes work at low temperatures (~80°C) [1-5, 7]
2) it is quick starting and suitable for intermittent use [3, 8]
3) it can be built very thin and compact [3]
4) there are no corrosive fluid safety hazards [2, 3, 7]
5) it can produce a high power density [2, 3, 5, 7]
6) it has ~40% efficiency, which is about 2-3 times better than an IC engine [4-6]

There are several disadvantages to the PEMFC. The polymer electrolyte must be kept hydrated with water, heat must be removed from the PEMFC, and the Pt anode is poisoned by trace quantities of CO [2-6]. The PEMFC must operate under conditions where H₂O formed in the cathode does not evaporate faster than it is produced to maintain the high conductivity of the polymer electrolyte. In fact, extra humidification of the reactant gases is required for PEMFCs operating above 60°C [3]. Therefore, keeping
the PEMFC cool is important, especially since H\textsubscript{2} oxidation is exothermic (\(\Delta H_{\text{rxn,298K}} = -242 \text{ kJ/mol}\)). Carbon monoxide poisons the Pt anode at lower temperatures, and needs to be removed to less than 10 ppm to prevent loss of activity of the Pt anode. Consequently, it is difficult to find an optimal operating temperature: at low temperatures, CO poisons the Pt anode but the electrolyte is conductive, and at high temperatures, CO poisoning is weakened but the electrolyte acts as an insulator. New technology on polybenzimidazole electrolytes are being developed to operate at higher temperatures (> 180°)C. Higher temperature electrolytes will tolerate more CO and remove humidification problems [5].

PEMFCs have already been tested for automotive transportsations. In the late 1980s – early 1990s, Ballard Power Systems developed a 30 ft commercial transit bus powered entirely by a 105 kW fuel cell system [9]. The bus was fueled by an on-board compressed H\textsubscript{2} storage cylinder, allowing it to travel at least 90 miles before refueling. In the mid-to-late 1990s, Daimler-Benz Chrysler-Ballard, with an investment from Ford (now called Xcellsis), started developing PEMFC vehicles [3, 5]. The vehicles, from NECAR 1 in 1994 to NECAR 4 in 2000, produced at least 50 kW of electricity (kW\textsubscript{e}). The power produced in the PEMFC vehicles were still far away from the 150 kW IC engines.

On-board compressed H\textsubscript{2} storage can be risky, so safety considerations must be scrutinized because H\textsubscript{2} is an extremely volatile and flammable gas. The H\textsubscript{2} LEL and HEL in air are 4.0 vol.% and 77 vol.%, respectively. Even with such a large ignition limit range, H\textsubscript{2} disperses upward very quickly because of its high buoyancy. Hydrogen
leaks 2.8 times faster than CH₄ and 3.3 times faster than air, so H₂ unlikely to reach its 4 vol% LEL. Also, H₂ detonation limits in air are much higher than common fuels like methane and propane. All things considered, H₂ is no more dangerous than commonly used fuels, contrasting what is typically thought of for compressed H₂ (Figure 2.2, [10]).

As research shifts from using on-board compressed H₂ to existing infrastructure reformer fuels, CO concentrations prior to the PEMFC have to be reduced to trace quantities. Preferential oxidation (PROX) reactor designs and full-scale models are already in development. Dudfield et al. [11, 12] produced a dual stage compact PROX reactor that reduced CO concentrations from 7000 ppm to less than 10 ppm. The optimal catalyst

Figure 2.2: The “Hindenburg Disaster” of May 6th, 1937, which gave H₂ a bad reputation. [10]
was a Pt/Ru mix promoted with a metal oxide, the optimal heat transfer design was a 0.5 liter capacity Al plate-fins, and the optimal temperatures for CO removal ranged from 145-170°C depending on the catalyst. When the PROX reactor was coupled with a methanol steam reformer, it reduced 2.7% CO to less than 20 ppm and produced 20 kW_e.

2.1.2 Reformer Technology

Hydrogen production in the chemical industry is typically accomplished by steam reforming. Two industries that use steam reforming for H_2 production are ammonia and methanol synthesis. There are four main steps required to generate pure H_2 [3, 5, 13]: 1) desulfurization, 2) steam reforming, 3) water-gas-shift (WGS), and 4) CO removal. In the desulfurization step, hydrocarbons (HC) are purified of sulfur and chlorine-containing compounds. The sulfur compounds are converted to H_2S, which is removed by adsorption on ZnO. In the steam reforming step, HCs are reacted with H_2O to produce H_2 and CO on a Ni-based catalyst. This reaction is highly endothermic and requires a lot of energy input (e.g., ΔH_{rxn,298K} = +206 kJ/mol for methane; ΔH_{rxn,298K} = +1108 kJ/mol for n-heptane). In general, steam reforming requires two steps. The effluent stream enters a high and low temperature WGS reactor. The WGS reactors convert about 10% CO to 0.5% CO using a Fe/Cr-based catalyst for the high temperature WGS and a CuO/ZnO/Al_2O_3 catalyst for the low temperature WGS. The final step for CO removal is achieved by methanation or pressure swing adsorption.
For automobile applications, traditional H\textsubscript{2} generation methods are not feasible [5]. The desulfurization step requires temperatures of 500°C and pressures over 10 MPa. The Ni-based catalyst for steam reforming is highly self-igniting when exposed to air. Also, the two WGS catalysts are also pyrophoric when reduced. Methanation is not usable because it consumes H\textsubscript{2} and requires an extra CO\textsubscript{2} removal step. Pressure swing adsorption requires pressures around 2 MPa. The onboard fuel processors need to be compact, quick starting, able to emit only low levels of pollutants, and able to manage a wide range of conditions [3].

Alternative technology must be developed to generate H\textsubscript{2} for PEMFC vehicles. Of major interest to automobile manufacturers is methanol reforming. In methanol reforming, gaseous methanol (B.P. = 64.5°C) is reacted with H\textsubscript{2}O to form H\textsubscript{2} and CO\textsubscript{2} (reaction R4):

\[
\text{CH}_3\text{OH}_{(g)} + H_2O \rightleftharpoons 3H_2 + CO_2 \quad (\Delta H_{\text{rxn,298K}} = +49.7 \text{ kJ/mol}) \quad \text{R4}
\]

The major advantages to methanol reforming are that it contains no sulfur, it can be reformed at moderate temperatures of 200-250°C, and it produces 3 moles of H\textsubscript{2} and only 1 mole of CO\textsubscript{2} [5]. Since the reaction is mildly endothermic, only a small amount of heat needs to be supplied. Inevitably, about 1% CO is produced from the reverse-WGS reaction, but it can be removed downstream using a PROX reactor. Overall, the desulfurization and WGS steps are averted, and the reforming step occurs at lower
temperatures compared to industrial production of H₂. The major disadvantages are the lack of infrastructure, water solubility, and toxicity problems.

2.1.3 Other Types of Fuel Cells

In addition to the PEMFC, there are many other types of fuel cells. Phosphoric acid fuel cells (PAFCs) use phosphoric acid soaked in a SiC matrix as the electrolyte. The PAFCs can tolerate up to 1.5% CO, but run at higher temperatures (150-200°C), generate low current and power and are larger in weight and size compared to other fuel cells [1, 5]. Molten carbonate fuel cells (MCFCs) use a liquid solution of lithium, sodium, or potassium carbonates soaked in a \( \gamma \)-LiAlO\(_2\) matrix as the electrolyte. The MCFCs have higher efficiencies (~60%), are not poisoned by CO, and do not require noble metal catalysts, but operate at 650°C to achieve adequate conductivity, making it more likely to corrode and break down [1, 5].

Solid oxide fuel cells (SOFCs) use solid zirconium oxide and small amounts of ytrria (Y\(_2\)O\(_3\)) instead of a liquid electrolyte. The SOFCs can achieve 60% efficiency, but require temperatures of 800-1100°C to make the zirconia conductive to O\(^{-}\) [1, 3, 5]. Alkaline fuel cells (AFCs) use an aqueous alkaline KOH solution soaked in a matrix as the electrolyte. The AFCs can achieve 70% efficiency because the cathode reaction operates at 150-200°C and is faster than the electrolyte permeation, but cost, reliability, safety, and low power output are major issues [1, 3]. There are also direct methanol, zinc-air, regenerative, and protonic ceramic fuel cells [1, 5], with more in development.
With so many alternatives, why is most research focused on PEMFCs? The AFCs are not realistic for automobiles with on-board reforming because CO₂ deactivates OH⁻ in the electrolyte, forming carbonate [3]. The SOFC, MCFC [5], and PAFC [3] operate at high temperatures, allowing them to convert CH₄ and CO to H₂ internally, without a separate fuel processing system. However, the overall H₂ concentration will always remain lower compared to an external reformer, reducing the overall current density. Furthermore, the MCFC, AFC, and PAFC use liquid solutions, which pose a safety hazard. Table 2.1 summarizes the fuel requirements for the principle types of fuel cells [3].

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>CO</td>
<td>Poison (&gt; 10 ppm)</td>
<td>Poison</td>
<td>Poison (&gt; 0.5%)</td>
<td>Fuel⁷</td>
<td>Fuel⁷</td>
</tr>
<tr>
<td>CH₄</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent⁶</td>
<td>Diluent⁶</td>
</tr>
<tr>
<td>CO₂ &amp; H₂O</td>
<td>Diluent</td>
<td>Poison³</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>S (as H₂S &amp; COS)</td>
<td>Few studies to date</td>
<td>Unknown</td>
<td>Poison (&gt; 50 ppm)</td>
<td>Poison (&gt; 0.5 ppm)</td>
<td>Poison (&gt; 1.0 ppm)</td>
</tr>
</tbody>
</table>

Table 2.1: The fuel requirements for the principal types of fuel cells [(3), Table 7.6]

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Fuel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>Poison (&gt; 10 ppm)</td>
<td>Poison</td>
<td>Poison (&gt; 0.5%)</td>
<td>Fuel⁷</td>
<td>Fuel⁷</td>
</tr>
<tr>
<td>CH₄</td>
<td>Diluent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ &amp; H₂O</td>
<td>Diluent</td>
<td>Poison³</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>S (as H₂S &amp; COS)</td>
<td>Few studies to date</td>
<td>Unknown</td>
<td>Poison (&gt; 50 ppm)</td>
<td>Poison (&gt; 0.5 ppm)</td>
<td>Poison (&gt; 1.0 ppm)</td>
</tr>
</tbody>
</table>

a In reality CO reacts with H₂O, producing H₂ and CO₂ via the WGS reaction, and CH₄ with H₂O reforms to H₂ and CO faster than reacting as a fuel at the electrode.
b A fuel in the internal reforming MCFC and SOFC
c The fact that CO₂ is a poison for the AFC more or less rules out its use with reformed fuels

2.2 CO Preferential Oxidation

2.2.1 Different Types of Metals

In 1960, Brown et al. [14] described pilot-plant operations for ammonia synthesis by preferential oxidation (PROX) of CO in the presence of a H₂-rich gas stream. The use of
PROX was an alternative to methanation, absorption on cuprous salts, or a liquid nitrogen wash. Reasonable CO selectivity was found at a limited temperature range of 130-160°C and O\textsubscript{2}/CO ratio of 2 on 0.5% Pt and Ru catalysts, but not on Pd, Ir, or Ru-Rh mix. In general, many different types of metal catalysts are available for the PROX reaction, from non-precious (base) metals like Cu and Mn, to the precious (noble) metals of Au, Ir, Os, Pd, Pt, Re, Ru, Rh, or combinations thereof.

2.2.1.1 Platinum, Palladium, Ruthenium, and Rhodium Catalysts

The PROX reaction has been extensively studied on noble metal catalysts. In 1991, Muraki et al. [15] studied 0.24 wt% Pt, Pd, and Rh catalysts deposited on α-Al\textsubscript{2}O\textsubscript{3} at 30,000 hr\textsuperscript{-1} gas hourly space velocity (GHSV). The Pt catalyst was found to have the highest CO oxidation rate compared to the Pd and Rh catalysts with 0-0.3 mol% H\textsubscript{2}, 1.0 mol% CO, and 0.44 mol% O\textsubscript{2} in the feed stream. In addition, Pt had the lowest H\textsubscript{2} oxidation rate in the presence of CO up to about 170°C with 0.08 mol% H\textsubscript{2}, 1.0 mol% CO, and 0.44 mol% O\textsubscript{2} in the feed stream.

Oh and Sinkevitch [16] studied both base and noble metal catalysts supported on Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}. They reported that the 0.5 wt% noble metals supported on Al\textsubscript{2}O\textsubscript{3} had a CO oxidation activity order of Ru > Rh > Pt > Pd between 100-300°C with 0.85 vol% H\textsubscript{2}, 900 ppm CO, 800 ppm O\textsubscript{2}, and balance N\textsubscript{2}. All four catalysts exhibited a maximum CO conversion with increasing temperature. For the Pt catalyst, the maximum was observed around 200°C. The decrease in CO conversion at higher temperatures was attributed to
the water-gas-shift equilibrium. In contrast, the Pt/Al₂O₃ catalyst reached and sustained 100% CO conversion at temperatures above ~200°C with no H₂ in the inlet feed. The Ru and Rh catalysts had a higher CO selectivity than the Pt catalyst at both lower (122-140°C) and higher temperatures (171-180°C). The base metal catalysts performed poorly compared to Pt/Al₂O₃, though catalysts containing several metals, like Co/Cu and Ni/Co/Fe, exhibited higher performances than the mono-metallic catalysts.

Kahllich et al. [17] observed a similar phenomenon of maximum CO conversion at 225°C for a 0.5 wt% Pt/Al₂O₃ with an inlet feed of 1% CO, 75% H₂, and balance N₂. At temperatures higher than 225°C, CO selectivity dropped. The Pt/Al₂O₃ catalyst reached and sustained 100% CO conversion at temperatures above 225°C with 1% CO and no H₂ in the inlet feed. Manasilp and Gulasi [18] synthesized 1 wt% and 2 wt% Pt/Al₂O₃ catalysts prepared by a single-step sol gel method using an inlet feed including CO₂ and H₂O. The catalyst had an activity and selectivity high enough to oxidize CO down to a few ppm in the presence of H₂. The CO conversion peaked at 170°C under reformate compositions (i.e., 40-75% H₂, 15-20% CO₂, ~10% H₂O, 0-35% N₂, and 0.5-1.0% CO).

Watanabe and co-workers explored the use of Pt on zeolites [19-21]. In 1995, Watanabe et al. [19] showed that a highly dispersed 6.4 wt% Pt/A-zeolite exhibited up to 10 times greater CO selectivity compared to Pt/Al₂O₃ at 200°C inlet temperature and 1.0% CO, 0.5% O₂ concentrations in balance H₂. In 1997, Igarashi et al. [21] investigated the effect of different zeolite supports on the activity and selectivity of 6 wt% Pt catalysts for CO
oxidation. The Pt/Al<sub>2</sub>O<sub>3</sub> catalyst had the highest CO conversion at 150-350°C reaction temperatures and a W/F ratio of 0.06 gr-sec/cm<sup>3</sup>. However, Pt supported on mordenite showed the highest CO conversion and selectivity at low O<sub>2</sub> concentrations and a W/F ratio of 0.12 gr-sec/cm<sup>3</sup>. The use of a two-stage reactor increased the effectiveness of the Pt/mordenite catalyst. There was no heat removal between the two reactors, the inlet temperature was 200°C, and the W/F ratio was 0.12 gr-sec/cm<sup>3</sup> in each reactor.

More recently, Kim and Lim [22] studied 0.04-1.0 wt% Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts using an integral reactor. The inlet feed contained 50% H<sub>2</sub>, 0.5-2.0% CO and O<sub>2</sub>, and balance He, with reactor temperatures of 150-400°C. The minimum temperature for complete O<sub>2</sub> conversion decreased from 300°C for 0.5 mol% O<sub>2</sub> to 270°C for 2.0 mol% O<sub>2</sub>. In addition, the maximum CO conversion increased from 45% for 0.5 mol% O<sub>2</sub> to 100% for 2.0 mol% O<sub>2</sub>. Different Pt wt% loadings and inlet feed rates did not affect CO selectivity, but feed compositions and temperatures did.

Syntnikov et al. [23] tested 1 wt% Pt-, Ru-, and Pd-supported on Sibunit (a porous carbonaceous material) catalysts with an inlet feed of 0.6 vol.% CO and O<sub>2</sub> in balance H<sub>2</sub>. The Ru and Pt catalysts showed higher CO activity and selectivity compared to Pd. The maximum CO conversion for the Ru and Pt catalysts were at temperatures around 105-120°C and 135-160°C, respectively. When the inlet CO concentration was increased from 0.6 vol% to 1.0 vol%, the O<sub>2</sub> concentration had to be increased from 0.6 vol% to 1.5 vol% to maintain less than 10 ppm CO in the effluent stream. A comparison study
revealed comparable CO selectivity on Ru/C and Pt/C to their Al₂O₃ support counterparts, but lower activity on the former. No mention was made in regards to the carbon support oxidizing to CO₂, but their mass balance on CO from outlet CO and CO₂ concentrations was closed, with a ± 5% accuracy.

De Wild et al. [24] filed a European patent showing complete CO oxidation on a Ru-Pt catalyst (< 0.5 wt% total noble metal) supported on α-Al₂O₃ at a temperature range of 120-180°C, an above stoichiometric O₂/CO ratio of 1, and a GHSV of 10,000-15,000 hr⁻¹. Minimal H₂ consumption was observed, even under reformate conditions with 0.5% CO and O₂, and varying CO₂, H₂O, H₂, and balance N₂ concentrations.

2.2.1.2 Gold Catalysts

In recent years, there has been significant interest in Au-based catalysts for CO oxidation. Since bulk Au is chemically inert and difficult to disperse, its use in heterogeneous catalysis has not been considered [25-28]. In the late 1980s, Haruta et al. [29] discovered that co-precipitation of Au with various metal oxides such as Fe₂O₃ or TiO₂ made it an extremely active CO oxidation catalyst. Later work by Haruta [28] showed that nano-Au particles (< 4 nm) provided reversible CO adsorption sites. Also, nano-Au particles increased O₂ adsorption on the TiO₂ support. Gold supported on TiO₂, α-Fe₂O₃, Co₃O₄, NiO, Be(OH)₂, and Mg(OH)₂ showed strong CO oxidation (50% conversion) at temperatures below 0°C using dried 1% CO in air. The Au/α-Fe₂O₃ catalyst reached 90% CO conversion at -50°C, and complete CO oxidation at 0°C. The CO and H₂
oxidation reactions were dependent on the calcination temperature; the optimal calcination temperatures for CO and H₂ oxidation at -70°C and 30°C, respectively, were 200°C and 300°C, respectively. Continuing work by Sanchez et al. [30] observed over 90% CO conversion on a Au-MnOₓ catalyst at temperatures of 50-80°C in 98 vol% H₂ and at an O₂/CO ratio of 1.0. There was no CO₂ or H₂O in the inlet feed, but it was suggested that Au catalytic activity would be enhanced by H₂O and insensitive to CO₂.

Since the co-precipitation study by Haruta and co-workers [29], a great deal of research on Au catalysts has been accomplished [26, 27, 31-37]. Bethke and Kung [32] studied 0.4% Au/γ-Al₂O₃ catalysts prepared with and without Mg citrate, which affected the Au particle size. The optimal Au particle size of 5-10 nm achieved ~35% CO conversion and 50% CO selectivity at 100°C, an O₂/CO ratio of 0.5, and 1% CO concentration in the presence of 48% H₂ and balance He. Studies on Au surface acidity modified with Y-type or Fe/Y-type zeolites in the presence of CO and air were conducted by Lin et al. [26]. At 0°C, the Au/Fe/Y-type zeolite showed full CO oxidation catalytic ability at initial time-on-streams (TOS), while the Au/Y-type zeolite showed low initial activity, requiring ~5 hours TOS before reaching steady-state CO conversions of 70%. The presence of Fe enhanced the Au loading on Y-type zeolites because Au could also react and deposit on Fe. Hence, the Au loading on the Fe/Y was two times more than on the pure Y-type zeolite. In 2000, Grigorova et al. [31] filed a patent for a Au-Sn-Co/CeO₂-TiO₂ catalyst tested for CO PROX between 80-130°C. In the presence of SnO₂ using a H₂:CO:O₂ ratio
of 2.0:0.5:0.8 in balance N₂, the CO conversion was greater than 70%, with less than 10% H₂ conversion.

Kahllich et al. [27] studied 3.15 wt% Au/α-Fe₂O₃ catalysts without CO₂ and H₂O in the inlet feed. A deactivation of ~30% was noted for the first 2 hours TOS. After 2 hours the activity increased and reached a steady-state after 10 hours. The major advantages of using Au/α-Fe₂O₃ instead of 0.5 wt% Pt/Al₂O₃ catalysts at their respective optimal operating temperatures of 80°C and ~200°C were threefold:

1) Au had comparable activity and higher selectivity compared to Pt at CO and O₂ partial pressures of 1 kPa
2) Au had lower activation energies for CO oxidation (115-183 kJ/mol for Pt (100), Pt (111), and Pt (110) vs. 58-33 kJ/mol for Au (100), Au (54), Au (332), and Au (110))
3) CO oxidation on Au/α-Fe₂O₃ involved a non-competitive Langmuir-Hinshelwood kinetic reaction mechanism (positive CO reaction order for CO on Au)

Both Kahlich et al. [27] and Schubert et al. [35] calculated a negative CO oxidation reaction order for CO on Pt and correlated it to near saturation of the Pt surface. Conversely, the CO reaction order for CO on Au was positive. This meant the reaction rate for CO oxidation was directly proportional to the amount of CO partial pressure. Schubert et al. [35] used in-situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) to determine a maximum of about 20% CO coverage on the Au surface using 1 kPa CO in balance N₂ at 80°C inlet temperature.
The main advantage of Pt over the Au catalyst is its stability [25]. Generally nano-Au catalysts go through rapid deactivation during CO oxidation [25, 34]. Oh et al. [34] conducted TOS studies at room temperature on a 0.38 wt% Au/γ-Al₂O₃ catalyst and observed deactivation during CO oxidation without H₂. In addition, thermal deactivation was observed at 100°C in He or O₂ gas flow. Thermally deactivated catalysts were regenerated by H₂O, and CO oxidation deactivation was regenerated by H₂. A CO oxidation reaction mechanism involving OH⁻ and bicarbonate was theorized, and the Au surface was poisoned by the oxidation of bicarbonate to carbonate. Similar carbonate species were seen using DRIFTS on a 1% Au/TiO₂ catalyst by Bollinger and Vannice [36] under 5% CO and O₂ in balance Ar.

2.2.1.3 Bimetallic and Metal Oxide Promoted Catalysts

In addition to using monometallic catalysts, activity and selectivity can be increased by promoting with a metal oxide or by creating a bimetallic catalyst. Metal oxide promotion provides additional sites for O₂ adsorption, creating a non-competitive dual site Langmuir-Hinshelwood reaction mechanism similar to that seen on Au / metal oxide catalysts. The first patent involving PROX using a promoted Pt/alumina catalyst was awarded to Straschil and Egbert [38] in 1963 for ammonia synthesis. The 0.5 wt% Pt/alumina was promoted with metals such as Fe, Ni, Mn, and Co, to form a metal oxide. A gas mixture of 0.1% CO₂, 0.5% CO, 0.75% O₂, ~74% H₂, and ~24% N₂ was used. The most active catalysts at 25-40°C inlet temperatures were the Pt/Fe and Pt/Ni catalysts,
with an outlet CO concentration of 10 and 20 ppm, respectively. At 0.5% \( \text{O}_2 \) concentration, Pt promoted with Mn, Mn + Fe, and Co catalysts had 25 ppm CO in the effluent gas, while a Pt/Fe catalyst supported on CaCO\(_3\)/bleached clay had 12 ppm CO. On the other hand, an unpromoted 0.5 wt% Pt/Al\(_2\)O\(_3\) catalyst showed little to no activity.

Korotkikh and Farrauto [39] investigated the effect of a promoter oxide (later revealed by Liu et al. [40] as Fe) on the activity of 5 wt% Pt/Al\(_2\)O\(_3\) catalysts in an isothermal reactor. With a base metal oxide promoter and an \( \text{O}_2/\text{CO} \) molar ratio of 0.5, the CO conversion significantly increased from 13.2% to 68% without affecting the selectivity at 90°C. At higher GHSV on a ceramic monolith Pt/Fe catalyst, the CO and \( \text{O}_2 \) conversion decreased, but the CO selectivity remained relatively constant. Watanabe et al. [20] tested different Pt:Fe ratios with a total of 6 wt% catalyst supported on a mordenite zeolite. At temperatures below 200°C and at 1.0% CO, 0.5% \( \text{O}_2 \), and \( \text{H}_2 \) balance concentrations, the 2:1 Pt/Fe catalyst exhibited 100% CO conversion and selectivity, while the unpromoted Pt catalyst reached a maximum of ~80% CO conversion and ~90% selectivity. At temperatures above 200°C, both catalysts decreased in CO conversion and selectivity.

Sakamoto et al. [41] used 3.50-3.70 wt% Pt promoted with 1.10 or 3.70 wt% Fe supported on \( \gamma \)-Al\(_2\)O\(_3\) catalysts for catalytic activity testing under stoichiometric and lean mixture simulated exhausts from an automotive internal combustion (IC) engine. The Pt/Fe catalysts reached 50% hydrocarbon conversion at the same or lower temperatures compared to the Pt catalyst under both stoichiometric and lean conditions and under
different pretreatment conditions. Grisel and Nieuwenhuys [33] studied 5 wt% Au/Al₂O₃ promoted with MnOₓ and/or MgO, which improved CO activity and selectivity, reaching 90% CO selectivity on the promoted catalysts at temperatures less than 100°C using a H₂:CO:O₂ ratio of 4:2:1 and a constant 4 vol.% reactant concentration in balance He. The MnOₓ promotion was thought to supply active O for CO oxidation, while MgO helped to stabilize the small Au particles.

Bimetallic Pt-Sn catalysts showed promise for CO oxidation at lower temperatures (120°C) [42, 43]. Aksoylu et al. [42] developed 1 wt% Pt / 0.25 and 0.5 wt% Sn on activated carbon (AC) catalysts for CO oxidation with a CO:O₂:He ratio of 15:20:65. The 0.25 wt% Sn performed better than the 0.5 wt% Sn catalyst, with an optimal Pt:Sn weight ratio of 4:1. Both Pt/Sn catalysts were more active than the unpromoted Pt/AC catalyst. For all catalysts, a reduction temperature of 400°C yielded higher activity than a 350°C reduction temperature. It was proposed that the Pt₃-Sn alloy could adsorb O₂ more readily than the Pt-Sn alloy. Schubert et al. [43] investigated low temperature CO oxidation using a 20 wt% Pt-Sn supported on carbon. At 80°C, the CO oxidation rate on the Pt-Sn catalyst was much faster than on a Pt/Al₂O₃ catalyst, with a turnover frequency (TOF) two orders of magnitude larger. In fact, the TOF of 0.7 s⁻¹ at 80°C was comparable to a Au/Fe₂O₃ catalyst studied by Kahllich et al. [27]. At 0-20°C, the Pt-Sn catalyst achieved 85% selectivity before decreasing, which was much higher than a Pt/Al₂O₃ catalyst under its optimal conditions. The O₂ was suggested to adsorb
predominately on the Sn sites and SnO_x islands adjacent to the bimetallic Pt-Sn sites, similarly to the metal oxides.

2.2.2 Kinetics

It is generally accepted that CO oxidation on Pt obeys a Langmuir-Hinshelwood (L-H) kinetic model rather than a Eley-Rideal model [13, 39, 40, 44, 45]. The elementary steps for CO oxidation are shown in Figure 2.3, reprinted from Farrauto & Bartholomew [13], where CO(g) and O_2(g) denote gas phase CO and O_2, Pt_s is the surface Pt atom or active site for the reaction, and CO-Pt_s, O-Pt_s, and CO_2-Pt_s are short-lived intermediate species on the Pt surface. \( K_1 \) and \( K_2 \) are adsorption equilibrium constants, defined as \( K_1 = k_1 / k_4 \) and \( K_2 = k_2 / k_{-2} \), or the kinetic rate constant \( k \) for the forward reaction divided by the reverse reaction.

\[
\begin{align*}
\text{CO}_\text{(g)} + \text{Pt}_s & \rightleftharpoons K_1 \text{CO-Pt}_s \quad \text{(quasi-equilibrium)} \\
\text{O}_2\text{(g)} + 2\text{Pt}_s & \rightleftharpoons K_2 \text{2O-Pt}_s \quad \text{(quasi-equilibrium)} \\
\text{CO-Pt}_s + \text{O-Pt}_s & \rightleftharpoons k_1 \text{CO}_2\text{-Pt}_s + \text{Pt}_s \quad \text{(slow, rate determining step)} \\
\text{CO}_2\text{-Pt}_s & \rightleftharpoons k_2 \text{CO}_2\text{(g)} + \text{Pt}_s \quad \text{(fast)}
\end{align*}
\]

Figure 2.3: Elementary steps for CO oxidation according to Langmuir-Hinshelwood reaction mechanism [13]

Carbon monoxide strongly adsorbs on the Pt surface [3, 13, 18, 22, 38-40, 44], causing CO saturation and inhibiting considerable O_2 adsorption on the Pt surface. Reactions that follow the L-H mechanism have a generalized form for the rate equation; for CO oxidation on Pt, the L-H rate equation in measurable quantities is shown in equation E1.
[13], where $P_{CO}$ and $P_{O2}$ are the partial pressures of CO and O$_2$, respectively, and $r$ is the rate expression for the rate determining step described in Figure 2.3.

$$r = \frac{k_1K_1^05P_{CO}^05}{1 + K_1P_{CO} + \left(K_2P_{O2}\right)^{05}2}$$

Figure 2.4: Generalized L-H schematic of the CO oxidation reaction rate as a function of CO partial pressure ($P_{CO}$) at a constant O$_2$ partial pressure ($P_{O2}$)

Figure 2.4 shows a schematic for the CO oxidation reaction rate, according to equation E1, as a function of $P_{CO}$ assuming a constant $P_{O2}$ [13]. At low $P_{CO}$ values, the reaction rate increases with increasing $P_{CO}$ (positive order) because of low CO coverages. At intermediate $P_{CO}$ values, the reaction rate reaches a maximum. At high $P_{CO}$ values, the reaction rate decreases with increasing $P_{CO}$ (negative order) because high CO coverages
inhibit O$_2$ adsorption, thereby reducing the rate of CO oxidation. Hence, the reaction rate for CO oxidation can be positive and negative order in CO depending on $P_{co}$, with a range between -1 and 1.

Kinetic studies of CO oxidation on unpromoted Pt catalysts have shown that the order of CO in the CO oxidation reaction is less than one. Sarkany & Gonzalez [46, 47] used differential flow measurements at 100°C and 170°C to calculate CO and O$_2$ reaction orders of -0.1 and +0.7, respectively. Zafris and Gorte [48] used a high pressure batch reactor with an isolated UHV chamber between 290-400°C to calculate CO and O$_2$ reaction orders of -0.6 and +1.3, respectively, for Pt on α-Al$_2$O$_3$. Muraki et al. [15] obtained CO and O$_2$ reaction orders of -1.5 and +1.0, respectively.

Kahlich et al. [17] used differential flow measurements between 150-250°C to calculate CO and O$_2$ reaction orders of -0.4 and +0.8, respectively. Schubert et al. [35] utilized DRIFTS to validate reaction orders for CO and O$_2$ from Kahlich et al. [17]. Kim and Lim [22] calculated CO and O$_2$ reaction orders of -0.51 and +0.76, respectively, from a differential reactor, and -0.50 and +0.81, respectively, from an integral reactor prediction model. Both Kahlich et al. [17] and Kim and Lim [22] described the CO oxidation intrinsic kinetics with a simple power-law expression.

These negative orders in CO were consistent with the observations mentioned above that CO effectively saturated the Pt surface [13, 22, 39, 44, 49], and were within the range for
a L-H reaction mechanism. Conversely, the reaction orders for O\textsubscript{2} in the literature ranged from 0.7-1.3. This range was higher than the maximum order of 0.5 for a L-H reaction mechanism described in equation E1. One hypothesis is that the rate-limiting step is molecular O\textsubscript{2} adsorbing on the Pt surface. Kahlich et al. [17] mentioned that the +0.8 O\textsubscript{2} reaction order was consistent with CO oxidation in the absence of H\textsubscript{2} occurring in the \textit{low-rate branch}. CO oxidation in the \textit{low-rate branch} means the catalyst surface is predominately covered with CO, and is characterized by a +1 O\textsubscript{2} reaction order. Zafris and Gorte [48] mentioned that the first-order dependence of O\textsubscript{2} is attributed to molecular O\textsubscript{2} adsorbing on the catalyst surface. The dissociation of O\textsubscript{2} occurred later, in a more rapid step. Therefore, CO oxidation occurs at the \textit{low-rate branch} under differential reactor analysis, which allows a +1 O\textsubscript{2} reaction order because molecular O\textsubscript{2} adsorption on the Pt surface is the rate-limiting step.

One way to overcome CO poisoning of the Pt surface is to promote the Pt catalyst with another metal. This promotion will form a metal oxide and create a non-competitive dual site reaction mechanism instead of the typical competitive dual site reaction mechanism observed from unpromoted Pt catalysts [50].

2.2.3 \textit{The Reverse Water-Gas-Shift Reaction}

Under reformate inlet feed compositions (i.e., 40-75\% H\textsubscript{2}, 15-20\% CO\textsubscript{2}, \sim 10\% H\textsubscript{2}O, 0-35\% N\textsubscript{2}, and 0.5-1.0\% CO), the reverse water-gas-shift (r-WGS) reaction, seen in reaction R3 from Chapter 1 and reproduced below, can severely limit CO conversion
when reactor temperatures are above 170-200°C. The thermodynamics of the r-WGS reaction are unfavorable ($\Delta G_{\text{rxn,298K}} = +28.6$ kJ/mol). However, even a small amount of shift increases the minimum outlet CO concentration. Therefore, the effect of CO$_2$ and/or H$_2$O must be considered.

\[
\text{CO}_2 + \text{H}_2 \underset{\text{R3}}{\rightleftharpoons} \text{CO} + \text{H}_2\text{O} \quad (\Delta H_{\text{rxn,298K}} = +41.2 \text{ kJ/mol})
\]

Brown et al. [14] stated that the breakdown of CO selectivity above 160°C on Pt catalysts was attributed to the r-WGS reaction. Moreover, this effect was magnified because the oxidation reactions were exothermic, causing a considerable temperature rise in the reactor. More recently, Korotkikh and Farrauto [39] carried out tests without CO$_2$ in the inlet feed to eliminate significant CO formation from the r-WGS reaction. They stated that tests were done with CO$_2$ but were not reported, and that the r-WGS reaction might limit the CO conversion at temperatures above 180°C. Watanabe et al. [20] noted that even without CO$_2$ and H$_2$O in the inlet feed, the rWGS reaction was observed at temperatures above 200°C on Pt and Pt/Fe supported on mordenite. Enough CO$_2$ was formed from the oxidation reaction to active the r-WGS reaction. Igarashi et al. [21] mentioned that the addition of H$_2$O decreased the CO and O$_2$ conversions, but not the CO selectivity, on Pt/zeolite catalysts. A CO conversion maximum was reported in the reaction studies at 200°C, but was not attributed to the r-WGS reaction.
Oh and Sinkevitch [16] saw a decrease in CO conversion with increasing temperatures on different noble metals supported on Al$_2$O$_3$. Maximum CO conversion on Pt was seen ~200°C. This decrease was explained by the r-WGS reaction, even without CO$_2$ and H$_2$O in the inlet feed. The r-WGS reaction equilibrium was calculated assuming complete O$_2$ conversion. Assuming equilibrium, the CO conversion was calculated to be 88% at 250°C, 78% at 350°C, and 60% at 450°C. Discrepancies between the measured and calculated CO conversions were attributed to insufficient time to reach equilibrium and temperature gradients in the catalyst bed, yielding a different value from the equilibrium constant based on the mid-bed temperature.

Kahlrich et al. [17] postulated that H$_2$ approximately doubled the CO oxidation rate at 150°C under integral and differential flow measurements. This increase was explained by formate species production on the Al$_2$O$_3$ surface from adsorbed hydroxyl groups (OH$^-$). The H$_2$ reacts to form H$_2$O, and the H$_2$O adsorbs on the Al$_2$O$_3$ surface to form OH$^-$. The OH$^-$ groups consume Pt-bonded CO to form a formate species, which frees up some Pt sites for O$_2$ adsorption and dissociation.

Manasilp and Gulari [18] studied the selectivity of a 2 wt% Pt/Al$_2$O$_3$ sol-gel catalyst with an inlet feed containing CO$_2$ and/or H$_2$O. Steam had a positive effect in reducing the activation energy for CO oxidation from ~74 to ~37 kJ, resulting in an up to ten-fold increase in CO conversion. The CO selectivity did not change significantly, indicating an increase in H$_2$ oxidation also. One hypothesis was that H$_2$O dissociatively adsorbed on
Pt, forming OH. The OH$^-$ provided a better oxidant than O$_2$ for CO and H$_2$ oxidation. Another hypothesis was that H$_2$O modified the Pt$^0$ surface to Pt(O)$_x$. Carbon dioxide in the inlet feed decreased the activity of the catalyst, possibly because of the $\tau$WGS reaction. In the presence of both CO$_2$ and H$_2$O, the positive effect of H$_2$O on CO oxidation dominated the negative effect of CO$_2$.

Muraki et al. [15] studied the effect of H$_2$ and H$_2$O on Pt, Pd and Rh catalysts supported on Al$_2$O$_3$. At 140°C, CO conversions for all catalysts were higher in the presence of H$_2$O, with an enhancement increasing order of Pt > Pd > Rh. The activation energies for CO oxidation were lowered in the presence of H$_2$O, with a decreasing activation energy order of Pt < Pd < Rh. The same effect on CO conversion was seen with H$_2$ addition because H$_2$ oxidized to H$_2$O. Steam adsorbed strongly on Al$_2$O$_3$, which might affect some Pt/Al$_2$O$_3$ interaction during CO oxidation. At temperatures below 200°C, no $\tau$WGS reaction activity was observed from flowing 1 mol% CO and 3 mol% H$_2$O on Pt/Al$_2$O$_3$.

Kim and Lim [22] did not see a CO conversion enhancement from H$_2$O addition on a Pt/Al$_2$O$_3$ catalyst. They hypothesized that enough H$_2$O was produced by H$_2$ oxidation for the enhancement to occur. Earlier, Nibbelke et al. [51] detected an enhancement on the rate of CO oxidation with H$_2$O partial pressures of less than 1 kPa at 210°C. An increase in H$_2$O pressure had no added effect on CO oxidation, and changed the CO oxidation reaction order in H$_2$O to zero. Also, they found a zero reaction order in CO$_2$ because the CO$_2$ partial pressure did not affect the CO$_2$ production rate.
Conversely, Snytnikov et al. [23] reported decreased CO conversions on Ru/C and Pt/C catalysts in the presence of 20 vol.% CO$_2$ and 3 vol.% H$_2$O. The minimum outlet CO concentration in the absence and presence of both CO$_2$ and H$_2$O was 9 ppm at 150°C and 20 ppm at 160°C on Pt/C, respectively, and 7 ppm at 105°C and 140 ppm at 110°C on Ru/C, respectively. The CO selectivity decreased in the presence of CO$_2$ and H$_2$O, while O$_2$ conversion was not affected. In separate tests, the presence of CO$_2$ facilitated the r-WGS reaction on Pt/C and Ru/C, and the CO hydrogenation reaction on Ru/C to form methane. The presence of H$_2$O might have blocked catalyst active sites by adsorbing on the catalyst surface, as well as forming CO-H$_2$O surface complexes.

2.2.4 Catalyst Characterization

Carbon monoxide adsorbs strongly to Pt metal, inhibiting O$_2$ and H$_2$ adsorption. Specifically, high CO coverage on Pt catalysts is common at lower temperatures. Adsorption of CO on Pt can have many different configurations, from linear (1:1 CO:Pt), to bridged (1:2), to bidentate (2:1) bonding [52]. The linear bond is predominant at coverages less than 50%, pressure of 0.101 MPa, and temperatures of 27-227°C [53, 54]. An example of linear and bridged bond configurations is depicted in Figure 2.5 [55].
Using Fourier transform infrared spectroscopy (FTIR), Dulaurent & Bianchi [49] observed complete linear CO coverage on Pt at room temperatures for 0.01-1.0% CO mixtures. Complete coverage of the linear CO species on Pt did not start to decrease until above 200°C for the 0.1% and 1.0% CO mixtures. Liu et al. [39, 40] experimentally confirmed the domination of CO adsorption on the Pt surface compared to H₂. Bourane and Bianchi [44] stated that CO oxidation on Pt/Al₂O₃ was only detected for reaction conditions allowing a decrease in the CO adsorbed species or a weakly adsorbed oxygen species. Manasilp and Gulari [18] predicted a desorption temperature of ~160°C for CO on Pt. Using CO temperature programmed desorption (TPD), Kahlich et al. observed three desorption peaks/shoulders at 120°C, 215°C, and 260°C for 0.5 wt% Pt. Schubert et al. [56] reported a higher desorption temperature of 210-240°C, but attributed it to formate decomposition from the hydroxylated alumina support (Al₂O₃-OH⁻).

Carbon monoxide adsorbs on metallic Fe in multiple configurations, with multiple desorption temperatures. At CO coverages less than 50%, CO desorbs from Fe (100) from four-fold hollow sites at two states: α₃ (167°C), an intermediate state between molecular and dissociated CO, and β (547°C), which occurs after dissociated CO
recombines on the Fe surface. At CO coverages higher than 50%, CO desorbs from Fe at two other states, in addition to $\alpha_3$ and $\beta$: $\alpha_1$ (-48°C) and $\alpha_2$ (32°C), which correspond to weakly bonded CO on the Fe surface.

Cameron and Dwyer [57] observed all four CO desorption peaks from TPD experiments. Using x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED), they saw CO adsorb on four-fold hollow sites on Fe (100), and the $\alpha_3$ state as the most strongly bonded to metallic Fe. At temperatures above 167°C, CO dissociated on Fe and each C and O required its own four-fold hollow site, until temperatures above ~450°C where they recombined and desorbed from at the $\beta$ state. Nassir et al. [58] furthered the theory of partial $\alpha_3$ dissociation by proposing a new mechanism called *dissociation-stimulated desorption*. Lu et al. [59] reported seeing all four CO peaks, with an $\alpha_2$' shoulder on a clean Fe (100) surface, but not on a precovered CO-Fe surface. The $\alpha_2$ and $\alpha_2$' were ascribed to bridge sites, while $\alpha_1$ was an on-top (linear) site.

Liu et al. [40] mentioned that CO did not or very weakly adsorbed on Fe oxide compared to Pt. They did not observe CO bands on Fe$^{2+}$ or Fe$^{3+}$ around 2140 cm$^{-1}$ wavenumber using DRIFTS. Jiang et al. [60] used DRIFTS to determine adsorption properties of precipitated Fe catalysts from pulse chemisorption. The catalyst was pretreated with He at 350°C for 1 hour. The CO pulses revealed two bands at 2187 and 2090 cm$^{-1}$ wavenumbers after a brief He flushing. The two bands were attributed to CO adsorption on Fe$^{3+}$ and Fe$^{2+}$. It is possible that the 2187 cm$^{-1}$ is from Fe$_2$O$_3$. After more time had
passed, the two bands disappeared. Therefore, the CO adsorption on Fe$^{3+}$ and Fe$^{2+}$ were short-lived. A carbonate species on the iron oxide surface was also observed at 1700-1100 cm$^{-1}$ wavenumbers. Harrison and Thornton [61] observed bidentate (2:1 CO:Pt) adsorption on an oxidized Fe$^{3+}$ surface supported on SnO$_2$. The CO adsorption was attributed to a carbonate species, not molecular CO. When the Fe/SnO$_2$ catalyst was reduced with CO at 350°C, no CO adsorption was seen. Therefore, from the literature, the Fe oxide surface can have many different CO adsorption configurations.

Moreover, CO can react with Fe to form iron pentacarbonyl [Fe(CO)$_5$], a volatile and toxic chemical. Farrauto and Bartholomew [13] revealed that Fe(CO)$_5$ could form at moderate to room temperatures (0-300°C) [13, 62] and volatize from the support. Blanchard [62] extensively described volatile metal carbonyls, and how Fe(CO)$_5$ quickly oxidized to Fe$_2$O$_3$ in the presence of air.

The amount of CO adsorbed on the catalyst surface can change significantly when Pt is promoted with Fe. Liu et al. [40] revealed that Fe preferred to deposit on Pt instead of Al$_2$O$_3$. Iron lowers CO adsorption on Pt because Fe oxide decorated the Pt surface. The CO adsorbed on the Pt/Fe/Al$_2$O$_3$ catalyst was only about 75% that of the Pt/Al$_2$O$_3$ catalyst. They also claimed that Fe oxide provided active O$_2$ for CO oxidation. Studies using DRIFTS on the Pt/Fe catalyst showed CO$_2$ adsorption, disturbed OH groups on Al$_2$O$_3$, and a ~3 cm$^{-1}$ wavenumber band shift from the linear CO-Pt band (2084 cm$^{-1}$), all of which were attributed to Fe oxide. The XPS results showed Fe was present in the form
of Fe\(^{2+}\) and Fe\(^{3+}\), but not Fe\(^{0}\). Using transmission electron microscopy (TEM), high resolution TEM (HRTEM), and X-ray diffraction (XRD), no effect was seen on the size and distribution of Pt (~ 2 nm) from the presence of Fe.

On a Pt/Fe/mordenite catalyst, Watanabe et al. [20] observed negligible CO adsorption using FTIR at 30°C in a flow of 1% CO, 0.5% O\(_2\), and balance H\(_2\). A CO TPD experiment showed only 1/3 of the CO peak size compared to an unpromoted Pt/M catalyst. Both observations were explained by lowered and weakened CO adsorption properties from neighboring Pt and Fe sites. The TEM and scanning TEM images did not show Fe decorating the Pt surface, but that the catalysts existed inside the mordenite cages. Sakamoto et al. [41] found using XRD that Fe dissolved into the Pt lattice after an 800°C O\(_2\)-H\(_2\) treatment to mimic thermal aging. The mean Pt diameter was 20-35 nm using TEM. They modeled the Pt/Fe/Al\(_2\)O\(_3\) catalyst after the O\(_2\)-H\(_2\) pretreatment as a homogeneous Pt-Fe alloy covered with a thin Fe\(_2\)O\(_3\) layer. Their catalyst was used for hydrocarbon conversion at stoichiometric conditions, not for the PROX reaction.

2.3 **Structured Supports**

2.3.1 *Ceramic Monoliths*

Uses for structured catalyst supports, such as ceramic monoliths, are well established. One of the most prominent examples is the catalyst in the catalytic converter of gasoline-powered automobiles. Many automotive catalysts are comprised of Pt/Pd/Rh washcoated on a ceramic honeycomb monolith. Ceramic monoliths frequently are made of a
cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) material composed of $2\text{MgO}$, $5\text{SiO}_2$, and $2\text{Al}_2\text{O}_3$. Cordierite monoliths have low thermal expansion coefficients ($\sim 10^{-6}$-$10^{-7}/°\text{C}$ [5, 63]) making them resistant to thermal shock, and well designed pore structures giving good chemical and mechanical bonding to the washcoat.

The advantages of using a ceramic monolith in an automobile compared to particulate catalysts are: lower pressure drop (dependent on washcoat thickness), good mechanical strength and attrition resistance, higher geometric surface areas, and availability of different cell densities or cells per square inch (cpsi) [5, 64, 65]. For example, a 400 cpsi ceramic monolith has an open frontal area of 71%, hydraulic diameter of 0.112 cm, and a geometric surface area of $2.8 \text{ cm}^2/\text{cm}^3$.

In addition to catalytic converters, ceramic monoliths are used in power plants for selective catalytic reduction (SCR) of $\text{NO}_x$ by $\text{NH}_3$ [5, 64]. For low- (175-250°C), medium- (300-450°C), and high-temperature SCR (350-600°C), the catalysts deposited on the monolith are Pt-based, $\text{V}_2\text{O}_5/\text{TiO}_2$, and zeolite-based, respectively. Korotkikh and Farrauto [39] investigated CO PROX reactions using a Pt/Fe/$\text{Al}_2\text{O}_3$ catalyst supported on a 400 cpsi cordierite monolith, and reported comparable CO conversion and selectivity to Pt/Fe/$\text{Al}_2\text{O}_3$ pellets at 90°C and 150°C.

Although ceramic monoliths have many advantages, there are disadvantages. The cordierite monoliths have parallel channels, essentially operating as adiabatic reactors,
which limit the control of temperature within the monolith [64]. This restricts their use in very exothermic or endothermic reactions that require operation in a narrow temperature range. In the 1990s, corrugated metallic monoliths became available, allowing better heat distribution because of their higher thermal conductivity. In addition, a thinner wall thickness will allow higher cell densities with lower pressure drop [5]. A 400 cpsi metal monolith has a 25% thinner wall thickness compared to its ceramic counterpart. The main disadvantage of metallic monoliths is their higher thermal expansion coefficients ($\sim 10^{-5}-10^{-6}/^\circ\text{C}$ [63]), requiring special bonding techniques for washcoat adherence.

2.3.2 Metal Foams

Metal foams offer a number of advantages over the ceramic honeycomb monolith: higher thermal conductivity, radial mixing and heat transport, and a durable, low density, high strength structure. Richardson et al. [66] showed ceramic foams had a pressure drop one order of magnitude lower than 0.5 mm spherical beads, and metal foams of the same structure should have the same advantage. Metal foams may have broad applicability, e.g., automotive, aerospace, and biomedical [67, 68].

Metal foams can be created with different morphologies and metallurgies, depending on the application and operating conditions. There are many techniques used to manufacture metal foams [67, 69-71]; currently there are nine processes in practice. The five processes that can be produced commercially are [71]:

41
1) Melt gas injection (bubbling) through molten Al-SiC or Al-Al₂O₃ alloys.

2) Gas-releasing particle decomposition by stirring a particulate foaming agent (typically TiH₂) into a molten alloy and controlling the pressure while cooling.

3) Gas-releasing particle decomposition by consolidation of a metal powder with a particulate foaming agent (typically TiH₂). This is followed by heating of the solid to a little above its solidus state (the highest temperature at which a metal or alloy is still completely solid) while the foaming agent releases H₂, expanding the material.

4) Manufacture of a ceramic mold from a wax or polymer foam precursor with the desired cell size and relative density. This step is followed by burning-out of the precursor to form a negative image, and pressure infiltration with a molten metal or a metal powder slurry which is then sintered.

5) Vapor phase deposition or electrodeposition of metal onto a polymer foam precursor which is subsequently burned out, leaving cell edges with hollow cores.

Figure 2.6: Range of cell size and relative density for the different metal foam manufacturing methods [71]
Each process can create metal foams with a range of relative densities, cell sizes, and cell types, as shown in Figure 2.6 [71]. There are two cell types: open and closed. In an open cell metal foam, the cells, or pores, are connected. In a closed cell metal foam, each cell is separated from another cell by thin walls of metal.

Pestryakov and co-workers [72-74] published data on metal foams (2-3 mm cell size or ~10 pores per inch, 4-7% cell density) used in hydrocarbon oxidation and automotive emissions abatement. The hydrocarbon oxidation studies of n-butane [72, 73] were tested between 250-350°C on 5-8 wt% CuCr$_2$O$_4$/γ-Al$_2$O$_3$ metal foam catalysts. The metal foam catalysts were comparable to granular catalysts, and more active than the block honeycomb monolith because of mixing turbulence in the former two compared to the parallel channels in the latter. The γ-Al$_2$O$_3$ washcoat was used to increase the surface area of the metal foams for catalytic deposition. Other catalyst compositions were tested, and the CuO-Co$_3$O$_4$ on Cu and Ni metal foams with no γ-Al$_2$O$_3$ had the highest activity.

Later work by Pestryakov et al. [74] studied 1 vol.% CO and propane oxidation reactions in air between 150-350°C using a 0.5 wt% Pt or Pd, or 10-12 wt% transition metals on metal foam supports coated with γ-Al$_2$O$_3$. The metal foam catalysts performed better than the ceramic monoliths and comparably to the granular catalysts with the same catalyst composition for propane oxidation. The Pd catalyst performed better than the transition metals for CO oxidation on the metal foams.
2.4 Other CO Reduction Methods

2.4.1 Methanation

Methanation offers another method to reduce residual CO, as described in reaction R5. The main disadvantage of using methanation for CO removal is hydrogen consumption. Three moles of H$_2$ are consumed per mole of CO during methanation. This requires a higher inlet feed to make up for the reacted H$_2$. To a lesser extent, CO$_2$ can also be hydrogenated (reaction R6), so it has to be removed prior to the methanation reactor.

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad (\Delta H_{\text{rxn},298K} = -206 \text{ kJ/mol}) \quad \text{R5} \\
\text{CO}_2 + 4\text{H}_2 & \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \quad (\Delta H_{\text{rxn},298K} = -165 \text{ kJ/mol}) \quad \text{R6}
\end{align*}
\]

Even though the thermodynamics for CO and CO$_2$ hydrogenation are favorable ($\Delta G_{\text{rxn},298K} = -142$ and -113 kJ/mol, respectively), the kinetics are unfavorable at lower temperatures. Typical methanation conditions are 250-300°C and 3.04 MPa over a Ni/Al$_2$O$_3$ catalyst promoted with MgO [13]. These conditions are higher than the temperatures and pressure exiting the WGS reactor [3, 5, 13]. Moreover, the high temperatures required for methanation in the presence of CO$_2$ generates additional CO from the r-WGS reaction [5, 16]. The Ni catalyst is self-igniting when exposed to air [5], which poses a considerable safety hazard. Therefore, methanation is not a practical option for CO reduction prior to the PEMFC.
Even under PROX conditions, there is a possibility of CO or CO$_2$ hydrogenation to CH$_4$, but generally Pt is a poor catalyst for methanation compared to Ni or Ru [17]. Korotkikh and Farrauto [39] reported no CH$_4$ formation at temperatures above 250°C on Pt/Fe/Al$_2$O$_3$. Manasilp and Gulari [18] similarly saw no CH$_4$ production up to 210°C on unpromoted Pt/Al$_2$O$_3$. Watanabe et al. [20] did not see any CH$_4$ production (lower limit was 10 ppm CH$_4$ detection) up to 300°C on Pt/Fe/zeolite. Snytnikov et al. [23] observed methanation on Ru/C catalysts at 100°C, but not on Pt/C catalysts at 140°C. Kahlich et al. [17] detected CH$_4$ formation at 250°C and insignificant amounts compared to the PROX reaction at 350°C. Kim and Lim [22] observed trace quantities of CH$_4$ at 350°C, and minor methanation at 400°C relative to the other CO reactions.

2.4.2 Pressure-Swing Adsorption

Pressure-swing adsorption (PSA) is an alternative to PROX and methanation because it does not require high temperatures. At ambient temperatures and high pressures (2.07 MPa), the high-pressure WGS effluent stream passes over an adsorbent bed of molecular sieves. The sieves remove all non-H$_2$ components to a purity of 99.95% H$_2$ [13, 75]. When the adsorbent bed is saturated, it is depressurized and regenerated by purging with H$_2$. A second PSA bed is required while the first bed regenerates. The use of PSA for CO removal in fuel cells is not a practical technique. Even though PSA eliminates the need for a second WGS reactor and the equipment cost is lower, the space requirements are greater because of the necessity of two PSA beds. Moreover, PSA operating pressure is too high [5].
2.4.3 Selective Membranes

Selective membrane reactors using a Pd or Pd-alloy allow only H$_2$ to permeate through the membrane [3, 75]. The two major advantages of using a selective membrane in conjunction with the reformer are: 1) H$_2$ removal during reforming can increase the CH$_4$ conversion above what is dictated thermodynamically by the operating temperature, and 2) high purity H$_2$ production suitable for PEMFCs. The major disadvantage is purity requirements for the inlet feed entering the membrane reactor. Impurities such as CO, H$_2$S, or aromatics poison the Pd surface. This causes lower rates of mass transport and decreases the working surface area [75].
2.5 References


23. Snytnikov, P.V., V.A. Sobyandin, V.D. Belyaev, P.G. Tsyrlunikov, N.B. Shitova and D.A. Shlyapin, *Selective oxidation of carbon monoxide in excess hydrogen over Pt-


CHAPTER 3 PREFERENTIAL OXIDATION STUDY

A preferential oxidation (PROX) study was conducted on four different types of structured supports: metal foams, ceramic straight-channel monoliths, metal monoliths, and ceramic foams. The PROX reactor was run at a total volumetric flow rate of ~12 L/min at standard conditions, a gas hourly space velocity of 30,000 hr$^{-1}$, and reactor inlet temperatures between 80-200°C. Carbon monoxide and O$_2$ conversions were measured, and selectivity was calculated for CO oxidation over H$_2$ oxidation. The gas composition of the effluent stream from a water-gas-shift (WGS) reactor in a typical fuel processor was modeled.

3.1 Experimental Design

The catalyst supports used in this study were cylindrically shaped with a 2.54 cm (1") inner diameter and 5.08 cm (2") length, as shown in Figure 3.1. The supports were supplied by Porvair Fuel Cell Technology, Hendersonville, NC. A series of Fe-promoted Pt catalysts were synthesized and washcoated on the supports, with a washcoat loading of about 0.098 g/cm$^3$ (1.6 g/in$^3$) of the gross catalyst support volume.

Figure 3.1: Catalyst support length and diameter
Four different types of support were tested: metal foams, ceramic straight-channel monoliths, ceramic foams, and corrugated metallic monoliths. Foams have two defining characteristics: pores per inch (ppi) and cell density ($\rho$). Monoliths are defined by their cells per square inch (cpsi).

Pores per inch is the number of pores in the foam per linear inch. The average diameter of a pore or channel varies inversely with ppi. For example, a 20 ppi foam has larger channels than a 40 ppi foam. Higher ppi foams have a greater tortuosity for the gas stream path. Cell density is the ratio of the actual volume of the foam to the gross geometric volume of the foam. Cell density is the complement of void volume; a foam with 12% $\rho$ has a void volume of 88%. The surface area per unit volume for a 20-40 ppi, 4-12% $\rho$ metal foam is about 1-4 mm\(^{-1}\) [1]. Assuming a dry washcoat density of 2.0 g/cm\(^3\), the calculated average washcoat thickness is ~10-60 µm.

Cells per square inch is the number of cells (open channels) per square inch of cross-sectional area. For the same cross-sectional area of monolithic support, a 400 cpsi (62 cells/cm\(^2\)) monolith has a smaller hydraulic diameter per cell than a 200 cpsi monolith. The surface area per unit volume is about 2.8 mm\(^{-1}\) for a 400 cpsi monolith [1]. Assuming a dry washcoat density of 2.0 g/cm\(^3\), the calculated average washcoat thickness is about 15-20 µm [2].
Metallic monoliths are fashioned out of spiral-wound, corrugated metal supports with a repeating pattern of ~3 mm. This results in an open face roughly equivalent to a 400 cpsi straight-channel monolith. The calculated average washcoat thickness is ~15-20 µm, the same as a 400 cpsi monolith. Examples of different supports are shown in Figure 3.2.

![Figure 3.2](image)

Figure 3.2: Sample pictures of a (a) 40 ppi, 4% ρ metal foam, (b) 400 cpsi ceramic straight-channel monolith, and (c) 400 cpsi equivalent metal monolith

3.1.1 Catalyst Preparation Procedure

There are many different types of catalyst preparation techniques, such as wet impregnation, ion-exchange, and precipitation [3, 4]. All catalysts used in this study were prepared by Environex Inc., located in Devon, PA. They dipped the support in a washcoat slurry, and utilized the incipient wetness technique to deposit the catalyst on the washcoat. Incipient wetness is accomplished by adding catalyst-containing solution onto the washcoat until the pores are just filled. Capillary forces draw the liquid solution into the pores and deposit the catalyst into the pores. The main advantages of incipient wetness are its relative simplicity, efficiency, and ability to deposit high metal loadings.
The two main disadvantages are non-uniform catalyst deposition along the pores, and oxidation of the base metal in the solution, causing unwanted interactions with the support and making it difficult to reduce [3].

The following procedure for synthesizing these types of catalyst support was provided by Environex:

**Fe-promoted Pt catalysts:**

1) The catalyst support (e.g. foam or monolith) was dipped into a slurry containing Al$_2$O$_3$ particles with an average particle size of 5 µm (after ball milling).

2) Excess slurry was blown off with compressed air.

3) The washcoated support was dried at 100$^\circ$C and then weighed to determine the amount of Al$_2$O$_3$ taken up. If the amount was less than the target washcoat loading of 0.098 g cat/cm$^3$ of gross catalyst volume, steps 1 through 3 were repeated until the target loading was achieved.

4) The washcoated support was calcined at 500$^\circ$C to promote washcoat adhesion.

5) The pore volume of the washcoat was determined by impregnating the support with deionized water.

6) The washcoated support was impregnated with a solution of tetraamine platinum (II) hydroxide [Pt(NH$_3$)$_4$(OH)$_2$] to achieve the desired Pt concentration. For most catalysts, this concentration was 5 wt% based on the amount of washcoat (0.080 grams Pt/in$^3$ of gross catalyst volume).

7) The catalyst was dried at 100$^\circ$C and calcined at 500$^\circ$C.
8) The catalyst was impregnated with a solution of iron (II) acetate anhydrous 
\[ \text{Fe(C}_2\text{H}_3\text{O}_2\text{)}_2 \] to achieve the desired Fe concentration. For most catalysts, this 
concentration was 0.5 wt.% based on the amount of washcoat (0.008 grams Fe/in\(^3\) of 
gross catalyst volume).

9) The catalyst was dried at 100°C and calcined at 500°C.

3.1.2 Equipment and Measurement

The experimental gases required to simulate the gas stream exiting the WGS reactor were 
CO, H\(_2\), O\(_2\), CO\(_2\), H\(_2\)O, and N\(_2\). Gas cylinders were supplied by National Welders, and 
the cylinder compositions for the reaction experiments were: 10% CO-balance N\(_2\); 10% 
O\(_2\)-balance N\(_2\); 17.6% CO\(_2\)-balance H\(_2\), and; pure N\(_2\). These compositions were chosen 
because of safety, compatibility, and lower explosive limit (LEL) levels. The H\(_2\)O was 
supplied via HPLC pump. A 900 ppm CO-balance N\(_2\) cylinder was used as a span gas 
for the gas analyzer.

Gas flow rates were controlled by four Brooks Instrument Model 5850E mass flow 
controllers. The maximum flow rates of the controllers for the 10% CO in N\(_2\), 10% O\(_2\) in 
N\(_2\), 17.6% CO\(_2\) in H\(_2\), and pure N\(_2\) gas cylinders were 3500 standard cubic centimeter per 
minute (sccm), 3500 sccm, 16,000 sccm, and 5,500 sccm, respectively. Standard 
conditions are defined here as 0.101 MPa (1 atm) pressure and 0°C temperature. The 
mass flow controllers were controlled by a Brooks Instrument Model 5878 control and 
read out equipment for thermal mass flowmeters. A LabAlliance series 1500 constant 
flow HPLC pump controlled the flow rate of deionized (DI) water.
The gases were initially preheated by an Omega FSB-1 fluidized sand bath, with a maximum temperature of 350°C. The effluent from the sand bath (FSB) was heated further by heating tapes. The heating tapes could achieve maximum temperatures of about 482°C (900°F). Five Variac Voltmeter transformers controlled the voltage to the heating tape, which determined the final temperature.

A model 3080SS thermoelectric two channel gas sample chiller, from Universal Analyzers, Inc., was used to cool down the reactor effluent gas stream to 4°C. This step was required to remove water from the system prior to entering the gas analyzer.

A Precision Scientific catalog # 63126 wet test meter was used to verify the flow rates from the mass flow controllers and as a vent stream. An Omega FL-1345-G variable area rotameter was used to gauge the gas stream flow rate directly before the gas analyzer.

A California Analytical Instruments, Inc. (CAI) nondispersive infrared (NDIR) gas analyzer model 300 was used to measure the CO and O₂ concentrations. The CO concentration is measured with IR analyzers. The O₂ concentration is measured by a paramagnetic oxygen analyzer. The NDIR has three components, each with four ranges listed in Table 3.1. Each component requires 0.5 – 2.0 L/min of gas for accuracy. There are two inlet gas streams for the NDIR. The inlet gas stream for components 2 and 3 are coupled, requiring a higher flow rate than component 1. The NDIR was interfaced with a
personal computer through a PCI-DAS6025 and CIO-MINI50 boards from Measurement Computing. Data acquisition was done using the LabTech Notebook software package.

Table 3.1: NDIR Components and Ranges

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR analyzer</td>
<td>IR analyzer</td>
<td>Paramagnetic analyzer</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>Carbon Monoxide</td>
<td>Oxygen</td>
</tr>
<tr>
<td><strong>Range 1</strong></td>
<td><strong>Range 2</strong></td>
<td><strong>Range 3</strong></td>
</tr>
<tr>
<td>0 – 3000 ppm</td>
<td>0.000 – 1.500%</td>
<td>--</td>
</tr>
<tr>
<td>0 – 200 ppm</td>
<td>0 – 1000 ppm</td>
<td>0.00 – 15.00%</td>
</tr>
<tr>
<td>0.000 – 1.000%</td>
<td>0.0 – 25.0%</td>
<td>--</td>
</tr>
</tbody>
</table>

In addition to the NDIR analyzer, a Perkin-Elmer Autosystem on-line gas chromatograph (GC) could be used. The GC consists of a dual-column, temperature-programmable instrument, equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The chromatograph was interfaced with a personal computer, and the Turbochrom 4 software package was used for data acquisition.

Thermocouples and pressure indicators were dispersed throughout the process. The thermocouples were monitored by Omega model CN 101 and 102 high temperature and low temperature alarm monitors, respectively. The reactor inlet and outlet temperatures were controlled and monitored, respectively, by Yokogawa model UT-14 digital indicating controllers. Pressure drop across the support was measured by an Omega model DP41-E 1/8” high performance process indicator.
The process system had 3 gas monitors: two MSA series 5000 CO gas monitor systems, and one MSA series 5000 combustible gas monitor system. The walk-in hood enclosure contained one CO and one combustible monitor. The lab contained one CO monitor. All 3 gas monitors were interfaced with a MSA model 5300 monitoring system with warning, caution, and alarm settings. If either monitor inside the walk-in hood reaches the alarm setting, power to the walk-in hood is automatically shut off.

3.1.3 Reactor Design

The fixed bed reactor consisted of 316/316L stainless steel tubing 30.5 cm (12”) in length and 2.86 cm (1.125”) in pipe diameter (3.12 cm, 1.25” tube). Inlet and outlet thermocouples in the reactor measured the inlet and outlet gas stream temperature, respectively, using 45.7 cm (18”) K-type Omega quick disconnect thermocouples with miniature connectors. Absolute pressure was measured in the reactor, along with the pressure drop across the catalytic support. A Tescom back pressure regulator downstream of the reactor controlled the reactor pressure. Two ceramic foam distributors were placed in the inlet and the outlet of the reactor to distribute the gas stream radially.

In the PROX reaction study, 2.86 cm (1.125”) Swagelok male-female threaded connections were used to seal the reactor. Figure 3.3 shows a schematic of this reactor design. Figure B.1 in Appendix B shows the dimensions of the threaded reactor.
Figure 3.3: Reaction reactor design schematic.
The reactor was held as close to adiabatic as possible. The 2.54 cm diameter catalytic support was wrapped with a low thermal conductivity aluminum oxide ULTRA-TEMP ceramic tape insulation supplied by McMaster-Carr. The outside of the reactor tube was first wrapped with insulation foam. Then it was wrapped with multiple layers of Fisher Scientific fiberglass cloth tape to minimize heat loss from the oxidation reactions. The reactor was then wrapped with heating tape to help maintain the reactor temperature. More fiberglass cloth tape was wrapped around the heating tape to suppress heat loss. Finally, aluminum foil was wrapped around the outside of the reactor.

3.1.4 Process Design

The four gas cylinders containing CO, O\textsubscript{2}, H\textsubscript{2}, CO\textsubscript{2}, and N\textsubscript{2} were piped from the manifolds in the gas station to the walk-in hood using 0.635 cm (¼”) Swagelok tubing. The CO in N\textsubscript{2} and O\textsubscript{2} in N\textsubscript{2} lines flowed through activated carbon (AC) traps to remove nickel and iron carbonyls, and other impurities. All lines except the pure N\textsubscript{2} line were set at fail closed. The pure N\textsubscript{2} line was set at fail open and was interconnected with the other lines in case the reactants needed to be shut off. The CO\textsubscript{2} / balance H\textsubscript{2} line had an extra vent to the atmosphere in the manifold in case of an overpressurization.

From the walk-in hood enclosure, the gas flow rates were controlled by mass flow controllers. The pure N\textsubscript{2} and CO\textsubscript{2} in H\textsubscript{2} lines flowed through two separate Alltech Oxytraps to remove O\textsubscript{2}. All four gas lines had pressure relief valves installed in case of overpressurization. The four gas lines entered two Swagelok crosses acting as a mixing
bowl for the gas. A HPLC pump introduced liquid water into the system downstream of the crosses. This stream entered the fluidized sand bath (FSB), where it was preheated and the water was vaporized. Downstream of the FSB, gas stream temperatures were maintained by heating tapes. Fiberglass cloth tape and aluminum foil were placed wherever heating tapes were used to reduce exposure to the ambient air.

The gas stream entered the fixed bed reactor and passed through a back pressure regulator (BPR). The BPR was set to control the reactor pressure at 0.2 MPa (2 atm). The reactor inlet feed simulated the gas composition leaving the WGS reactor in a typical fuel processor: 42% H\textsubscript{2}, 9% CO\textsubscript{2}, 12% H\textsubscript{2}O, 1% CO, 0.25-1.0% O\textsubscript{2}, and 35-35.75% N\textsubscript{2}. The reactor was run at a total volumetric flow rate of ~12 L/min at standard conditions, a gas hourly space velocity of 30,000 hr\textsuperscript{-1}, and reactor inlet temperatures between 80-200°C. Part of the reactor effluent gas was diverted to a steam trap before leaving through the first vent. The remaining reactor effluent gas entered a 7 \textmu m particle filter prior to the cooling system. The cooling system cooled the effluent gas stream to 4°C.

The remaining gas stream was split into three lines: the first line passed through the wet test meter and acted as a second vent line, the second line operated as the GC inlet gas stream, and the third line operated as the NDIR inlet gas stream. A rotameter measured the gas flow rate entering the NDIR. The NDIR inlet stream was split in two because there were two NDIR inlets, as described in section 3.1.2. The effluent gas from the GC and NDIR was vented.
3.2 Data Analysis

The CO concentration (% and ppm) and O\textsubscript{2} concentration (%) data were collected from the NDIR gas analyzer. CO conversion (X\textsubscript{CO}), CO selectivity (S\textsubscript{CO}), and O\textsubscript{2} conversion (X\textsubscript{O2}) were used to compare the various catalysts. These variables were calculated using equations E2 through E4.

\[
X_{\text{CO}} = \frac{[\text{CO}]_{\text{inlet}} - [\text{CO}]_{\text{outlet}}}{[\text{CO}]_{\text{inlet}}} \quad \text{E2}
\]

\[
S_{\text{CO}} = \frac{1/2\{[\text{CO}]_{\text{inlet}} - [\text{CO}]_{\text{outlet}}\}}{[\text{O}_2]_{\text{inlet}} - [\text{O}_2]_{\text{outlet}}} \quad \text{E3}
\]

\[
X_{\text{O2}} = \frac{[\text{O}_2]_{\text{inlet}} - [\text{O}_2]_{\text{outlet}}}{[\text{O}_2]_{\text{inlet}}} \quad \text{E4}
\]

The stoichiometric O\textsubscript{2}/CO ratio for CO oxidation is 0.5. To measure the true kinetic selectivity, the O\textsubscript{2}/CO ratio must be less than stoichiometric, or the O\textsubscript{2} conversion must be less than what would result if only CO is oxidized. For example, if the O\textsubscript{2}/CO ratio is greater than stoichiometric and the O\textsubscript{2} conversion is 100%, it is impossible to determine whether all the CO oxidizes first and then H\textsubscript{2} oxidation proceeds, or whether H\textsubscript{2} and CO are oxidized simultaneously.
Many variables were studied in these experiments: Fe weight loading, support structure, inlet temperature \( (T_{in}) \), inlet CO concentration, inlet \( O_2 \) concentration, linear velocity, and gas hourly space velocity (GHSV). GHSV is measured in inverse hours (hr\(^{-1}\)) and is shown in equation E5.

\[
GHSV = \frac{\dot{V}_{\text{inlet}}}{V} \quad \text{E5}
\]

\[
\dot{V} = \omega_{\text{inlet}} A_{xs} \quad \text{E6}
\]

where \( \dot{V}_{\text{inlet}} \) is the inlet gas stream volumetric flow rate measured in standard cubic centimeters per minute (sccm), \( V \) is the gross catalyst support volume measured in cubic centimeters (cm\(^3\)), \( A_{xs} \) is the cross-sectional area of the cylindrical catalyst defined by \( \pi r^2 \) (cm\(^2\)), and \( v_{\text{inlet}} \) is the inlet linear velocity of the gas stream measured in centimeters per second (cm/sec) at standard conditions. For a constant catalyst support volume, equations E5 and E6 show that the GHSV and the linear velocity are directly related to each other. These two effects need to be decoupled to evaluate their individual effects. An in-depth analysis is shown in Chapter 4.

Thermocouples in the reactor inlet and outlet were used to determine the temperature difference across the reactor. The change in temperature in the reactor is mostly associated with the oxidation reactions. This temperature difference was compared to the theoretical adiabatic temperature rise (\( \Delta T_{ad} \)), shown in equation E7. The \( \Delta T_{ad} \) equation
assumes complete O₂ conversion. In order to calculate the adiabatic outlet temperature, multiply ΔT_{ad} with the O₂ conversion, and add it to the inlet temperature.

\[
\Delta T_{ad} = - \left( 2 * F_{O₂} * \Delta H^o_{RX} \right) \sum_{i=1}^{n} \theta_i \hat{C}_{pi} \over F_0
\]

where \( F_{O₂} \) is the O₂ inlet flow rate, \( F_0 \) is the total inlet flow rate, \( \Delta H^o_{RX} \) is the heat of reaction of either CO or H₂ oxidation, \( \theta_i \) is the fractional composition of species \( i \) in the gas stream, and \( \hat{C}_{pi} \) is the average heat capacity of species \( i \) in the gas stream. The \( F_{O₂} \) is multiplied by 2 because of the 2:1 CO:O₂ and H₂:O₂ stoichiometric ratio for the oxidation reactions. Equation E7 plays an important role in determining the proximity to the r-WGS reaction equilibrium line, discussed in Chapter 4. Table 3.2 shows ΔT_{ad} calculations for different CO inlet concentrations and O₂/CO ratios. The ΔT_{ad} calculations assume: 1) 100% O₂ conversion, 2) CO oxidation occurs before H₂ oxidation, and 3) at above stoichiometric O₂/CO ratios, residual O₂ is consumed by H₂ oxidation.

Table 3.2: ΔT_{ad} calculations for various CO inlet concentrations and O₂/CO ratios

<table>
<thead>
<tr>
<th>Inlet CO concentration (%)</th>
<th>O₂/CO ratio</th>
<th>ΔT_{ad} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>169</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5</td>
<td>91</td>
</tr>
<tr>
<td>1.0</td>
<td>0.25</td>
<td>46</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>85</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>46</td>
</tr>
</tbody>
</table>
Methane could not be measured in this research, but its production by methanation is not considered. As discussed in the literature, Kim and Lim [5] observed trace quantities of CH$_4$ at 350°C. Even at the highest inlet temperatures, O$_2$ inlet concentrations, and $\Delta T_{ad}$, the outlet temperature in these experiments only approached 350°C. Therefore, based on previous research [5-9], it is assumed that CO hydrogenation does not occur to any significant extent.

### 3.3 Ceramic Monoliths Results and Discussion

It is well known that Pt-based supported catalysts are active oxidation catalysts [7, 10-13]. However, CO adsorbs very strongly to Pt under PROX conditions [5, 7, 8, 14-18] and covers the Pt surface. Carbon monoxide oxidation is very slow because there are no empty Pt sites for O$_2$ adsorption. The CO oxidation reaction occurs via a Langmuir-Hinshelwood (L-H) mechanism [3, 8, 18, 19], which requires both O$_2$ and CO adsorption on the Pt surface for the reaction to occur. Oxidation of CO can be facilitated if there is an alternative site for the O$_2$ to adsorb and react.

Previous research found that promotion with a base metal minimized inhibition caused by strong CO adsorption on the Pt surface [6, 8, 15]. Liu et al. [14] found that iron oxide promoted Pt/alumina catalyst provided the active oxygen for CO oxidation. Iron oxide on the Pt promoted catalyst is located either on or adjacent to the Pt surface, creating a non-competitive dual site adsorption pathway and enhancing CO oxidation. Iron reacts strongly with O$_2$, and does not spillover to the Pt surface.
Based on this understanding, initial experiments were conducted on 0.5 wt% Pt catalyst promoted with 0.005 wt% Fe. This catalyst formulation was the most active in a series studied by Straschil and Egbert [15]. A catalyst was washcoated with this formulation onto a 2.54 cm ID and 5.08 cm length ceramic monolith.

3.3.1 Low Pt / Fe Catalyst Loading

The 0.5 wt% Pt / 0.005 wt% Fe / γ-Al₂O₃ catalyst was washcoated on a 40 ppi, 12% ρ metal foam and on a 400 cpsi ceramic straight-channel monolith. At an inlet CO concentration of 1.0%, both catalysts showed an O₂ conversion of less than 10%. The low O₂ conversion indicated that both CO and H₂ oxidation were inhibited. Even at an inlet temperature of 170°C, there was no significant temperature difference across the reactor. As mentioned in section 3.3, CO can poison the Pt surface. Thus, CO inhibition of the Pt surface would explain the overall low conversions and temperature rise.

To test this theory, the CO inlet gas was shut off, allowing only H₂ oxidation. At inlet temperatures of 100°C and 170°C, O₂ conversion increased to ~100%. The ΔTₐd was 65-90°C, which significantly increased the reactor outlet temperature. When CO was re-introduced in the inlet feed, O₂ conversion decreased and the reactor outlet temperature quickly dropped back to the inlet temperature. The strong CO inhibition suggests that a 0.005 wt% Fe concentration does not provide enough active sites for O₂ adsorption. As a result, it would not be an effective PROX catalyst.
3.3.2 5 wt% Pt / Varying Fe weight loading study

Subsequently, 5 wt% Pt/γ-Al₂O₃ ceramic straight-channel monoliths were synthesized with four different Fe weight loadings: 0, 0.05, 0.5, and 1.0 wt%. The ceramic monolith supports had a 2.54 cm ID, 5.08 cm length, and 400 cpsi. At 170°C inlet temperature, all four catalysts exhibited similar results. Figure 3.4b shows that the CO conversion and selectivity, and O₂ conversion are independent of Fe loading. These results indicate the need for lower inlet temperatures.

Figure 3.4a shows the catalyst performance at 100°C inlet temperature, 1% CO inlet concentration, O₂/CO ratio = 1.0, and 30,000 hr⁻¹ GHSV. At these conditions, there were distinct differences in the CO conversion and selectivity. At lower Fe loadings (0 and 0.05 wt% Fe), the CO conversion was less than 40% and the O₂ conversion was less than 30%. At higher Fe loadings (0.5 and 1.0 wt% Fe), the activity of the catalysts increased significantly; CO conversion was ~80%, and O₂ conversion was ~100%.

As mentioned previously, it is impossible measure the true kinetic CO selectivity above the stoichiometric O₂/CO ratio over certain O₂ conversions. At an O₂/CO ratio = 1.0, the O₂ conversions for the lower 0 wt% and 0.05 wt% Fe promoted catalysts measured the true kinetic CO selectivity of 62% and 98%, respectively. The higher 0.5 wt% and 1.0 wt% Fe promoted catalysts did not measure the true kinetic CO selectivity because the O₂ conversions were too high (> 50%).
Figure 3.4: Effect of Fe weight loading on 400 cpsi, 5 wt% Pt / γ-Al₂O₃ ceramic straight-channel monoliths at inlet gas temperatures of (a) 100°C and (b) 170°C (1% CO inlet concentration, O₂/CO ratio = 1.0, GHSV = 30,000 hr⁻¹)
Korotkikh and Farrauto [8] observed a similar increased activity on a 400 cpsi cordierite monolith with the addition of an unspecified base metal oxide, presumably Fe [14], to a 5% Pt/\(\gamma\)-Al\(_2\)O\(_3\) catalyst. On the other hand, they did not observe a significant effect on CO selectivity at a given inlet temperature. Figure 3.4a shows a decline in CO selectivity with Fe concentration at 100°C inlet temperature. This trend may seem inconsistent with Korotkikh and Farrauto [8]. However, their experiments were run isothermally, while the data from Figure 3.4a were obtained adiabatically. Under adiabatic conditions, the reactor temperature increases for exothermic reactions. Figure 3.4a shows increasing O\(_2\) conversion with higher Fe loading, leading to higher reactor temperatures. Data from Farrauto and Korotkikh [8], reproduced in Table 3.3, also show that under isothermal conditions, CO selectivity declines with increasing reactor temperatures.

Table 3.3: Effect of CO concentration on the monolith promoted Pt catalyst performance (GHSV=20,000 hr\(^{-1}\), 2000 ppm CO inlet concentration, from Korotkikh and Farrauto [8] Table 2)

<table>
<thead>
<tr>
<th>Run #</th>
<th>Inlet Temperature (°C)</th>
<th>O(_2)/CO mole ratio</th>
<th>(X_{\text{CO}}) (%)</th>
<th>(S_{\text{CO}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>0.5</td>
<td>68.9</td>
<td>66.1</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>0.75</td>
<td>96.8</td>
<td>64.4</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>1.0</td>
<td>100</td>
<td>50.7</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>0.5</td>
<td>61.2</td>
<td>57.7</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>0.75</td>
<td>90.6</td>
<td>57.8</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>1.0</td>
<td>100</td>
<td>50.6</td>
</tr>
</tbody>
</table>

Moreover, the CO selectivity in Figure 3.4b is insensitive to Fe loading at \(T_m=170^\circ\)C because the O\(_2\) conversion is about 100% for all four Fe loadings. The adiabatic temperature rise and reactor outlet temperature should be similar for all Fe loadings,
which simulated the isothermal conditions Korotkich and Farauto [8] used. Hence, the
data from Figure 3.4 is consistent with their data.

3.4 Metal Foam Results and Discussion

3.4.1 No Catalyst Pretreatment

A 5 wt% Pt / 0.5 wt% Fe catalyst was washcoated on a series of metal foams with the
same washcoat loading (0.098 g/cm\(^3\)). The four different metal foams, all with 2.54 cm
ID and 5.08 cm length, were 40 ppi 4% \(\rho\), 40 ppi 12% \(\rho\), 20 ppi 4% \(\rho\), and 20 ppi 12% \(\rho\).
Figure 3.5 shows the CO conversion and selectivity for these different metal foams.

The data shows that higher ppi, lower \(\rho\) (higher void volume) metal foams have greater
CO conversion and selectivity compared to their counterparts at all inlet temperatures.
Higher ppi foams allow a more tortuous flow path, thinner washcoat layers, and better
mixing both axially and radially. The \(\text{O}_2\) conversion was \(\sim 100\%\) for all cases except the
two lower CO conversions from the 12% \(\rho\) foams. At 100\(\text{o}^\circ\)C inlet temperature, the 12% \(\rho\)
foams had very low CO conversions (< 22%). The order of activity for CO oxidation is:

\[ 20 \text{ ppi, 12% } \rho \sim 40 \text{ ppi, 12% } \rho \lllll 20 \text{ ppi, 4% } \rho \sim 40 \text{ ppi, 4% } \rho \]
Figure 3.5: (a) CO conversion and (b) CO selectivity for four different metal foams as a function of inlet gas temperature (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ catalysts, 1% CO inlet concentration, O₂/CO ratio = 1.0, GHSV = 30,000 hr⁻¹)
Increasing inlet temperatures resulted in decreasing CO conversion and selectivity on the 4% $\rho$ metal foams. As the inlet temperature increases, CO starts to desorb from the Pt surface [7, 20]. The desorption temperature for CO on Pt is about 120-160°C [7, 13]. Therefore, CO conversion decreases at higher temperatures. Since $O_2$ conversion was still about 100% (not shown) at higher temperatures, the decrease in CO conversion was followed by the decrease in CO selectivity.

3.4.2 Catalyst Pretreatment

The low CO conversion exhibited on the 12% $\rho$ foams at 100°C inlet temperature led to a pretreatment study. The pretreatment procedure was comprised of an oxidation and a reduction step. The oxidation step consisted of a 10% $O_2$-balance $N_2$ gas flow at 230°C for 2 hours to purge and oxidize the catalyst surface. Next, the reduction step consisted of a 15% $H_2$-balance $N_2$ gas flow at 230°C for 2 hours to reduce the catalyst surface. No reactor temperature rise was observed during either pretreatment step.

A retest of the 20 ppi, 12% $\rho$ metal foam after pretreatment revealed a much higher CO conversion than without pretreatment. At 100°C inlet temperature, CO conversion increased from 15% to 84%. At 170°C inlet temperature, the activity increase was less, from 62% to 67%. Overall, the CO selectivity is higher for the pretreated catalyst. Figure 3.6 summarizes the pretreatment effect on the 20 ppi, 12% $\rho$ metal foam. This activity increase is permanent; a repeat experiment of the 20 ppi, 12% $\rho$ metal foam produced similar results to its first pretreatment test.
Figure 3.6: Effect of pretreatment on (a) CO conversion and (b) CO selectivity as a function of inlet temperature for the 20 ppi, 12% \( \rho \) metal foam (5 wt% Pt / 0.5 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\) catalyst, 1% CO inlet concentration, O\(_2\)/CO ratio = 1.0, GHSV = 30,000 hr\(^{-1}\))
To see if similar results could be achieved on the catalysts with higher initial activity, the same pretreatment procedure was applied to the 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 400 cpsi ceramic monolith studied in section 3.3.2. No significant difference in CO conversion and selectivity was observed. The ceramic monolith was taken out of the reactor, exposed to air, and replaced in the reactor, but still no effect was seen. Figure C.1 and Table C.1 in Appendix C summarize these results.

These data indicated that the pretreatment activated the 20 ppi, 12% ρ metal foam at low inlet temperatures, but did not affect the catalysts with high initial activity. One explanation is that the 12% ρ metal foams were not calcined properly. This could have lead to the low initial activity seen at 100°C inlet temperature. Further characterization studies on the Pt/Fe state and the Pt/Fe distribution on the catalyst surface are needed to understand the differences in CO conversion at low inlet temperatures of these supported catalysts.

3.5 Metal Monolith and Ceramic Foam Results and Discussion

5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ catalysts were also washcoated on a 400 cpsi equivalent corrugated metal monolith and a 20 ppi, 11% ρ ceramic foam. Tests were carried out under these conditions: 80°C and 150°C inlet temperatures, 15,000-45,000 hr⁻¹ GHSV, 1.0% CO inlet concentration, and 0.5 and 1.0 O₂/CO ratios. The ceramic foam had a 2.54 cm ID and a 5.08 cm length. The metal monolith had a 2.54 cm ID and a 3.81 cm (1.5”) length. Similarly to the metal foam and ceramic monolith, a washcoat loading of 0.098
g/cm$^3$ was used. The results are graphed in Figure 3.7, in addition to a 40 ppi, 4% $\rho$ metal foam for comparison.

At 80°C inlet temperature, the CO conversion and selectivity were higher for the metal monolith than the ceramic foam but lower than the metal foam. At 150°C inlet temperature, the metal monolith, ceramic foam, and metal foam had similar CO conversions and selectivities. There is no obvious reason why the metal foam is superior to the ceramic foam and metal monolith at 80°C. At the lower inlet temperature, the ceramic foam and metal monolith also might have been affected by an improper calcination.

The data described above, in addition to that for a 400 cpsi ceramic monolith, is shown in Table C.2 in Appendix C. At 150°C, the ceramic monolith had the highest CO conversion and selectivity compared to the metal foam, ceramic foam, and metal monolith. The metal foam and ceramic monolith used in this comparison are not the same pieces of catalyst studied in sections 3.4.1 and 3.3.2, respectively. They are “newer” pieces of 5 wt% Pt / 0.5 wt% Fe / $\gamma$-Al$_2$O$_3$ catalyst with the same nominal washcoat loading of 0.098 g/cm$^3$. More detail on this topic will be presented in chapter 4, section 4.3.3.
Figure 3.7: 400 cpsl equivalent metal monolith, 20 ppi, 11% ρ ceramic foam, and 40 ppi, 4% ρ “newer” metal foam comparison of (a) CO conversion and (b) CO selectivity as a function of inlet temperature (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 0.098 g/cm³ washcoat loading, 1% CO inlet concentration, O₂/CO ratio = 0.5, GHSV=30,000 hr⁻¹)
3.6 References


CHAPTER 4 PROX CATALYST SUPPORT COMPARISON

In chapter 3, the preferential oxidation (PROX) reaction was studied for several structured supports, with a focus on varying Fe concentrations and inlet temperatures. In chapter 4, the effects of the reverse water-gas-shift reaction and transport resistances on the PROX reaction were studied. Additionally, a comparison of the ceramic monolith and metal foam was conducted for the effects of inlet temperature, O₂/CO ratio, and transient responses.

4.1 Significance of the Reverse Water-Gas-Shift Reaction

The decrease in CO conversion at higher temperatures seen in chapter 3 suggested CO formation by the reverse water-gas-shift (r-WGS) reaction. Experiments with no CO in the inlet gas stream (shutting off the CO inlet line) were carried out to determine the adiabatic temperature rise (ΔT_{ad}) from H₂ oxidation for these reactions. The theoretical ΔT_{ad} was calculated using equation E7 in chapter 3.

The PROX reactor inlet gas stream was modeled after the effluent stream exiting a WGS reactor. Using typical gas stream compositions (i.e. 40-75% H₂, 15-20% CO₂, ~10% H₂O, 0-35% N₂, and 0.5-1.0% CO), the r-WGS reaction could severely limit CO conversion [1-3]. The significance of the r-WGS reaction in PROX processes is well studied [1-6]. Limitations caused by the r-WGS reaction can be significant at higher
temperatures (i.e. > 150°C), where the oxidation catalyst is moderately active and the 
r-WGS equilibrium favors CO formation.

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad (\Delta H_{\text{rxn,298K}} = +41.2 \text{ kJ/mol}) \quad \text{R3}
\]

Carbon monoxide was removed from the inlet stream to test the catalysts’ activity for the 
r-WGS reaction. Under this condition, any CO detected in the outlet stream could be 
attributed to the r-WGS reaction (reaction R3). A r-WGS equilibrium curve was 
computed by a theoretical model with the following five assumptions:

1) No CO was in the inlet gas stream
2) Hydrogen oxidation consumed all of the O\(_2\)
3) The r-WGS reaction reached equilibrium at the outlet temperature
4) The ideal gas law (PV=nRT) was valid
5) The C\(_p\)’s and \(\Delta H_{\text{rxn}}\) were constant over a given range of temperatures

The r-WGS equilibrium, shown as the solid green line in Figure 4.1a, could limit the 
minimum outlet CO concentration exiting the PROX reactor under these conditions. 
Figure 4.1a shows the outlet CO concentration as a function of the measured reactor 
outlet temperature for the 5 wt% Pt / 0 & 0.05 wt% Fe / γ-Al\(_2\)O\(_3\) ceramic straight-channel 
monoliths at different O\(_2\) inlet concentrations and/or inlet temperatures. The 5 wt% Pt / 
0.5 & 1.0 wt% Fe / γ-Al\(_2\)O\(_3\) ceramic monolith data was not graphed, but exhibited a 
similar behavior.
Figure 4.1: CO formed by the r-WGS reaction on 5 wt% Pt / 0-1 wt% Fe / γ-Al$_2$O$_3$ ceramic straight-channel monoliths as a function of (a) the measured outlet temperature and (b) the adiabatic reaction outlet temperature (no CO in the feed, varying O$_2$ concentration and/or inlet temperature, GHSV=30,000 hr$^{-1}$)
The two catalysts shown in Figure 4.1a were active WGS catalysts because they approached, and in some cases exceeded, the r-WGS equilibrium. No correlation between the measured outlet temperature and the approach to the r-WGS equilibrium could be determined from this graph. The second and fourth outlet CO concentration points were above the predicted r-WGS equilibrium curve, while first and third data points were below, causing a decrease in outlet CO concentration from the second to third point albeit the increased outlet temperature.

An explanation for this anomaly is transport limitations in the support, causing a temperature gradient between the catalyst surface and the bulk gas. The CO and H$_2$ oxidation reactions are very exothermic ($\Delta H^\circ_{\text{rxn},298K} = -283$ and -242 kJ/mol, respectively); if the heat transfer coefficient $h_i$ between the catalyst surface and the bulk gas is small, then the catalyst surface temperature will exceed the measured bulk gas temperature, especially at high H$_2$ concentrations.

When the catalyst surface temperature is higher than the measured bulk gas temperature, the r-WGS reaction can equilibrate at a higher temperature than the measured bulk outlet temperature and increase the outlet CO concentration. This shift in the equilibrium is one explanation of why several outlet CO concentrations in Figure 4.1a are above the r-WGS equilibrium curve. Moreover, the location of the “hot spot” in the support affects the extent of the equilibrium shift. If the “hot spot” is located towards the inlet region of the
catalyst, then the r-WGS reaction can re-equilibrate to a lower temperature in the latter portion of the catalyst before leaving the reactor. If the “hot spot” is located towards the outlet region of the catalyst, then the r-WGS reaction may not re-equilibrate to a lower outlet CO concentration. An illustration of a “hot spot” located towards the inlet region is shown in Figure 4.2.

Figure 4.2: Illustration of the r-WGS reaction re-equilibrating at a lower temperature when the “hot spot” is located towards the inlet region.

Figure 4.1b is a re-plot of the data in Figure 4.1a with two differences: 1) the abscissa is the adiabatic reaction temperature instead of the measured outlet temperature, and 2) all the 5 wt% Pt / varying wt% Fe data is graphed. The adiabatic reaction temperature was
calculated assuming 100% O\textsubscript{2} conversion. Every data point fell below the r-WGS equilibrium curve. In addition, the outlet CO concentration for each catalyst increased monotonically with the adiabatic outlet temperature. No obvious relationship between the Fe weight loading and the outlet CO concentration formed by the r-WGS reaction was discerned from Figure 4.1b. Even without the presence of Fe, the unpromoted Pt catalyst was active WGS catalyst because it approached the r-WGS equilibrium [2, 5, 7].

![Graph showing CO concentration vs outlet temperature](image)

Figure 4.3: CO formed by the r-WGS reaction on the 5 wt% Pt / 0.5 wt% Fe / γ-Al\textsubscript{2}O\textsubscript{3} ceramic straight-channel monolith (no CO in the feed, 0-1% O\textsubscript{2} inlet concentration, 170°C inlet temperature, GHSV=30,000 hr\textsuperscript{-1})

Based on Figure 4.1, a graph of outlet CO concentration versus measured outlet temperature for the 5 wt% Pt / 0.5 wt% Fe / γ-Al\textsubscript{2}O\textsubscript{3} ceramic monolith is shown in Figure 4.3. At T\textsubscript{in}=170°C, the data points in Figure 4.3 from left to right correlated to 0%, 0.1%,...
0.5%, and 1.0% O$_2$ inlet concentrations. Only 158 ppm CO was formed by the r-WGS reaction with no O$_2$ in the inlet feed, and no temperature rise was observed in the reactor. As the inlet O$_2$ concentration increased, it was consumed by H$_2$ oxidation. This caused the measured outlet temperature to increase, and shifted the r-WGS equilibrium towards higher CO concentrations. The outlet CO concentration was 0.44% at a 308°C measured outlet temperature, which reached 65% of the predicted equilibrium model.

For the 5 wt% Pt / 0.5 wt% Fe ceramic monolith, the r-WGS reaction constituted a potential barrier to achieving ppm level outlet CO concentrations. The reactor must be maintained at low temperatures (< 150°C) to limit the significance of this reaction in a PROX system. One way to achieve this goal is running the reactor isothermally instead of adiabatically to sustain low outlet temperatures and to suppress the r-WGS reaction.

Figure 4.4 shows the 5 wt% Pt / 0-1 wt% Fe monoliths’ activity for the r-WGS reaction at 170°C inlet temperature, gas hourly space velocity (GHSV) of 30,000 hr$^{-1}$, 0.1-1.0% O$_2$ inlet concentration, and no CO in the inlet gas feed. Similarly to Figure 4.1, “hot spots” on the catalyst surface was an explanation for the higher outlet CO concentrations exceeding the r-WGS equilibrium. The 0.5 wt% Fe ceramic monolith was furthest away from the r-WGS equilibrium curve, but no other relationships between the Fe weight loading and the outlet CO concentration were discerned from Figure 4.4.
4.2 Metal Foam / Ceramic Monolith Comparison

4.2.1 Reverse Water-Gas-Shift Activity

Based on the results from section 4.1, in addition to the catalyst performance study in section 3.3.2 of chapter 3, the 5 wt% Pt / 0.5 wt% Fe ceramic straight-channel monolith was chosen for a comparison study to the metal foams. Figure 4.5 shows the affinity towards the r-WGS reaction as a function of the adiabatic outlet temperature for the 40 ppi, 4\% ρ metal foam (circle) and the 400 cpsi ceramic monolith (square). The inlet feed contained 0.1-1.0\% O_2 concentrations and no CO, and inlet temperature varied between 100-170°C. The metal foam was further away from the r-WGS equilibrium than the
ceramic monolith at all adiabatic outlet temperatures. Therefore, the ceramic monolith was a more active WGS catalyst than the metal foam.

![Graph showing CO formed by r-WGS reaction on ceramic monolith and metal foam](image)

**Figure 4.5:** CO formed by the r-WGS reaction on the 40 ppi, 4% metal foam and 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, no CO in the feed, 0.1-1.0% O₂ inlet concentration, 100-170°C inlet temperatures, GHSV = 30,000 hr⁻¹)

The difference in WGS activity between the ceramic monolith and metal foam can be explained by the higher thermal conductivity and better radial and axial mixing in metal foams. The thermal conductivities of a cordierite ceramic monolith and a FeCrAl alloy are 2-3 and 15-25 W/m°K, respectively, at temperatures of 25-1000°C [8]. Higher thermal conductivities improve heat transfer on the support and minimize the possibility of “hot-spots” on the catalyst surface. Better mixing promotes heat transfer by distributing heat more uniformly from the catalyst surface to the bulk gas.
4.2.2  PROX Reaction Comparison (No Pretreatment)

The 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ catalyst composition (0.098 g/cm³ washcoat loading) was used for a PROX comparison study of the 400 cpsi ceramic straight-channel monolith and 40 ppi, 4% ρ metal foam. Both supports had a 2.54 cm ID and 5.08 cm length and the following operating conditions were used: 1.0% CO inlet concentration, O₂/CO ratio = 1.0, and GHSV = 30,000 hr⁻¹. The results are summarized in Figure 4.6.

Overall, CO conversion and selectivity were slightly higher on the metal foam. At 100°C inlet temperature, the metal foam achieved 83% CO conversion and 41% CO selectivity compared to 79% and 40%, respectively, on the ceramic monolith. At 170°C inlet temperature, CO conversion and selectivity decreased for both supports, but the metal foam still performed better than the ceramic monolith – 70% vs. 53% CO conversion, and 34% vs. 27% CO selectivity. These results are consistent with the fact that the WGS activity is worse on the ceramic monolith than on the metal foam, as seen in Figure 4.5.

Since the O₂/CO ratio was 1.0 (twice stoichiometric), CO selectivity was below 50% because O₂ conversion reached 90-100% under all conditions. The CO conversion and selectivity decreased when the inlet temperature increased from 100°C to 170°C because H₂ oxidation and the r-WGS reaction were preferred at higher temperatures. The data indicates that metal foams are comparable to ceramic monoliths of the same metal loading for the PROX reaction.
Figure 4.6: Comparison of CO (a) conversion and (b) selectivity on a 40 ppi, 4% ρ metal foam and a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1.0% CO inlet concentration, O₂/CO ratio = 1.0, GHSV=30,000 hr⁻¹, varying inlet temperatures)
4.2.3 Transient study

A transient study was carried out to test CO oxidation as a function of time on the 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 400 cpsι ceramic straight-channel monolith and on the 20 ppi, 12% ρ metal foam after pretreatment. The study was carried out by shutting off the O₂ inlet gas until the reactor temperature rise was zero. Prior to shutting off the O₂, the inlet feed simulated typical gas compositions leaving the WGS reactor, in addition to 1.0% O₂ concentration. The O₂ inlet gas was turned on to an O₂/CO ratio of 1.0 at time zero.

Figure 4.7 shows the transient CO concentration and measured outlet temperature from 0 to 15 minutes. Figure D.1a in Appendix D is an enlarged graph of Figure 4.7a, with a time abscissa of 0 to 120 seconds. Both supports exhibited an initial decrease to below the steady-state outlet CO concentration before increasing to steady-state at about 400 seconds. The response time for CO oxidation from 0 to 20 seconds on the metal foam is faster than the ceramic monolith, as seen in the enlarged graph of Figure 4.7a.

The measured outlet temperature on the metal foam was higher than the ceramic monolith. This data indicates that the metal foam oxidizes more readily than the ceramic monolith because the outlet temperature rises more quickly on the metal foam. Unfortunately, since the steady state outlet CO concentration for the metal foam is higher than the ceramic monolith, this means the metal foam oxidizes more H₂ than the ceramic monolith to reach the higher outlet temperature.
Figure 4.7: Transient effects on the (a) outlet temperature and (b) outlet CO concentration for the 400 cpsi ceramic straight-channel monolith and 20 ppi, 12% \( \rho \) metal foam after pretreatment (5 wt% Pt / 0.5 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\), 1% CO inlet concentration, O\(_2\)/CO ratio = 1.0, inlet temperature = 109°C, GHSV=30,000 hr\(^{-1}\))
More data on the transient outlet O\textsubscript{2} concentration at an O\textsubscript{2}/CO ratio of 1.0 and the outlet CO concentration at an O\textsubscript{2}/CO ratio of 0.5 as a function of time can be found in Figures D.1b and D.2 in Appendix D.

4.2.4 \textit{O\textsubscript{2}/CO ratio study}

The effect of O\textsubscript{2}/CO ratio on CO conversion and selectivity was studied at a 1\% CO inlet concentration. Figure 4.8 shows this effect on the 5 wt\% Pt / 0.5 wt\% Fe / $\gamma$-Al\textsubscript{2}O\textsubscript{3} 40 ppi, 4\% $\rho$ metal foam and 400 cpsi ceramic monolith at $T_{\text{in}}$=80\textdegree{}C and 30,000 hr\textsuperscript{-1} GHSV. As expected, CO conversion increased at higher O\textsubscript{2} inlet concentrations. Moreover, as the O\textsubscript{2}/CO ratio increased, CO selectivity decreased for both supports because more H\textsubscript{2} oxidized at higher O\textsubscript{2}/CO ratios, especially above the stoichiometric value.

Figure D.3 in Appendix D shows a performance comparison between the same metal foam and ceramic monolith graphed in Figure 4.8. Overall the two supports were comparable, except at an O\textsubscript{2}/CO ratio of 1.0 when CO conversion for the ceramic monolith was substantially higher than the metal foam. It is unclear what caused the higher CO and O\textsubscript{2} conversions on the ceramic monolith compared to the metal foam at the above stoichiometric O\textsubscript{2}/CO ratio. This data may be an anomaly, and further experiments are needed to confirm the results.
Figure 4.8: Effect of O$_2$/CO ratio on a (a) 40 ppi, 4% $\rho$ metal foam and (b) 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / $\gamma$-Al$_2$O$_3$, 1% CO inlet concentration, 0.25-1.0 O$_2$/CO ratio, 80°C inlet temperature, GHSV=30,000 hr$^{-1}$)
The 40 ppi, 4% ρ metal foam and the 400 cpsi ceramic monolith used here are not the same pieces used in chapter 3, sections 3.3.2 and 3.4.1, but “newer” pieces of synthesized catalyst. The “newer” pieces of catalyst are used in the metal monolith and ceramic foam study in chapter 3, section 3.5. Despite a conscious effort to create identical catalysts, there are subtle differences between the “newer” catalyst pieces studied here and the “older” catalyst pieces studied in chapter 3. More detail on this topic will be presented in section 4.3.3.

4.3 Transport Effects Results and Discussion

A comparison of the 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 40 ppi, 4% ρ metal foam and the 400 cpsi ceramic straight-channel monolith as a function of GHSV and linear velocity revealed comparable activity and selectivity on both supports. These results are depicted in Figure 4.9.

The CO conversion, selectivity, and O₂ conversion for the metal foam and ceramic monolith followed the same trends of decreasing CO and O₂ conversions and increasing CO selectivity at increased GHSV. The outlet temperature also decreases because ΔT_ad declines with decreasing CO and O₂ conversions for exothermic reactions and under adiabatic conditions. Shorter contact time increases CO selectivity because CO oxidation is relatively faster than H₂ oxidation and occurs more readily under certain conditions [4, 9]. Conversely, CO and O₂ conversions decrease at higher GHSV because of shorter contact time with the catalyst.
Figure 4.9: GHSV and linear velocity comparison between the 40 ppi, 4% ρ metal foam and 400 cpsi ceramic monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 10,000-45,000 hr⁻¹ GHSV)

Figure 4.10 is a re-plot of Figure 4.9 with only the 40 ppi, 4% ρ metal foam data. Even though CO conversion and selectivity, and O₂ conversion followed the expected trends, the CO conversion line was flatter than expected. The CO conversion could be estimated by making two assumptions:

1) The CO oxidation reaction was first-order in CO
2) The reactor operated isothermally, allowing the use of a constant reaction rate constant $k_{CO}$
The first-order kinetic calculation for CO consumption is explained in Figure D.4 in Appendix D. Using these assumptions and 45,000 hr\(^{-1}\) GHSV as a basis for the reaction rate constant \(k_{CO}\), CO conversion at 10,000 hr\(^{-1}\) was predicted to be 60-70%, substantially higher than the measured value of 52% seen in Figure 4.10. Similar calculations on the ceramic monolith, shown in Figure D.5 in Appendix D, predicted 82% CO conversion at 10,000 hr\(^{-1}\) instead of a 47% measured value. Moreover, \(\Delta T_{ad}\) was greater at 10,000 hr\(^{-1}\) than 45,000 hr\(^{-1}\) because more O\(_2\) was consumed, increasing the reactor temperature and \(k_{CO}\) at lower GHSV. Therefore the CO conversion calculated at 10,000 hr\(^{-1}\), assuming isothermal operation, served as a lower bound on the actual conversion because the reactor was run close to adiabatic.

![Figure 4.10: Effects of GHSV & linear velocity on the 40 ppi, 4% \(\rho\) metal foam (5 wt% Pt / 0.5 wt% Fe / \(\gamma\)-Al\(_2\)O\(_3\), 1% CO inlet concentration, O\(_2\)/CO ratio = 0.5, 80°C inlet temperature, 10,000-45,000 hr\(^{-1}\) GHSV)](image)
Oxidation of CO occurs via the Langmuir-Hinshelwood reaction mechanism, and kinetic studies of CO oxidation on unpromoted Pt catalysts at similar operating conditions show the order of CO to be less than one [4, 10-14]. The first-order assumption was used above because the use of a zero or negative reaction order would result in 100% CO conversion at 10,000 hr\(^{-1}\) GHSV. This result solidified the first-order reaction CO conversion prediction as a lower bound on the actual conversion. Additionally, the first-order behavior assumption may be more consistent with the Pt/Fe catalyst than the negative-order behavior seen on the unpromoted Pt catalyst. Liu et al. [9] suggested a dual-site mechanism for Fe oxide promoted Pt catalysts. For Pt/Fe catalysts, CO saturation of the Pt surface would not lead to negative orders in CO because there would be no self-poisoning effect of the CO oxidation reaction by CO adsorption [14]. Dual-site mechanisms of CO and O\(_2\) adsorbed on Pt or Fe yield a rate law shown in equation E8 [15], where \(r_{CO}\) is the reaction rate expression for CO oxidation, \(K_{CO} = k_{f,CO}/k_{r,CO}\) or the kinetic rate constant for the forward reaction \(k_{f,CO}\) divided by that of the reverse reaction \(k_{r,CO}\), and \(C_{CO-Pt}\), \(C_{O2-Fe}\), and \(C_{CO2-Pt}\) are intermediate CO, O\(_2\), and CO\(_2\) concentrations on the Pt or Fe surface.

\[
r_{CO} = k_{f,CO} \left( \frac{C_{CO-Pt} C_{O2-Fe}}{C_{CO2-Pt}} \frac{C_{CO2-Pt}}{K_{CO}} \right)
\]

E8

The relative insensitivity of CO conversion as a function of GHSV for the metal foam and ceramic monolith in Figure 4.9 could be the result of the r-WGS reaction, discussed
in section 4.1. As mentioned above, the outlet temperature increased at lowered GHSV. Therefore, CO production by the r-WGS reaction could have played an important role in limiting CO conversion at lower GHSV.

However, transport effects occurring in the reactor provide a complementary explanation to the insensitivity of CO conversion as a function of GHSV. If CO or O\textsubscript{2} mass transfer from the bulk inlet gas to the catalyst surface limits the CO oxidation rate, then the linear velocity through the reactor will affect CO conversion. Heat and mass transfer coefficients are directly proportional to linear velocity.

Linear velocity and GHSV were coupled in Figure 4.9 and Figure 4.10. To increase the GHSV, the inlet volumetric flow rate through the 5.08 cm catalysts was increased proportionately; for example, to increase the GHSV from 10,000 hr\textsuperscript{-1} to 30,000 hr\textsuperscript{-1} the inlet volumetric flow rate was increased by a factor of 3, so the inlet linear velocity increased by the same factor, as shown in equations E5 and E6 in chapter 3 and reproduced below. Higher GHSV reduced the contact time in the reactor, but higher linear velocity increased the heat and mass transfer coefficients. These two competitive effects offset each other and may account for the “flatness” of the CO conversion curve as a function of GHSV. A schematic of heat and mass transport resistances under PROX conditions is shown in Figure 4.11. The H\textsubscript{2} concentration stayed relatively flat because of its high concentration compared to CO and O\textsubscript{2}. 
In order to separate the effects of GHSV and linear velocity ($\bar{v}_{inlet}$), the reactor length ($V$) was increased from 5.08 cm to 15.2 cm by placing a series of three 5.08 cm catalysts together and varying the inlet gas flow rate ($\dot{V}_{inlet}$). Modifying the reactor length allowed...
the GHSV to be held constant for different linear velocities, and vice versa. The individual performances of the three 5.08 cm catalysts which comprised the 15.2 cm catalysts were also analyzed in section 4.3.3.

### 4.3.1 Linear Velocity (Constant GHSV) Study

Experimental constraints limited the linear velocity study on the 40 ppi, 4% ρ metal foams to GHSV of 10,000 and 15,000 hr\(^{-1}\). At these GHSV, the 15.2 cm catalyst had linear velocities of 42.7 and 64.0 cm/sec, respectively, three times higher than 14.2 and 21.3 cm/sec, respectively, for the 5.08 cm piece. The results are shown in Figure 4.12.

![Figure 4.12: Effect of linear velocity at a constant GHSV on a 40 ppi, 4% ρ metal foam (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 10,000 and 15,000 hr\(^{-1}\) GHSV)](image)
At a fixed GHSV, the 15.2 cm catalyst had a higher CO conversion and selectivity, and O\textsubscript{2} conversion compared to the lower linear velocity 5.08 cm catalyst. These results are consistent with the hypothesis of significant transport resistance between the bulk inlet gas and the catalyst surface. The CO and O\textsubscript{2} conversion increased with higher linear velocity because the heat and mass transfer coefficients increased. The CO selectivity is affected because H\textsubscript{2} oxidation is slow compared to CO oxidation [4, 9], and therefore not as sensitive to transport resistances. Thus, CO selectivity was lowest at the lowest linear velocity.

A similar analysis was done on the 5 wt% Pt / 0.5 wt% Fe / γ-Al\textsubscript{2}O\textsubscript{3} 400 cpsi ceramic straight-channel monoliths. These GHSV and linear velocities corresponded to Reynolds numbers between 10-40 based on an open channel (cell) hydraulic diameter of 0.11 cm and on inlet gas conditions [16]. The results, shown in Figure D.6 in Appendix D, were similar to the 40 ppi, 4% \textrho metal foams.

4.3.2 Space Velocity (Constant Linear Velocity) Study

Data at 5,000 hr\textsuperscript{-1} GHSV were added to the data from Figure 4.10 and Figure 4.12 to illustrate the effect of GHSV at constant linear velocity. Figure 4.13 shows these results for the 40 ppi, 4% \textrho metal foams. The linear velocity for a 15.2 cm catalyst operating at a given GHSV was the same as a 5.08 cm catalyst operating at three times the GHSV. For example, a 15.2 cm catalyst running at 5,000 hr\textsuperscript{-1} GHSV had the same linear velocity as a 5.08 cm catalyst running at 15,000 hr\textsuperscript{-1}. Similarly, the data points at 10,000 and
30,000 hr\(^{-1}\), and 15,000 and 45,000 hr\(^{-1}\), on a 15.2 cm and 5.08 cm catalyst, respectively, had the same linear velocity.

As expected, CO conversion (solid lines) at constant linear velocity was much more sensitive to GHSV than shown in Figure 4.9 and Figure 4.10. At 42.7 cm/sec linear velocity, CO conversion dropped from 69% to 35% when GHSV increased from 10,000 hr\(^{-1}\) to 30,000 hr\(^{-1}\), respectively. Using the GHSV at 10,000 hr\(^{-1}\) for the \(k_{CO}\) constant and the first order assumption, the predicted CO conversion at 30,000 hr\(^{-1}\) is 32%. Therefore, the first-order in CO assumption for the CO oxidation reaction provides a reasonable estimate for the CO conversion when linear velocity is held constant.
The CO selectivity (dashed lines) behavior also depended on linear velocity. At the highest linear velocity (64.0 cm/sec), CO selectivity increased with increasing GHSV because of shorter residence time and CO oxidation was relatively faster than H₂ oxidation [4, 9], as discussed in section 4.3. At the intermediate linear velocity (42.7 cm/sec), CO selectivity did not depend appreciably on GHSV. At the lowest linear velocity (21.3 cm/sec), CO selectivity decreased significantly with higher GHSV.

At the lowest linear velocity (21.3 cm/sec), the CO conversion and O₂ conversion (not shown) increased from 45% to 73% and 84% to 100%, respectively, when the GHSV was decreased from 15,000 hr⁻¹ to 5,000 hr⁻¹. Since the reactor was essentially adiabatic, at 5,000 hr⁻¹ GHSV the outlet temperature was higher and CO and O₂ concentrations were lower than at 15,000 hr⁻¹. In general, CO selectivity will decrease with increasing reactor temperature and with decreasing reactor CO concentrations, as observed by Korotkikh and Farrauto [1]. At lower linear velocities, heat and mass transfer coefficients are low, which can cause a temperature gradient between the catalyst surface and the measured outlet gas stream. Moreover, in a H₂-rich gas mixture, the catalyst surface temperature can exceed the adiabatic outlet temperature because H₂ is not hindered considerably by mass transfer at high concentrations, as seen in Figure 4.11. Therefore, the ε-WGS reaction can equilibrate at a higher temperature than the measured outlet temperature, which will lower the CO conversion and selectivity.
At a low linear velocity (21 cm/sec), Figure 4.14 shows that the CO conversion was 45%, and O$_2$ conversion was 84% at 15,000 hr$^{-1}$ GHSV. Decreasing the GHSV to 5,000 hr$^{-1}$ while keeping the linear velocity at 21 cm/sec required tripling the catalyst length at the same inlet gas flow rate. The catalyst performance at 15,000 hr$^{-1}$ reflected the first (inlet) third of the catalyst at 5,000 hr$^{-1}$. The O$_2$ conversion increased from 84% to 100% when GHSV decreased from 15,000 to 5,000 hr$^{-1}$. However, at the 5,000 hr$^{-1}$ GHSV, 84% of the O$_2$ reacted in the first (inlet) third of the catalyst, as shown in Figure 4.14. Since most of the O$_2$ conversion and heat evolution occurred in the first third of the catalyst, this
catalyst section had the severest heat and mass transport limitations. In the downstream two thirds of catalyst length at the 5,000 hr\(^{-1}\) GHSV, the oxidation rate was much slower and the transport resistances were less severe. Heat dissipation could occur, and the catalyst surface could re-equilibrate to a lower temperature in the downstream two thirds of catalyst length. Thus the extent of the ε-WGS reaction would be less severe in this downstream section than in the upstream first third of the catalyst, and CO selectivity would increase as the GHSV was reduced from 15,000 hr\(^{-1}\) to 5,000 hr\(^{-1}\), as observed.

At the 21 cm/sec linear velocity under stoichiometric conditions, the difference in CO conversion from 15,000 hr\(^{-1}\) to 5,000 hr\(^{-1}\) (ΔX\(_{CO}\)) is 28%, while the difference in O\(_2\) conversion (ΔX\(_{O2}\)) is only 16%. It seems that more CO is reacted than O\(_2\) is consumed when the GHSV is decreased to 5,000 hr\(^{-1}\). One explanation is that H\(_2\) oxidation decreases, which allows a greater ΔX\(_{CO}\) compared to ΔX\(_{O2}\). This decrease in H\(_2\) oxidation leads to a higher CO selectivity at 5,000 hr\(^{-1}\) GHSV, which is observed. Another explanation is that at a GHSV of 15,000 hr\(^{-1}\), the amount of CO oxidized is higher than reported in the data, but because of heat transfer resistance, the ε-WGS reaction produced CO and H\(_2\)O. Hence, the outlet CO concentration is higher and the calculated CO conversion is lower than the actual amount of CO oxidized.

At the high linear velocity (64.0 cm/sec), Figure 4.15 shows this phenomenon disappeared. The O\(_2\) conversion was only 33% at 45,000 hr\(^{-1}\) GHSV, so the heat evolution for the upstream first (inlet) third of catalyst was less than the 21 cm/sec case.
Moreover, heat and mass transfer coefficients are higher at higher linear velocities. Thus the original conclusion of higher CO selectivity at faster GHSV held. However, the data from Figure 4.13 and Figure 4.15 did not indicate whether transport effects were absent at 64 cm/sec linear velocity, only that they were less than the 21 cm/sec case.

Figure 4.15: Schematic drawing of Figure 4.13, linear velocity of 64.0 cm/sec (5 wt% Pt / 0.5 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\) 40 ppi, 4% \( \rho \) metal foam, 1% CO inlet concentration, \( \mathrm{O}_2/\mathrm{CO} \) ratio = 0.5, 80°C inlet temperature, 15,000 and 45,000 hr\(^{-1}\) GHSV)

The 5 wt% Pt / 0.5 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\) 400 cpsi ceramic monoliths produced similar results to the 40 ppi, 4% \( \rho \) metal foams. Figures D.7, D.8, and D.9 in Appendix D are analogous to the graphs shown in Figure 4.13, Figure 4.14, and Figure 4.15.
4.3.3 “Identical” Pieces Similarity Study

As noted in section 4.3, the 15.2 cm length reactor for the 40 ppi, 4% ρ metal foams and 400 cpsι ceramic monoliths consisted of three separate pieces of catalyst with a 5 wt% Pt / 0.5 wt% Fe metal loading washcoated on γ-Al₂O₃ (0.098 g/cm³ washcoat loading). The three pieces were made up of two “newer” pieces, placed at the first (inlet) and second (middle) third of the 15.2 cm reactor, and one “older” piece placed at the end of the reactor. One of the “newer” pieces was used in the O₂/CO ratio study described in section 4.2.4 and the metal monolith and ceramic foam comparison in chapter 3, section 3.5. The “older” pieces were used in the experiments described in chapter 3, sections 3.3 and 3.4. The performance of the three separate pieces of catalyst is shown in Figure 4.16. The “older” metal foam catalyst was not tested at an O₂/CO ratio of 0.25.

The performance of the two “newer” pieces of metal foam catalyst is almost identical, but their CO conversion and selectivity are substantially lower than the original “older” piece. At an O₂/CO ratio of 0.5, CO conversions of the two “newer” pieces were 35% and 37%, while the original “older” piece exhibited 50% CO conversion. Similarly, the CO selectivities of the “newer” pieces were 33% and 32%, while the “older” piece exhibited 47% CO selectivity. The activity and selectivity numbers are shown in Table D.1 in Appendix D.
Figure 4.16: (a) CO conversion and (b) CO selectivity of the three separate 40 ppi, 4% ρ metal foams (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, 0.25-1.0 \( \text{O}_2/\text{CO} \) ratio, 150°C inlet temperature, GHSV=30,000 hr\(^{-1} \))
Nominally “identical” catalysts with similar metal loadings should exhibit comparable CO conversion and selectivity, but the data indicates otherwise. It is not known why the “identical” catalysts with similar metal loadings are so different. A possible explanation for this discrepancy is that although the catalysts have similar metal loadings, the amount of Pt and Fe acting as active sites for CO and O\textsubscript{2} adsorption is different.

The activity and selectivity of the two “newer” pieces of 400 cpsi ceramic monoliths were not the same. Overall, the performance of the “older” ceramic monolith piece was better than the two “newer” pieces. The data is shown in Table D.2 and Figure D.10 in Appendix D.
4.4 References


CHAPTER 5  CATALYST SUPPORT CHARACTERIZATION

Two catalyst characterization techniques were utilized to help explain the differences in the activity and selectivity seen in Chapters 3 and 4: CO pulse chemisorption and CO temperature programmed desorption (TPD). The size of the supports inhibited the use of other characterization techniques, since it was decided that the catalysts should not be destroyed at this time. Table 5.1 shows typical results obtainable for pulse chemisorption and TPD. In addition, the bulk elemental composition and surface area of one catalyst slurry from Environex and of powdered catalysts made at NCSU were done using Inductively Coupled Plasma (ICP) and Brunauer-Emmett-Teller (BET).

Table 5.1: Obtainable results from pulse chemisorption and TPD

<table>
<thead>
<tr>
<th>Data Interpretation Results</th>
<th>Pulse Chemisorption</th>
<th>TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of adsorbate adsorbed</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Metal dispersion</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Desorption temperature</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Average metal crystalline size</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Activation energy of desorption</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Kinetic rate constant of desorption</td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

5.1  Experimental Design

5.1.1  Equipment & Process Design

The process and equipment design for the characterization system was similar to the preferential oxidation (PROX) reaction system described in Chapter 3, sections 3.1.2 and 3.1.4. Pure N₂ was fed from the gas cylinder through the mass flow controller to control the inlet feed rate at 1.0-1.5 L/min. The inlet feed passed through the fluidized sand bath
and heating tapes until it reached the GC sampling valve, where CO could be pulsed into
the system prior to the reactor. The GC sampling valve was a Valco Instruments 6-port
manual switching valve, product # 6UWE with \( \frac{1}{8}'' \) connections, 400 psi and 225°C
maximum pressure and temperature rating, respectively. A 1 mL sample loop from
Valco was utilized in conjunction with the switching valve to pulse a known volume of
gas into the reactor. The gas stream passed through the reactor, back pressure regulator,
cooling system, rotameter, and finally the NDIR, where the outlet CO concentration was
detected. A schematic of the process design is found in Figure B.4 in Appendix B. More
detail on the procedure for running pulse chemisorption and TPD experiments are found
in their respective sections of 5.2.3 and 5.3.3.

5.1.2 Reactor Design

For the characterization experiments, the Swagelok threaded connections described in
Chapter 3, section 3.1.3 were replaced with four A-351 MSS 150-lbs A370 SC flanges
with 3.12 cm (1.25”) I.D. / 10.80 cm (4.25”) O.D.. Figure 5.1 shows a schematic of this
reactor design. Figures B.2 and B.3 in Appendix B describe the reactor, flange, and
gasket dimensions for this reactor.

Two McMaster-Carr 3.12 cm (1.25”) I.D. / 6.67 cm (2.625”) O.D. pure graphite spiral-
wound gaskets and eight Grade L9 hex head cap screws (4.45 cm (1.75”) length, 1.27 cm
(0.5”) thread diameter, 1.91 cm (0.75”) head height, 20 threads per inch), nuts, washers,
and lock washers were used to seal the reactor.
Figure 5.1: Characterization reactor design schematic.
5.2 CO Pulse Chemisorption

5.2.1 Theory

Pulse chemisorption is used to determine the amount of adsorbate that adsorbs on the catalyst surface. This study utilized CO as the adsorbate gas. Pulse chemisorption is accomplished by sending pulses of CO from the switching valve to the reactor until all the catalyst sites are saturated. The amount of CO pulsed to the reactor is known through the sample loop size and the CO gas composition in the sample loop. The amount of CO adsorbed from each pulse is calculated by subtracting the molar amount of CO in the sample loop ($n_{CO,\text{loop}}$) from the molar amount of CO detected downstream of the reactor by the NDIR ($n_{CO,\text{NDIR}}$), defined in equation E9.

$$\text{CO uptake (per pulse)} = n_{CO,\text{loop}} - n_{CO,\text{NDIR}}$$  \hspace{1cm} \text{E9}

Pulse chemisorption goes through three phases, seen in Figure 5.2. In the first phase (pulses 0-1 in Figure 5.2), all of the CO pulsed into the reactor is adsorbed by the catalyst. No CO is detected downstream of the reactor. In the second phase (pulses 2-5 in Figure 5.2), the amount of CO detected by the NDIR after each pulse gradually rises. In the third phase (pulses 6-8 in Figure 5.2), CO has saturated the catalyst surface, and no more CO adsorbs on the catalyst. This final phase is represented by peaks of similar magnitude and area.
In general, \( \text{H}_2 \) is used as the adsorbate gas to study chemisorption on metals because \( \text{H}_2 \) adsorption occurs by dissociation into two H atoms with a 1:1 H:metal atom relationship. This confidence allows for consistent results [1]. The stoichiometry of CO adsorption on metals is variable because of the possibility of multiple adsorption geometries [2, 3]. However, since the desired PROX reaction involves CO, it was used as the chemisorption adsorbate gas.

### 5.2.2 Data Analysis

The amount of CO adsorbed and the metal dispersion can be calculated from pulse chemisorption results. To calculate the amount of CO adsorbed, \( n_{\text{CO,loop}} \) and \( n_{\text{CO,NDIR}} \) from equation E9 must be calculated. The value of \( n_{\text{CO,loop}} \) is obtained from equation E10, where \( P_{\text{loop}}, V_{\text{CO,loop}}, \) and \( T_{\text{loop}} \) are the pressure, CO volume, and temperature in the 1 mL sample loop, respectively, and R is the universal gas law constant, 8.314 J/(mol°K). The value of \( V_{\text{CO,loop}} \) is obtained from the certificate of analysis for the CO in \( \text{N}_2 \) gas cylinder, supplied by National Welders. To calculate \( n_{\text{CO,NDIR}} \), a conversion from ppm to molar values is needed because the NDIR reads ppm CO values. Equation E11 defines
the required relationship. In equation E11, $\dot{N}_{\text{total}}$ is the molar total gas flow rate entering the NDIR defined by the mass flow controllers under standard conditions, neglecting the additional gas from the sample loop, and $\int_0^\infty (\text{ppm CO}) \, dt$ is the integrated area under the ppm versus time curve.

The integration of the CO concentration (ppm) versus time curve was done initially using the trapezoidal rule in Microsoft Excel. After the experiment was finished, the spline function in Matlab was used with a step size of 0.001 seconds for higher accuracy. The Matlab program has the ability to input the time interval for the integration, which allows for a more accurate and defined integration of the CO pulse curve as a function of time. Appendix F contains the Matlab code for the integration under the curve. An example of a CO pulse on an uncatalyzed, unwashcoated “blank” metal foam is shown in Figure E.1 in Appendix E.

$$\begin{align*}
n_{\text{CO,loop}} &= \frac{V_{\text{CO,loop}} * R * T_{\text{loop}}}{P_{\text{loop}}} \quad \text{E10} \\
N_{\text{CONDIR}} &= \int_0^\infty (\text{ppm CO})(\dot{N}_{\text{total}}) \, dt = \dot{N}_{\text{total}} \int_0^\infty (\text{ppm CO}) \, dt \\nE11 \\
n_{\text{metalactive}} &= \frac{n_{\text{CO, saturate}} * N_A \left( \frac{\text{CO atoms}}{\text{mol}} \right)}{N_A \left( \frac{\text{metal atoms}}{\text{mol}} \right)} \quad \text{E12}
\end{align*}$$

Sample loop pulses are sent to the reactor until the catalyst surface is saturated with CO (third phase in Figure 5.2 in section 5.2.1). The value of $n_{\text{CO,NDIR}}$ is the same as $n_{\text{CO,loop}}$.
for subsequent pulses and equation E9 equals zero. The total CO adsorbed to saturate the catalyst \(n_{CO,saturate}\) is calculated from the summation of equation E9 for all pulses.

Assuming a 1:1 relationship for CO:Pt and CO:Fe adsorption, the molar value of active metal sites \(n_{metal,active}\) is calculated from equation E12, where \(N_{AV}\) is Avogadro’s number, \(6.023 \times 10^{23}\) atoms/mol. The CO adsorbed on Pt can have many different configurations, from linear (1:1) to bridged (1:2) to bidentate (2:1) bonding [2], but the predominant bond relationship is the linear bond [4-6].

The role of Fe is not completely understood in the characterization calculations. Fe, like Pt, does not always have a linear bond relationship. The CO can adsorb on Fe in a linear, bridged, bidentate [7], or four-fold (1:4) CO:Fe bond [7-9]. Also, CO can weakly chemisorb on Fe oxide and slowly desorb off the surface. Because the particular configuration is not known, the Fe weight loading is relatively low compared to Pt, and the bridged and four-fold configurations are unlikely because of low Fe loading, a 1:1 CO:Fe adsorption assumption acts as a lower bound for the calculations.

Metal dispersion is defined in equation E13 as the ratio of the amount of metal that actively adsorbs CO \(n_{metal,active}\) from equation E12 to the total amount of metal washcoated on the support \(n_{metal,total}\). Higher dispersion values equate to a more efficient metal atom usage for catalytic reaction [10]. For example, a catalyst with 100% dispersion has every metal atom available for adsorption.
Dispersion (%) = \frac{\text{grams of CO-adsorbing metal}}{\text{total grams of catalytic metal}} \times 100\% = \frac{n_{\text{metal active}}}{n_{\text{metal total}}} \times 100\% \quad \text{E13}

Average metal crystallite sizes are not calculated for chemisorption because the data is unclear whether the Pt or Fe chemisorbs CO, and the calculation is dependent on the metal physical properties $\rho$ and $S_g$, explained in the section 5.3.2.

5.2.3 Experimental Procedure

The experimental procedure for pulse chemisorption experiments on the system described in section 5.1 was:

1) Pretreated the catalyst with 15% H$_2$ in N$_2$ (~ 6000 sccm) at 350°C to reduce the catalyst surface. The pretreatment time was 2 hours (1 hour of start-up heating to reach 350°C, 1 hour pretreatment)
2) Lowered H$_2$ reduction temperature to 250°C and continued to pretreat for 1 hour
3) Purged catalyst surface with a N$_2$ pretreatment (~3500 sccm) at 250°C for 1 hour
4) Ramped temperature down to 40°C in pure N$_2$ (~1000 sccm)
5) Zeroed and spanned the NDIR using pure N$_2$ and span gas (~1000 sccm)
6) Pulsed 10% CO in N$_2$ gas to the reactor at 40°C until the catalyst was saturated

5.2.4 Background Study

A background study was conducted on: 1) a blank reactor; 2) an uncatalyzed, unwashcoated “blank” metal foam wrapped with ceramic fiber insulation; 3) ceramic fibers with no support, and; 4) a blank metal foam wrapped in glass wool insulation. In
addition, all runs had 2 ceramic foam distributors, one upstream and one downstream of the reactor, to ensure proper mixing of the gas stream, as shown in Figure 5.1.

The background study was performed to see if any of the items described above adsorbed CO. Sets of 10 pulses were done for each N\textsubscript{2} flow rate, and the \( n_{CO,NDIR} \) values were averaged. Table 5.2 summarizes the pulse chemisorption results on the background tests. The \% error was calculated by equation E14. The blank reactor experiment and all tests using ceramic fibers were pretreated at 250ºC instead of 350ºC.

<table>
<thead>
<tr>
<th></th>
<th>( n_{CO} ) in 1 mL sample loop (( \mu )mol)</th>
<th>( n_{CO} ) from NDIR (( \mu )mol) (1 L/min N\textsubscript{2})</th>
<th>% error</th>
<th>( n_{CO} ) from NDIR (( \mu )mol) (1.5 L/min N\textsubscript{2})</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank Reactor + 2 ceramic foam distributors</td>
<td>4.17 (T = 25°C)</td>
<td>4.80</td>
<td>~15%</td>
<td>4.92</td>
<td>~18%</td>
</tr>
<tr>
<td>Ceramic Fibers</td>
<td>4.17 (T = 25°C)</td>
<td>4.94</td>
<td>~18%</td>
<td>5.04</td>
<td>~21%</td>
</tr>
<tr>
<td>Blank Foam + Ceramic Fibers</td>
<td>4.18 (T = 24°C)</td>
<td>4.88</td>
<td>~17%</td>
<td>5.02</td>
<td>~20%</td>
</tr>
<tr>
<td>Blank Foam + Glass Wool</td>
<td>4.20 (T = 23°C)</td>
<td>4.99</td>
<td>~19%</td>
<td>5.11</td>
<td>~22%</td>
</tr>
</tbody>
</table>

\[
\% \text{ Error} = \frac{n_{CO,NDIR} - n_{CO,loop}}{n_{CO,loop}} \times 100\%
\]

Positive error results when \( n_{CO,NDIR} \) is greater than \( n_{CO,loop} \). Equation E9 is negative when \( n_{CO,NDIR} \) is greater than \( n_{CO,loop} \), which is not possible; the gas analyzer can not detect more CO coming out of the reactor than is pulsed in. It is possible that the NDIR has a
slow response time, causing it to overshoot CO values at faster flow rates. The error at higher N₂ flow rate runs (1.5 L/min) was 3% greater than at the lower N₂ flow rate.

Each experiment consisted of 10 pulses from a 1 mL sample loop containing 10% CO in N₂. The standard deviation for $n_{CO,NDIR}$ is small within each set of 10 pulses and the error does not fluctuate substantially (~ 1-2%). The certificate of analysis provided by National Welders has a ±2% variation for their 10% CO in N₂ gas cylinders (i.e., 9.8% to 10.2%). Therefore, the variation in $n_{CO,NDIR}$ can be accounted for from the variations in the 10% CO in N₂ gas cylinder. Hence, it is assumed that the blank reactor, ceramic fiber, glass wool, and blank metal foam do not adsorb CO.

5.2.5 Initial Results

CO pulse chemisorption was performed on four catalysts wrapped with glass wool insulation: 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 40 ppi, 4% ρ metal foam, and three 5 wt% Pt / 0, 0.05, & 0.5 wt% Fe / γ-Al₂O₃ 400 cpsi ceramic straight-channel monoliths. The results are summarized in Table 5.3. The term “used glass wool” means the reactor has not been opened prior to the second run and the same glass wool is used from the first run, but it is no longer virgin. The metal dispersion numbers are calculated either assuming CO adsorption on Pt and Fe, or CO adsorption only on Pt.
Table 5.3: CO pulse chemisorption results on the initial set of catalysts

<table>
<thead>
<tr>
<th>Test</th>
<th>$n_{\text{CO}}$ (µmol) adsorbed</th>
<th>Dispersion (%) (Pt only)</th>
<th>Dispersion (%) (Pt + Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ppi, 4% ρ (5% Pt, 0.5% Fe) metal foam with virgin glass wool “newer” front piece of 6” reactor</td>
<td>78.9</td>
<td>12.3%</td>
<td>11.1%</td>
</tr>
<tr>
<td>40 ppi, 4% ρ (5% Pt, 0.5% Fe) metal foam with used glass wool (2nd run) “newer” front piece of 6” reactor</td>
<td>67.0</td>
<td>10.4%</td>
<td>9.46%</td>
</tr>
<tr>
<td>5% Pt, 0.5% Fe (400 cpsi) ceramic monolith with virgin glass wool “newer” front piece of 6” reactor</td>
<td>101</td>
<td>15.7%</td>
<td>14.3%</td>
</tr>
<tr>
<td>5% Pt, 0.5% Fe (400 cpsi) ceramic monolith with used glass wool (2nd run) “newer” front piece of 6” reactor</td>
<td>85.3</td>
<td>13.2%</td>
<td>12.0%</td>
</tr>
<tr>
<td>5% Pt, 0% Fe (400 cpsi) ceramic monolith with virgin glass wool</td>
<td>90.4</td>
<td>14.0%</td>
<td>--</td>
</tr>
<tr>
<td>5% Pt, 0.05% Fe (400 cpsi) ceramic monolith with virgin glass wool</td>
<td>104</td>
<td>16.1%</td>
<td>15.9%</td>
</tr>
</tbody>
</table>

The values in Table 5.3 are adjusted to take into account that $n_{\text{CO,NDIR}}$ can be 15-19% greater than $n_{\text{CO,loop}}$ when no more CO adsorbs on the catalyst surface, as discussed in the background study. Therefore, the negative numbers computed from equation E9 are not included in the metal dispersion and $n_{\text{CO}}$ calculations.

The 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ metal foam and ceramic monolith do not have reproducible $n_{\text{CO}}$ values; the first runs are 12-15 µmol (~2% dispersion) higher than the second runs. Regardless of whether or not Fe is taken into account for the dispersion calculation, the trend remains the same. It is not understood why $n_{\text{CO}}$ varies so considerably for different runs of the same catalyst.
Liu et al. [11], Sakamoto et al. [12], and Watanabe et al. [13] claimed that on Pt/Fe catalysts, Fe blocked CO adsorption on some Pt sites. Therefore, a higher Fe loading should inhibit CO adsorption on the Pt particles for the 5 wt% Pt / 0, 0.05, 0.5 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\) ceramic monoliths. However, the data showed the reverse trend: the 0 wt% Fe monolith adsorbed 90.4 \( \mu \)mol CO, while the 0.05 wt% Fe monolith adsorbed 104 \( \mu \)mol CO. It is possible that at low Fe loadings (0-1 wt% Fe), Fe does not have a significant inhibition effect on Pt. Sakamoto et al. [12] and Watanabe et al. [13] used Pt:Fe ratios of 3:1 and 2:1, respectively, much lower than the minimum 10:1 ratio seen in Table 5.3. Thus, because of the low Fe loading and high Pt:Fe ratio, the Fe might not significantly inhibit CO adsorption on the Pt sites.

A peculiar observation was seen on all four washcoated supports. As described in Figure 5.2 in section 5.2.1, there should be three phases in pulse chemisorption. On the washcoated supports, the first stage of complete CO uptake was observed. In the second stage, an elongated tail was seen at the end of the pulse. The elongated tail often lasted longer than 10 minutes and did not drop to 0 ppm CO. The elongated tail was not seen on the unwashcoated metal foam. Figure 5.3 shows a graphical representation of this behavior. In the third stage, no CO uptake occurred, but the value of \( n_{CO,NDIR} \) was up to 25% greater than \( n_{CO,loop} \). This error was higher than the 15-19% seen in the background study. An example of an elongated tail CO pulse is shown in Figure E.2 in Appendix E.
Two possibilities could explain the elongated tail. The first possibility is that Fe weakly chemisorbs CO and slowly desorbs off the catalyst. Liu et al. [11] stated that iron oxide could weakly adsorb CO. Farrauto and Bartholomew [1] mentioned that iron carbonyl \([\text{Fe(CO)}_5]\) could form at moderate to room temperatures (273-573 K) and volatize off the support [1, 14]. Assuming Fe weakly adsorbs CO, the CO might slowly desorb off the Fe and create the long tail. It was hypothesized that the long tail would be absent if Fe was not present. To test this theory, pulse chemisorption was done on the 5 wt% Pt / 0 wt% Fe / \(\gamma\text{-Al}_2\text{O}_3\) ceramic monolith. The results showed that a tail developed, similarly to Figure E.2 in Appendix E. Therefore, this theory was discarded.

The second possibility is the \(\gamma\text{-Al}_2\text{O}_3\) washcoat or surface impurities are physisorbing CO, which causes the slow desorption from the support. The exact catalyst preparation procedure used by Environex is unknown, but binding agents and other chemicals that are typically used in a washcoating process may physisorb CO. It was hypothesized that after the catalyst was saturated with CO, more CO would adsorb after a long period of
time had passed. Pure N₂ was flowing through the catalyst during the long period of time. This test was done on all four catalysts. More CO was adsorbed after hours passed, even though the active sites were saturated already. Therefore, either the γ-Al₂O₃ washcoat or surface impurities might be physisorbing or weakly chemisorbing CO and causing the CO to slowly desorb out of the reactor. Moreover, mass transfer resistances in the reactor can cause readsorption of CO on the γ-Al₂O₃ or on surface impurities before reaching the bulk gas. This will amplify the slow desorption from the support.

5.3 CO Temperature-Programmed Desorption (TPD)

5.3.1 Theory

Similarly to pulse chemisorption, TPD measures the strength of adsorbate (CO) that adsorbs on the catalyst surface. Instead of pulsing CO into the reactor to measure CO adsorption, TPD data measures the amount of CO desorbed from the catalyst surface [15]. This result is used to calculate the number of active sites.

In TPD, the catalyst is flooded with CO at a given temperature so that all the catalyst active sites are saturated. Then, with an inert gas flowing through the reactor, the catalyst temperature is raised linearly, with a ramp rate measured in °C/minute. As the temperature increases, CO desorbs from the catalyst surface and is measured with the NDIR gas analyzer. Desorption occurs at higher temperatures because there is enough energy to break the adsorbate:catalyst bond. Higher desorption temperatures equate to stronger bonds. The catalyst temperature is increased until all of the CO has desorbed.
from the catalyst surface. Each adsorbate:catalyst pair will have a different temperature range for desorption. It is possible to have multiple desorption temperature ranges for each adsorbate:catalyst pair, causing bimodal or trimodal desorption peaks. Herein, for bimodal peaks, the first peak is called the low temperature peak (LTP), while the second peak is called the high temperature peak (HTP).

The maximum of the CO concentration versus time curve is called the desorption temperature. The desorption temperature is dependent on the porosity of the catalyst and its support [2, 5], the linear temperature ramp rate, and the inert gas flow rate [15]. The faster the linear ramp rate, the higher the desorption temperature. If the catalyst or its support is porous, readsorption of CO onto another metal after it desorbs is possible. This effect shifts the desorption temperature higher because CO diffusion out of the catalyst requires a longer time. A slower inert gas flow rate leads to a greater time difference between the reactor and the gas analyzer, increasing the apparent desorption temperature. Compounding these three effects of a fast linear ramp rate, multiple readsorption sites, and a slow inert gas flow rate, the TPD desorption temperature peak may not reflect values reported in the literature for other sets of conditions.

Integration of the area under the CO versus time curve is done using equation E11 in section 5.2.2. The integration result indicates the amount of CO desorbed from the catalyst \( n_{CO,saturate} \). From \( n_{CO,saturate} \), the metal dispersion and average metal crystallite size are calculated. Multiple TPD tests on the same catalyst using different ramp rates or
CO coverages are required to compute the activation energy and kinetic rate constant of desorption. Unfortunately, the temperature ramp rate could not be controlled accurately, so the activation energy and kinetic rate constant of desorption are not calculated.

5.3.2 Data Analysis

Similarly to pulse chemisorption, TPD can be used to determine the metal dispersion and $n_{CO,saturate}$. The equations behind these calculations are found in the pulse chemisorption theory in section 5.2.2, except in TPD $n_{CO,saturate}$ equals $n_{CO,NDIR}$. A typical graphical representation of TPD data is shown on Figure 5.4.

![Graphical representation of TPD data](image)

Figure 5.4: Typical graphical representation of TPD data: reactor inlet temperature and CO concentration as a function of time.
For the TPD calculations, it is assumed that CO desorption from the catalyst is attributed to Pt. This assumption is justified because the catalyst is flooded with CO, to saturate the active sites, hours before the TPD run. This time difference between the CO flood and the TPD experiment allows the physisorbed and weakly chemisorbed CO to bleed off the catalyst. As discussed in section 5.2.5, any CO adsorbed on the Fe, $\gamma$-Al$_2$O$_3$ washcoat, or surface impurities are presumed to fall into these categories, leaving only chemisorbed CO on Pt during the TPD run.

In addition, TPD can be used to determine the desorption temperature and the average metal crystallite size. The CO desorption temperature ($T_{\text{des}}$) is determined from the location of the CO maximum, as seen in Figure 5.4. $T_{\text{des}}$ is often reported as the typical temperature that CO desorbs off the metal. The strength of the CO:metal bond is associated with its desorption temperature: the higher the desorption temperature, the stronger the bond and the adsorption site. For CO adsorbed on Pt, Manasilp and Gulari [16] observed the $T_{\text{des}}$ peak at $\sim$160°C, while Kahlich et al. [17] reported the main peak at 120°C, with shoulders at 215°C and 260°C.

The average metal crystallite size ($d_{\text{metal}}$) is a physical parameter which can be computed from metal dispersion [10]. To find $d_{\text{metal}}$, a geometric model that describes the shape of the deposited metal must be assumed. The formula for a spherical model is shown in equation E15 [10].
\[ d_{metal} = \frac{6}{\rho \cdot S_g \cdot \text{Dispersion}} \]

where \( \rho \) is the density of the metal (g metal/cm\(^3\)) and \( S_g \) is the maximum surface area possible per gram metal basis (cm\(^2\)/g metal). Other geometric models can be used to describe the shape of the deposited metal, such as a cubic model [2]. Without knowing the actual geometry of the metal, \( d_{metal} \) is a rough estimate of the actual particle size. Larger \( d_{metal} \) values indicate clumping and clusters of metal, translating into poor dispersion of the metal on the support.

5.3.3 Experimental Procedure

The experimental procedure for TPD tests on the system described in section 5.1 was:

1) Pretreated the catalyst with 15% \( \text{H}_2 \) in \( \text{N}_2 \) (~6000 sccm) at 350°C to reduce the catalyst surface. The pretreatment time was 2 hours (1 hour of start-up heating to reach 350°C, 1 hour pretreatment)
2) Lowered \( \text{H}_2 \) reduction temperature to 250°C and pretreated for 1 hour
3) Purged catalyst surface with a \( \text{N}_2 \) pretreatment (~3500 sccm) at 250°C for 1 hour
4) Ramped temperature down to 40°C in pure \( \text{N}_2 \) (~1000 sccm)
5) Flowed 10% \( \text{CO} \) in \( \text{N}_2 \) gas (~2000 sccm) for 1 hour to saturate all metal active sites on the catalyst surface
6) Flowed pure \( \text{N}_2 \) (~500 sccm) overnight at 40°C to remove any physisorbed or weakly chemisorbed \( \text{CO} \) from the catalyst surface
7) Zeroed and spanned NDIR thrice using pure \( \text{N}_2 \) and span gas (~1000 sccm)
8) Flowing pure \( \text{N}_2 \) (~1000 sccm), ramped temperature up to 430°C
9) After reaching 430°C, slowly ramped the temperature to ambient conditions
5.3.4 Background Study

A background study was conducted on: 1) a blank reactor; 2) a blank metal foam wrapped with ceramic fiber insulation; 3) ceramic fibers with no support, and; 4) a blank metal foam wrapped in glass wool insulation. All runs included 2 ceramic foam distributors, as shown in Figure 5.1. A background study was performed to see if any CO desorbed from these items. Table 5.4 summarizes the TPD results on the background tests with ramp rates ~ 5-15°C/min. The blank reactor experiment and all tests using ceramic fibers were pretreated at 250°C instead of 350°C. The blank reactor was only tested up to 330°C because the old insulation wrapped around the heating tapes did not allow for temperatures above 350°C.

Table 5.4: TPD results on a background study of the blank reactor, ceramic fibers, uncatalyzed, unwashcoated blank metal foam, and glass wool with ramp rates of ~ 5-15°C/min

<table>
<thead>
<tr>
<th>Date</th>
<th>Test</th>
<th>nCO High Temp (µmol)</th>
<th>Tdes High Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/12/04</td>
<td>Blank Reactor (&amp; 2 ceramic foam distributors)</td>
<td>~ 2.1</td>
<td>No Peak</td>
</tr>
<tr>
<td>03/03/04</td>
<td>Virgin Ceramic Fibers / No support</td>
<td>117</td>
<td>385°C</td>
</tr>
<tr>
<td>03/04/04</td>
<td>2nd Used Ceramic Fibers / No support</td>
<td>6.67</td>
<td>430°C</td>
</tr>
<tr>
<td>03/08/04</td>
<td>Virgin Ceramic Fibers / No support</td>
<td>120</td>
<td>380°C</td>
</tr>
<tr>
<td></td>
<td>(no pretreatment)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>03/10/04</td>
<td>Used Ceramic Fibers / Blank Metal Foam</td>
<td>8.45</td>
<td>440°C</td>
</tr>
<tr>
<td>03/10/04</td>
<td>Used Ceramic Fibers / Blank Metal Foam (2nd run)</td>
<td>~ 1.1</td>
<td>435°C</td>
</tr>
<tr>
<td>03/26/04</td>
<td>Virgin Glass Wool / Blank Metal Foam</td>
<td>^ 3.24</td>
<td>260-180°C</td>
</tr>
<tr>
<td>03/29/04</td>
<td>Used Glass Wool / Blank Metal Foam (2nd run)</td>
<td>~ 1.1</td>
<td>No Peak</td>
</tr>
</tbody>
</table>

^ -- Broken inlet heating tape caused a large ΔT between inlet and outlet reactor temperatures
No LTP typically observed from CO desorption (120-160°C [16, 17]) was seen in any of the background tests. Sometimes the HTP did not occur until after the temperature ramping (step 8 in section 5.3.3) ended.

TPD results showed the blank reactor and two ceramic foam distributors did not desorb much CO (~2 µmol) up to 330°C. The virgin ceramic fibers with no support desorbed 117 µmol CO, and a subsequent run released 7 µmol CO, totaling ~125 µmol CO desorbed. The term “used ceramic fibers” means some CO has already desorbed from previous runs using them. An experiment was done using virgin ceramic fibers with no pretreatment or CO flooding prior to the TPD. These ceramic fibers desorbed 120 µmol CO, with a similar T_{des} of 380-385°C. Therefore, the ceramic fibers desorbed a significant amount of CO or some interference gas that was detected as CO by the NDIR. It is unlikely that the ceramic fibers give off CO because they are made of ultra-high pure Al₂O₃ based refractory fiber.

Experiments on a blank metal foam wrapped in used ceramic fiber insulation showed low CO desorption (8 µmol CO) on the first run, and little/no CO desorption (~1 µmol CO) on the second run. The CO desorption on the first run might be attributed to leftover CO on the used ceramic fibers. Therefore, it is assumed that a blank metal foam does not desorb CO. These background tests indicated that considerable CO desorption from ceramic fibers could convolute TPD results on catalyzed, washcoated supports, and they should not be used.
Instead of ceramic fiber insulation, glass wool was used. TPD results on the blank foam wrapped in glass wool showed low CO desorption on the first run (~3 µmol CO) and little/no CO desorption on the second run (~1 µmol CO). The term “used glass wool” in Table 5.4 means the reactor has not been opened prior to the second run and the same piece is used in the first run. The CO desorption from the first run using virgin glass wool might be attributed to sunlight hitting the NDIR, causing an ambient temperature rise. The NDIR is sensitive to temperature; CO measurements from the NDIR can increase up to 1.5% of its full scale per °C increase in ambient temperature. From the test with ceramic fiber insulation wrapped around a blank metal foam, it is assumed the blank foam does not desorb CO. The glass wool should not desorb CO since it is typically used in quartz tube reactors. Therefore, the 3 µmol CO from the first run using virgin glass wool is attributed to temperature fluctuations affecting the NDIR, not CO desorption.

The variance in $T_{\text{des}}$ for this test was caused by a broken inlet heating tape.

The blank metal foam tests wrapped in used ceramic fiber insulation and used glass wool insulation showed ~1 µmol CO desorbed. The blank reactor TPD test resulted in ~2 µmol CO desorbed. A blank, empty reactor can not desorb more CO than a reactor with a blank metal foam inside. Therefore, the experimental results from Table 5.4 indicate that there is a range of error for the TPD data of at least +3 µmol CO.
5.3.5 *Initial Results*

The TPD experiments were performed on four supports wrapped with glass wool insulation: 5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$ 40 ppi, 4% ρ metal foam, and three 5 wt% Pt / 0, 0.05, & 0.5 wt% Fe / γ-Al$_2$O$_3$ 400 cpsi ceramic straight-channel monoliths. The results for the low temperature peak (LTP) are summarized in Table 5.5. Prior to these results, all but the 5 wt% Pt / 0.5 wt% Fe / γ-Al$_2$O$_3$ ceramic monolith had seen temperatures of 330°C.

**Table 5.5: Low temperature peak CO TPD results on the initial set of four catalyst supports with ramp rates ~8-11°C/min**

<table>
<thead>
<tr>
<th>Test</th>
<th>( n_{\text{CO LTP}} ) (µmol)</th>
<th>( T_{\text{des LTP}} ) (°C)</th>
<th>Dispersion LTP (%) (Pt only)</th>
<th>( d_{\text{Pt LTP}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ppi, 4% ρ (5% Pt, 0.5% Fe) metal foam w/ virgin glass wool</td>
<td>54.9</td>
<td>~205°C</td>
<td>8.52%</td>
<td>14</td>
</tr>
<tr>
<td>“newer” front piece of 6” reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 ppi, 4% ρ (5% Pt, 0.5% Fe) metal foam w/ used glass wool (2nd run)</td>
<td>55.1</td>
<td>Shoulder: 165°C Peak: 222°C</td>
<td>8.55%</td>
<td>14</td>
</tr>
<tr>
<td>“newer” front piece of 6” reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Pt, 0.5% Fe (400 cpsi) ceramic monolith w/ virgin glass wool</td>
<td>59.7</td>
<td>240°C</td>
<td>9.27%</td>
<td>13</td>
</tr>
<tr>
<td>“newer” front piece of 6” reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Pt, 0.5% Fe (400 cpsi) ceramic monolith w/ used glass wool (2nd run)</td>
<td>69.5</td>
<td>Shoulder: 210°C Peak: 260°C</td>
<td>10.8%</td>
<td>11</td>
</tr>
<tr>
<td>“newer” front piece of 6” reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Pt, 0% Fe (400 cpsi) ceramic monolith w/ virgin glass wool</td>
<td>53.8</td>
<td>250°C</td>
<td>8.36%</td>
<td>14</td>
</tr>
<tr>
<td>5% Pt, 0.05% Fe (400 cpsi) ceramic monolith w/ virgin glass wool</td>
<td>67.0</td>
<td>245°C</td>
<td>10.4%</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^{\wedge} -- \) Broken inlet heating tape caused large ΔT between inlet and outlet reactor temperatures
The second runs on the 5 wt% Pt / 0.5 wt% Fe metal foam and ceramic monolith showed similar, somewhat reproducible low temperature $n_{CO}$ and dispersion values. The difference in $n_{CO}$ value between the first and second run was 0.2 µmol CO for the metal foam, and 10 µmol CO for the ceramic monolith. The difference in dispersion value was 0.03% for the metal foam, and 1.5% for the ceramic monolith.

The TPD results on the varying Fe loading ceramic monoliths do not show any trends. The 0 wt% Fe adsorbed 53.8 µmol CO (8.36% dispersion), the 0.05 wt% Fe adsorbed 67.0 µmol CO (10.4% dispersion), and the 0.5 wt% adsorbed 60-70 µmol CO (9.27-10.8% dispersion). Even though TPD data only accounts for CO adsorbed on Pt sites, as discussed in section 5.3.2, the effect of lowered CO adsorption on Pt from Fe inhibition [11-13] should still be observed. The Pt:Fe ratios used in this study were high, so the low Fe loading might not be enough to block the Pt sites and to affect CO adsorption.

The TPD results are very different compared to the pulse chemisorption results in section 5.2.5. The pulse chemisorption data in Table 5.3 (76-104 µmol CO) are higher than the TPD data in Table 5.5 (54-70 µmol CO). One explanation is that TPD only accounts for CO adsorbed on Pt sites. Pure N$_2$ gas flowed through the catalyst for hours prior to the TPD experiment, so physisorbed and weakly chemisorbed CO was given sufficient time to desorb from those sites. Pulse chemisorption accounts for physisorbed and weakly chemisorbed CO, which increases the value of $n_{CO}$. Even so, the pulse chemisorption $n_{CO}$ values should not be 20-25 µmol CO higher than the TPD values.
Considerable scatter in the $T_{\text{des}}$ value is seen between the catalysts. The ceramic monoliths had a LTP $T_{\text{des}}$ of 240-260°C. On the second run of the 0.5 wt% Fe monolith, a shoulder appeared at 210°C. The metal foam had a LTP $T_{\text{des}}$ of 205-222°C. On the second run, a shoulder appeared at 165°C. It is not understood why the second runs of the metal foam and ceramic monolith show a shoulder, but their first runs do not.

The LTP $T_{\text{des}}$ values are much higher than 160°C seen by Manasilp and Gulari [16] or 120°C seen by Kahlich et al. [17]. High linear ramp rates or CO readsorption on porous catalysts, discussed in section 5.3.1, can increase the value of $T_{\text{des}}$. Additionally, mass transport resistances, discussed in Chapter 4, section 4.3, can increase the time required for CO to diffuse to the bulk gas, which increases $T_{\text{des}}$. Typically, the lower LTP $T_{\text{des}}$ on the metal foam equates to weaker CO:Pt bond strengths compared to the ceramic monoliths. This may not be true if the metal foam experiences less mass transport resistances than the ceramic monolith. Lowered mass transport on the metal foam would decrease $T_{\text{des}}$ compared to the ceramic monolith.

The average diameter of the Pt particles ($d_{\text{Pt}}$) for the LTP is also summarized in Table 5.5. Liu et al. [11] used transmission electron microscopy (TEM) and high resolution TEM (HRTEM) to view dispersed Pt particles with a $d_{\text{Pt}}$ of ~2 nm for a 5% Pt/Fe/γ-Al$_2$O$_3$ catalyst, while Sakamoto et al. [18] used x-ray diffraction (XRD) and dark field TEM to determine an average $d_{\text{Pt}}$ of ~20 nm for 3.70% Pt/1.10% Fe/γ-Al$_2$O$_3$ and 3.50% Pt/5.10%
Fe/γ-Al₂O₃ catalysts. The \( \text{d}_{\text{Pt}} \) results (11-14 nm) from the TPD study fall in between these data. Sakamoto et al. [18] postulated that one of the roles of Fe was to create a layer of Fe₂O₃ to prevent Pt sintering. Farrauto and Bartholomew [1] stated that pores and support surface defects impeded surface migration of metal particles. Therefore, it is unlikely that the higher LTP \( \text{d}_{\text{Pt}} \) values compared to Liu et al. [11] are caused from Pt agglomeration or sintering. Better agreement may be obtained with Liu or Sakamoto if a cubic geometric model [2] or a combination of a spherical model with flat sides is used. Particle measurements using XRD or TEM are needed to make conclusive comparisons.

Table 5.6: High temperature peak CO TPD results on the initial set of four catalyst supports with ramp rates \( \sim 8-11 \text{°C/min} \)

<table>
<thead>
<tr>
<th>Test</th>
<th>( n_{\text{CO HTP}} ) (( \mu \text{mol} ))</th>
<th>( T_{\text{des HTP}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ppi, 4% ( \rho ) (5% Pt, 0.5% Fe) metal foam w/ virgin glass wool “newer” front piece of 6” reactor</td>
<td>^ 23.7</td>
<td>~405°C</td>
</tr>
<tr>
<td>40 ppi, 4% ( \rho ) (5% Pt, 0.5% Fe) metal foam w/ used glass wool (2(^{\text{nd}}) try) “newer” front piece of 6” reactor</td>
<td>~ 0</td>
<td>No Peak</td>
</tr>
<tr>
<td>5% Pt, 0.5% Fe (400 cpsi) ceramic monolith w/ virgin glass wool “newer” front piece of 6” reactor</td>
<td>11.9</td>
<td>400°C</td>
</tr>
<tr>
<td>5% Pt, 0.5% Fe (400 cpsi) ceramic monolith w/ used glass wool (2(^{\text{nd}}) try) “newer” front piece of 6” reactor</td>
<td>~ 0</td>
<td>No Peak</td>
</tr>
<tr>
<td>5% Pt, 0% Fe (400 cpsi) ceramic monolith w/ virgin glass wool</td>
<td>3.29</td>
<td>415°C</td>
</tr>
<tr>
<td>5% Pt, 0.05% Fe (400 cpsi) ceramic monolith w/ virgin glass wool</td>
<td>9.74</td>
<td>425°C</td>
</tr>
</tbody>
</table>

^ -- Broken inlet heating tape caused large \( \Delta T \) between inlet and outlet reactor temperatures
The results for the high temperature peak (HTP) on the four catalysts are summarized in Table 5.6. It is not understood why the first runs of the 5 wt% Pt, 0.5 wt% Fe metal foam and ceramic monolith exhibit CO desorption ($n_{CO} > 0$) at high temperatures, but their second runs show no CO desorption ($n_{CO} \sim 0$).

The HTP $T_{des}$ for the metal foam and ceramic monoliths ranged from 400-425°C, which fell in a smaller range than the LTP $T_{des}$ (205-260°C). The similar HTP $T_{des}$ equates to similar CO bond strengths.

A comparison of the HTP $n_{CO}$ values is performed on the catalyzed supports wrapped with virgin glass wool in Table 5.6 and the blank metal foam wrapped with virgin glass wool in Table 5.4. The HTP $n_{CO}$ values on the catalyzed supports are too large (3-24 µmol CO) to be completely attributed to the virgin glass wool or blank metal foam (3 µmol CO). Thus, the high temperature CO peaks seen on catalyzed supports are not attributed the virgin glass wool or blank metal foam, but to the catalyst, $\gamma$-Al$_2$O$_3$ washcoat, or an interference gas detected as CO by the NDIR.

5.4 Washcoating ICP / BET Results

In-house catalyst preparation was examined in an attempt to reduce inconsistencies in the catalyst loading on the washcoat made by others. Future work will include testing in-house catalyzed supports. Therefore, Pt, Pt/Fe, and Pt/Ni catalysts washcoated on $\gamma$-Al$_2$O$_3$ powder were synthesized and analyzed by two methods: Inductively Coupled
Plasma (ICP) and Brunauer-Emmett-Teller (BET). ICP is used to measure the catalyst bulk elemental composition, and BET is used to determine the total surface area per gram of catalyst. In addition to the eleven in-house catalysts, a 0.5 wt% Pt / 0.005 wt% Fe catalyst slurry provided by Environex was tested. This catalyst slurry was used by Environex to washcoat the ceramic monolith studied in Chapter 3, section 3.3.1.

5.4.1 NC State Wet Impregnation Procedure

Kyle Bishop, a summer student in the Green Processing research experience for undergraduates (REU) program, applied the incipient wetness impregnation method to synthesize powder samples that were used to washcoat blank metal foams supplied by Porvair Fuel Cell Technologies. In incipient wetness impregnation, metal-containing liquid is contacted with a dry, porous support, and capillary pressures draw the liquid into the pores [1, 19, 20]. More liquid is contacted with the support until incipient wetness occurs (i.e. the support began to look wet or shiny). The catalyst preparation technique is outlined below.

**Pt catalysts:**

1) Use a $\gamma$-Al$_2$O$_3$ powder [21, 22] (Alfa Aesar, 99.5% purity aluminum oxide) with a particle size ranging from 63-200 $\mu$m. Determine the pore volume to mass ratio of the $\gamma$-Al$_2$O$_3$ by impregnating to incipient wetness with deionized water.

2) Calculate the appropriate concentration of hydrogen hexachloroplatinate (IV) hexahydrate (H$_2$Cl$_6$Pt-6H$_2$O) solution to achieve the desired platinum loading. Impregnate to incipient wetness.
3) Dry in a 110°C oven for 12 hours to remove all water.

4) Calcine in air at 450°C for 5 hours.

Fe-promoted Pt catalysts:

1) Start with Pt/γ-Al₂O₃ powder. Determine the pore volume to mass ratio by impregnating to incipient wetness with deionized water. (Note: The ratio may or may not be less than the pure alumina depending on the platinum loading.)

2) Calculate the appropriate concentration of iron (III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O] to achieve the desired iron loading. Impregnate the Pt/γ-Al₂O₃ powder to incipient wetness.

3) Dry in a 110°C oven for 12 hours to remove all water.

4) Calcine in air at 300°C for 2-3 hours.

Ni-promoted Pt catalyst:

The wet impregnation procedure for the Ni-promoted Pt catalyst is the same at the Fe-promoted Pt catalysts, except nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O] is used as the nickel precursor.

5.4.2 ICP Results and Discussion

The samples were sent to the Soil Science Department at North Carolina State University for ICP analysis using a Perkin-Elmer Model 2000 DV with an ICP-Emission Spectrometer. The metal was removed from the support by reacting a sample with
concentrated HF acid, drying it, and refluxing it on a hot plate in the presence of Aqua Regia. The final solution then underwent ICP testing.

The ICP results summarized in Table E.1 in Appendix E show variations between the calculated composition from incipient wetness and the measured elemental composition from ICP analysis. One sample of specific interest is the Environex slurry, lab i.d. #80. For this sample, the measured Fe composition indicated 300% more Fe than the calculated composition. This suggested that the metal loadings provided by Environex might be inaccurate on the washcoated structured supports. The catalysts made in-house were more consistent, with the measured Pt composition only ± 10% from the calculated composition. The measured Fe composition often exceeded the calculated composition, as much as 30%. The measured Ni composition was about 6% below the calculated composition for lab i.d. #79.

5.4.3 BET Results and Discussion

BET analysis was done using an in-house Micrometrics Flowsorb II 2300 with BET capability. Surface area measurements are based on BET surface area theory, which assumes a clean surface and a monolayer adsorption of the adsorbing gas. Surface area is calculated using equation E16, where $S$ is the surface area of the monolayer, $V$ is the volume of gas adsorbed, $A$ is Avogadro’s number, $N$ is the area per adsorbed gas molecule, $P$ is the pressure at which the gas is adsorbed, $P_0$ is the saturation pressure of liquefied gas at the adsorbing temperature, and $M$ is the gas molar volume [23]. For
liquid N₂, the adsorbing gas, \( P_o \) and \( N \) at 77 K are 0.101 MPa and 0.16 nm² [24], respectively. Catalysts were degassed at 240°C for 2 hours, and tests were run according to the instruction manual [23].

\[
S = V * A * N * \left[ 1 - \frac{P}{MP_0} \right] \tag{E16}
\]

Comprehensive BET results are summarized in Table E.2 in Appendix E, while Table 5.7 shows the average BET surface areas. For the 11 samples made in-house, the average BET surface areas for the pure Pt and Pt/Fe impregnated on \( \gamma \)-Al₂O₃ are similar (3-8 m²/g standard deviation). This is expected because generally surface area is dependent on the washcoated powder, not the metal type and loading. The 5 wt% Pt / 0.66 wt% Ni / \( \gamma \)-Al₂O₃ powder made in-house had a lower surface area of 106 m²/g. It is not understood why the Pt/Ni catalyst has a lower surface area using the same \( \gamma \)-Al₂O₃ powder as the pure Pt and Pt/Fe catalysts. Inconsistent balance readings on the 5 wt% Pt catalysts may have caused this discrepancy.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Average BET Surface Area (m²/g)</th>
<th>Std Dev BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-5 wt% Pt / ( \gamma )-Al₂O₃ (3 samples)</td>
<td>127</td>
<td>3</td>
</tr>
<tr>
<td>0.5-5 wt% Pt / 0-2 wt% Fe / ( \gamma )-Al₂O₃ (7 samples)</td>
<td>134</td>
<td>8</td>
</tr>
<tr>
<td>5 wt% Pt / 0.66 wt% Ni / ( \gamma )-Al₂O₃ (1 sample)</td>
<td>106</td>
<td>--</td>
</tr>
<tr>
<td>0.5 wt% Pt / 0.005 wt% Fe / ( \gamma )-Al₂O₃ (1 sample) from Environex</td>
<td>172</td>
<td>--</td>
</tr>
</tbody>
</table>
The 0.5 wt% Pt / 0.005 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\) slurry from Environex had the highest surface area of 172 m\(^2\)/g. Environex used a different \( \gamma \)-Al\(_2\)O\(_3\) powder than the one used in-house. Different \( \gamma \)-Al\(_2\)O\(_3\) powders can have different porosities and internal surface areas. Environex ball milled their \( \gamma \)-Al\(_2\)O\(_3\) to 5 \( \mu \)m, which was smaller than the 63-200 \( \mu \)m \( \gamma \)-Al\(_2\)O\(_3\) particle sizes used in-house.

5.5 References


CHAPTER 6  CONCLUSIONS

6.1   Conclusions

Four 5 wt% Pt, 400 cpsi ceramic straight-channel monolith catalysts were synthesized with different Fe loadings. The \( \gamma\)-Al\(_2\)O\(_3\) washcoat loading was about 0.098 g/cm\(^3\) of the gross support volume, and the Pt loading was 0.005 g Pt/cm\(^3\). At 100°C inlet temperature and using an adiabatic reactor, higher Fe loadings increased CO and O\(_2\) conversions and decreased CO selectivity. At 170°C, the conversions and selectivity were independent of Fe loading. This data was consistent with Korotkikh and Farrauto [1] under isothermal conditions. At a 0.5 wt% Pt / 0.005 wt% Fe loading, CO poisoned the catalyst surface. The 0.005 wt% Fe loading did not provide enough active sites for O\(_2\) adsorption.

Four metal foams, with a 5 wt% Pt / 0.5 wt% Fe / \( \gamma\)-Al\(_2\)O\(_3\) washcoat, were tested under various operating conditions. The 40 ppi, 4% density (\( \rho \)) metal foam had the highest CO conversion and selectivity compared to the other three (20 ppi 4% \( \rho \), 20 ppi 12% \( \rho \), and 40 ppi 12% \( \rho \)) metal foams. The two 12% \( \rho \) metal foams exhibited low CO conversions (~15-20%) at 100°C inlet temperature. However, a pretreatment consisting of an oxidation and reduction step at 230°C permanently increased their activity. Pretreatment of the catalysts with high initial activity did not affect their CO conversions.
A comparison study was conducted on the 400 cpsi ceramic monolith and 40 ppi, 4% ρ metal foam with a 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ washcoat. At 100°C and 170°C inlet temperatures, 10,000-30,000 hr⁻¹ gas hourly space velocity (GHSV), and 0.25 and 0.5 O₂/CO ratios, the CO conversion and selectivity of the metal foam were comparable to those of the ceramic monolith. At 45,000 hr⁻¹ GHSV and 1.0 O₂/CO ratio, the ceramic monolith performed slightly better than the metal foam. Comparison tests at 80°C inlet temperature of the 400 cpsi equivalent metal monolith and the 20 ppi, 11% ρ ceramic foam resulted in lower CO conversion and selectivity compared to the ceramic monolith and the metal foam.

The reverse water-gas-shift (r-WGS) reaction was a significant side reaction under adiabatic conditions. This reaction made it impossible to achieve low outlet CO concentrations. Experiments were run simulating gas compositions exiting the WGS reactor, except with no CO in the inlet feed. The 5 wt% Pt / 0.5 wt% Fe ceramic monolith reached 65% of the r-WGS equilibrium at a 308°C outlet reactor temperature. There was no relationship between the Fe loading and the outlet CO concentration on the ceramic monoliths. The 40 ppi, 4% ρ metal foam was further away from the r-WGS equilibrium than the 400 cpsi ceramic monolith with the same catalyst composition.

Heat and mass transfer resistances were observed at some testing conditions. A study of the individual effects of linear velocity and GHSV on 5.08 cm and 15.2 cm catalyst lengths revealed significant transport effects at lower linear velocities. At 21.3 cm/sec
linear velocity and 5,000-15,000 hr\(^{-1}\) GHSV, most of the oxidation reactions occurred in the inlet 5.08 cm portion of the catalyst. This observation will allow the catalyst surface to re-equilibrate at a lower temperature and will decrease the significance of “hot spots” in the latter 10.1 cm portion of the 15.2 cm catalyst length. Both the r-WGS reaction and transport resistances must be overcome to reach low outlet CO concentrations.

Characterization techniques were used in an attempt to explain the differences in the activity and selectivity between the catalysts. Pulse chemisorption and temperature programmed desorption (TPD) is used to determine the amount of CO that will adsorb on the catalyst surface. A background study using pulse chemisorption on the blank reactor, ceramic fiber insulation, glass wool insulation, and uncatalyzed, unwashcoated metal foam indicated no CO adsorption. Pulse chemisorption results showed about 18% (~0.75 µmol) more CO detected by the NDIR gas analyzer than actually pulsed into the reactor. A background study using TPD showed considerable CO desorption from the virgin ceramic fiber insulation. The TPD results had a ±3 µmol CO error.

On catalyzed supports, the amount of CO adsorbed on the catalyst surface using pulse chemisorption was higher than for TPD. This might be possible because chemisorption accounted for CO adsorption on both Pt and Fe, while TPD only accounted for CO adsorption on Pt. Literature data [2-4] indicated lower CO adsorption on Pt/Fe catalysts than on unpromoted Pt catalysts. This lower CO adsorption effect was not seen on the ceramic monolith catalysts containing different Fe concentrations, possibly because of
the high Pt:Fe ratios used in this study compared to the literature data. An elongated tail was observed during the pulse chemisorption tests, possibly attributed to CO adsorption on the $\gamma$-$\text{Al}_2\text{O}_3$ washcoat or to surface impurities. Mass transfer resistances in the reactor can cause readsorption of CO on the $\gamma$-$\text{Al}_2\text{O}_3$ or on surface impurities before reaching the bulk gas, increasing the elongated tail. The desorption temperatures for CO on Pt determined by TPD were higher than reported in the literature [5, 6]. The higher desorption temperatures may be caused by mass transfer resistances, high linear ramp rates, or CO readsorption on Pt. The average Pt crystallite diameter based on a spherical model was 11-14 nm, which fell in between the values reported by Liu et al. [2] and Sakamoto et al. [3]. Overall, the pulse chemisorption and TPD results did not describe the catalyst performance results. Higher values of the number of CO adsorbed on the catalyst surface were not associated with higher CO conversions from the PROX reaction.

The ICP analysis on a catalyst slurry provided by Environex showed the measured Fe composition to be 300% greater than the calculated Fe composition. Therefore, the calculated catalyst compositions provided by Environex might be inaccurate. This hypothesis was reinforced when multiple “identical” metal loading catalyst supports were tested and exhibited different activity and selectivity.

6.2 Recommendations

Of the four catalyzed supports characterized to date, all but the 5 wt% Pt / 0.5 wt% Fe / $\gamma$-$\text{Al}_2\text{O}_3$ 40 ppi, 4% $\rho$ metal foam should be retested for the appearance of a high
temperature CO peak. As observed with the 5 wt% Pt / 0.5 wt% Fe ceramic monolith and the 40 ppi, 4% ρ metal foam (“newer” front pieces of 15.2 cm catalyst lengths), these subsequent runs should not exhibit a high temperature CO peak. They should also have similar low temperature CO adsorption values compared to their initial runs.

The rest of the supports from the preferential oxidation (PROX) reaction study were wrapped in ceramic fiber insulation. These supports should be wrapped in glass wool, and the pretreatment temperature should be increased from 350°C to 400°C. These nine supports should either exhibit a small high temperature CO peak, or no peak at all, because the pretreatment temperature will be raised to 400°C.

To make a direct comparison with the Pt diameters seen in the literature [2, 3], transmission electron microscopy (TEM) or x-ray diffraction (XRD) should be conducted to determine the actual Pt and Fe particle sizes. Also, inductively coupled plasma (ICP) analysis should be performed to verify the actual Pt and Fe compositions. This analysis will help explain the differences between the “identical” metal loading catalysts. In order to accomplish these studies, the catalysts must be destroyed.

Since the catalysts experienced transport limitations under testing conditions, the mass transfer coefficient $k_g$ can be calculated for the ceramic straight-channel monoliths. Using a correlation for the Nusselt mass transfer (Sherwood) number as a function of the Reynolds and Prandtl mass transfer (Schmidt) numbers, $k_g$ can be computed if the
diffusivity of the gases and the hydraulic diameter of the monolith are known [7]. Similarly, the heat transfer coefficient $h$ can be calculated for the ceramic monoliths.

Other catalysts should be synthesized and tested using different metals and promoters. Ru and Rh are considered active PROX catalysts [8-11], while low temperature PROX on Au has been the focus of more recent studies [12-15]. The use of other promoters for Pt-based catalysts, such as Mn [16], Co [16, 17], and Sn [18, 19], should also be considered. In-house catalyst production should be examined to help reduce the catalyst composition variability. Further research on catalyst preparation techniques is required.

In addition to testing new catalysts, the reactor design should be modified to allow the testing of catalysts containing cylindrical tubes in metal foams, as seen in Figure A.2 in Appendix A. As discussed in the conclusions and in Chapter 4, the r-WGS reaction severely inhibits the ability to achieve low outlet CO concentrations. The cylindrical tubes will be filled with a cooling fluid to allow for isothermal operation. An isothermal reactor will help suppress the r-WGS reaction by keeping the reactor at low temperatures. Additionally, kinetic parameters and reaction orders for CO and $O_2$ can be computed at low CO conversions, simulating differential reactor conditions. The reactor should be operated isothermally with no gradients, and the rate of reaction should be measured as a function of CO concentration or partial pressure [20]. The rate of reaction in a fixed bed reactor can be calculated using the continuous-stirred tank reactor (CSTR) design equation, assuming the reactor is gradientless.
6.3 References


APPENDICES
APPENDIX A  Metal Foam Pictures

Figure A.1: Different shapes of metal foams.

Figure A.2: Metal foams inserted with metal tubes.
Figure B.1: Threaded reactor design dimensions.
Figure B.2: Characterization reactor design dimensions.
Figure B.3: Flange and Gasket dimensions

304SS A-351 MSS 150-lb-rated A370 SC flanges

*Tube OD = 1.25”*

Flange ~ 4.25” diameter

5/8” Bolt holes
(4 holes using ¼” bolts)
Symmetric holes on flange

PureGraphite Gasket
(from McMaster-Carr)

1 1/4” ID & 2 5/8” OD
Gasket’s sealing element is raised @ 1 7/8”
Figure B.4: Process Flow Diagram
**Process Flow Diagram Notation**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Regular valve" /></td>
<td>Regular valve;</td>
</tr>
<tr>
<td><img src="image" alt="Back pressure regulator" /></td>
<td>Back pressure regulator;</td>
</tr>
<tr>
<td><img src="image" alt="Regular valve" /></td>
<td>Regular valve;</td>
</tr>
<tr>
<td><img src="image" alt="Front pressure regulator" /></td>
<td>Front pressure regulator;</td>
</tr>
<tr>
<td><img src="image" alt="Mass flow rate controller" /></td>
<td>Mass flow rate controller;</td>
</tr>
<tr>
<td><img src="image" alt="Needle Valve" /></td>
<td>Needle Valve;</td>
</tr>
<tr>
<td><img src="image" alt="Pressure relieve valve" /></td>
<td>Pressure relieve valve;</td>
</tr>
<tr>
<td><img src="image" alt="Check Valve" /></td>
<td>Check Valve;</td>
</tr>
<tr>
<td><img src="image" alt="Filter (7 micro meters)" /></td>
<td>Filter (7 micro meters);</td>
</tr>
<tr>
<td><img src="image" alt="Main flow line (black)" /></td>
<td>Main flow line (black);</td>
</tr>
<tr>
<td><img src="image" alt="GC Sampling Valve" /></td>
<td>GC Sampling Valve;</td>
</tr>
<tr>
<td><img src="image" alt="Heated line (red)" /></td>
<td>Heated line (red);</td>
</tr>
<tr>
<td><img src="image" alt="Temperature indicator" /></td>
<td>Temperature indicator;</td>
</tr>
<tr>
<td><img src="image" alt="Gas sampling line (green)" /></td>
<td>Gas sampling line (green);</td>
</tr>
<tr>
<td><img src="image" alt="Temperature controller" /></td>
<td>Temperature controller;</td>
</tr>
<tr>
<td><img src="image" alt="Cable line (blue)" /></td>
<td>Cable line (blue);</td>
</tr>
<tr>
<td><img src="image" alt="Pressure indicator" /></td>
<td>Pressure indicator;</td>
</tr>
</tbody>
</table>
Table C.1: Effect of pretreatment on a 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ ceramic monolith and metal foam

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>O₂/CO ratio</th>
<th>CO Conversion (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No Pretreatment</td>
<td>After Pretreatment</td>
<td>Pretreatment + re-exposure to air</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 ppi, 12% ρ metal foam support</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>1.0</td>
<td>14.7</td>
<td>83.7</td>
<td>80.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>9.00</td>
<td>55.3</td>
<td>55.4</td>
<td></td>
</tr>
<tr>
<td>170°C</td>
<td>1.0</td>
<td>61.9</td>
<td>67.0</td>
<td>48.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>47.2</td>
<td>54.5</td>
<td>46.8</td>
<td></td>
</tr>
<tr>
<td>400 cpsi ceramic straight-channel monolith support</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100°C</td>
<td>1.0</td>
<td>78.8</td>
<td>85.4</td>
<td>88.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>59.6</td>
<td>52.1</td>
<td>59.4</td>
<td></td>
</tr>
<tr>
<td>170°C</td>
<td>1.0</td>
<td>53.1</td>
<td>57.4</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>58.6</td>
<td>49.0</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Fig. C.1: Effect of pretreatment on (a) CO conversion and (b) CO selectivity as a function of inlet temperature for the 5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 400 cpsi ceramic straight-channel monolith (1% CO inlet concentration, O₂/CO ratio = 1.0, GHSV = 30,000 hr⁻¹)
Table C.2: Comparison of Catalyst Performance for the Ceramic Foam, Metal Monolith, Metal Foam and Ceramic Monolith

(testing conditions: 1.0% CO inlet concentration, \(O_2/CO\) ratio = 0.5)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>GHSV (hr(^{-1}))</th>
<th>Ceramic Foam 20 ppi, 11% density</th>
<th>Metal Monolith 400 cpsi equivalent</th>
<th>“newer” Metal Foam 40 ppi, 4% density</th>
<th>“newer” Ceramic Monolith (400 cpsi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Xco (%)</td>
<td>Sco (%)</td>
<td>Xo₂ (%)</td>
<td>Xco (%)</td>
</tr>
<tr>
<td>80°C</td>
<td>15,000 hr(^{-1})</td>
<td>4.5</td>
<td>40.2</td>
<td>10.6</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>30,000 hr(^{-1})</td>
<td>6.3</td>
<td>40.1</td>
<td>15.0</td>
<td>41.8</td>
</tr>
<tr>
<td>150°C</td>
<td>15,000 hr(^{-1})</td>
<td>31.3</td>
<td>35.6</td>
<td>84.1</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td>30,000 hr(^{-1})</td>
<td>22.2</td>
<td>35.5</td>
<td>60.0</td>
<td>40.2</td>
</tr>
</tbody>
</table>
Figure D.1: Transient effects on the outlet concentrations of (a) CO (enlarged) and (b) O\textsubscript{2} for the 400 cpsi ceramic straight-channel monolith and 20 ppi, 12% ρ metal foam after pretreatment (5 wt% Pt / 0.5 wt% Fe / γ-Al\textsubscript{2}O\textsubscript{3}, 1% CO inlet concentration, O\textsubscript{2}/CO ratio = 1.0, inlet temperature = 109°C, GHSV=30,000 hr\textsuperscript{-1})
Figure D.2: Transient effects on the outlet temperature at an O₂/CO ratio = 0.5 for the 400 cpsi ceramic straight-channel monolith and 20 ppi, 12% ρ metal foam after pretreatment (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, inlet temperature = 109°C, GHSV=30,000 hr⁻¹)
Figure D.3: $O_2/CO$ ratio comparison between the 40 ppi, 4% $\rho$ metal foam and 400 cpsi ceramic monolith (5 wt% Pt / 0.5 wt% Fe / $\gamma$-Al$_2$O$_3$, 1% CO inlet concentration, 0.25-1.0 $O_2/CO$ ratios, 80°C inlet temperature, GHSV=30,000 hr$^{-1}$)
Assumptions

1. First-order kinetics in CO \( r_{CO} = -k_{CO}[CO] \)
2. Isothermal reactor conditions \( k_{CO} \) is constant and not a function of \( T_{in} \)

\[
\begin{align*}
\text{Mass Balance:} & \quad F_{CO, in} = \left(F_{CO, in} + dF_{CO}\right) - r_{CO} dV \\
& \quad F_{CO, in} = \left[F_{CO, in} + d\left[F_{CO, in}(1 - X_{CO})\right]\right] - r_{CO} dV \\
& \quad F_{CO, in} \, dX_{CO} = r_{CO} dV
\end{align*}
\]

\[
\begin{align*}
dF_{CO} & = r_{CO} dV \\
\dot{V}_{CO} \frac{d[CO]}{dV} & = -k_{CO} [CO] \\
d[CO] & = -k_{CO} [CO] \\
\int_{[CO]_o}^{[CO]} \frac{d[CO]}{[CO]} & = -k_{CO} \int_{0}^{t} dt \\
\ln \left( \frac{[CO]}{[CO]_o} \right) & = -k_{CO} t \\
\ln \left( \frac{[CO]_o \left(1 - X_{CO}\right)}{[CO]_o} \right) & = -k_{CO} t \\
\ln (1 - X_{CO}) & = -\frac{k_{CO}}{\text{GHSV}}
\end{align*}
\]

Final Solution:

\[
\ln (1 - X_{CO}) = -\frac{k_{CO}}{\text{GHSV}}
\]

Figure D.4: First-Order CO Isothermal Kinetic Calculations
Nomenclature

\( F_{CO,in} = \) Mass flowrate of CO, inlet
\( F_{CO} = \) Mass flowrate of CO
\( dF_{CO} = \) Differential mass flowrate of CO
\( \dot{V}_{CO} = \) Volumetric Flowrate of CO
\( [CO]_o = \) initial CO concentration
\( \tau = \) residence time

\( r_{CO} = \) Reaction term for CO
\( X_{CO} = \) CO conversion
\( k_{CO} = \) CO reaction rate constant
\( dV = \) Differential Volume
\( [CO] = \) CO concentration
\( \text{GHSV} = \) Gas Hourly Space Velocity

Figure D.4 (continued)

Figure D.5: Effects of GHSV & linear velocity on a 400 cps ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / \( \gamma \)-Al\(_2\)O\(_3\), 1% CO inlet concentration, O\(_2\)/CO ratio = 0.5, 80°C inlet temperature, 10,000-45,000 hr\(^{-1}\) GHSV)
Figure D.6: Effect of linear velocity at constant GHSV on a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 10,000 and 15,000 hr⁻¹ GHSV)
Figure D.7: Effect of GHSV at constant linear velocity on a 400 cpsi ceramic straight-channel monolith (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 5,000-45,000 hr⁻¹ GHSV)
Figure D.8: Schematic drawing of Figure D.7, linear velocity of 21.3 cm/sec (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 400 cpsi ceramic monolith, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 5,000 and 15,000 hr⁻¹ GHSV)
Figure D.9: Schematic drawing of Figure D.7, linear velocity of 64.0 cm/sec (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃ 400 cpsi ceramic monolith, 1% CO inlet concentration, O₂/CO ratio = 0.5, 80°C inlet temperature, 15,000 and 45,000 hr⁻¹ GHSV)

- SV = 45,000: C₀ = 31%, S₀ = 70%, X₀₂ = 43%
- SV = 15,000: C₀ = 75%, S₀ = 70%, X₀₂ = 100%
Table D.1: Comparison of catalyst activity and selectivity for three “identical” 40 ppi, 4% ρ metal foams (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 1.0, 150°C inlet temperature, GHSV=30,000 hr⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Xₙ (%)</th>
<th>Sₙ (%)</th>
<th>X₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Older” Piece</td>
<td>51.3</td>
<td>46.9</td>
<td>104.7</td>
</tr>
<tr>
<td>“Newer” Piece #1</td>
<td>36.9</td>
<td>33.4</td>
<td>105.9</td>
</tr>
<tr>
<td>“Newer” Piece #2</td>
<td>34.5</td>
<td>32.0</td>
<td>103.3</td>
</tr>
</tbody>
</table>

Table D.2: Comparison of catalyst activity and selectivity for three “identical” 400 cpsi ceramic straight-channel monoliths (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, O₂/CO ratio = 1.0, 150°C inlet temperature, GHSV=30,000 hr⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Xₙ (%)</th>
<th>Sₙ (%)</th>
<th>X₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Older” Piece</td>
<td>53.3</td>
<td>54.9</td>
<td>96.1</td>
</tr>
<tr>
<td>“Newer” Piece #1</td>
<td>47.2</td>
<td>42.9</td>
<td>105.4</td>
</tr>
<tr>
<td>“Newer” Piece #2</td>
<td>37.7</td>
<td>34.3</td>
<td>105.2</td>
</tr>
</tbody>
</table>

*: Tₘ = 170°C

Note: This was the only set of operating condition tested for all three pieces of “identical” nominal metal loading catalysts, monolith and foam.
Figure D.10: (a) CO conversion and (b) CO selectivity comparison of the three separate 400 cpsi ceramic straight-channel monoliths (5 wt% Pt / 0.5 wt% Fe / γ-Al₂O₃, 1% CO inlet concentration, 0.25-1.0 O₂/CO ratios, GHSV = 30,000 hr⁻¹, 150°C or 170°C inlet temperature)
Appendix E  Catalyst Characterization Data

Figure E.1: An example of a CO pulse on an uncatalyzed, unwashcoated “blank” metal foam.
Figure E.2: An example of an elongated pulse chemisorption data.

- 5 wt% Pt, 0.5 wt% Fe
- 40 ppi, 4% Pt metal foam
- Pulse run #29
- NDIR read 5 ppm at the end of run
Table E.1: ICP Analysis of Pt, Pt/Fe, and Pt/Ni catalysts washcoated on γ-Al$_2$O$_3$ made in-house or by Environex

Analysis for Kylo bishop and Paul Chin, Chemical Engineering  
Prepared By: Wayne P. Robarge  
Date: July 28, 2002

Results for Fe and Ni are average of duplicate analyses.

<table>
<thead>
<tr>
<th>Lab. ID</th>
<th>Spl. ID</th>
<th>Calculated Composition</th>
<th>Measured Composition</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt (%)</td>
<td>Fe (%)</td>
<td>Ni (%)</td>
</tr>
<tr>
<td>75</td>
<td></td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>76</td>
<td></td>
<td>5</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>77</td>
<td></td>
<td>5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>78</td>
<td></td>
<td>5</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>79</td>
<td></td>
<td>5</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>Environex</td>
<td>0.5</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>81</td>
<td>020000</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>82</td>
<td>020005</td>
<td>2</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>83</td>
<td>020050</td>
<td>2</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>84</td>
<td>005000</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>85</td>
<td>005005</td>
<td>0.5</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>86</td>
<td>005050</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Digestion Procedure:
1) Sample Amount: 0.100 - 0.200 grams
2) React sample with 3 mL of concentrated HF acid in Teflon beaker. Take to dryness.
3) Add 15 mL of aqua regia and allow to refux on hot plate for 30 - 45 minutes.
4) Remove from hot plate and allow to cool. Make to volume in appropriate volumetric flask.
5) Dissolution of sample material is essentially complete except for few fine particles in solution.
6) Elemental analyses were conducted on Perkin-Elmer Model 2000 DV in axial mode.
Table E.2: BET surface area results for pure Pt, Pt/Fe, and Pt/Ni catalysts washcoated on γ-Al₂O₃ made in-house or by Environex

<table>
<thead>
<tr>
<th>Catalyst Composition</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% Pt</td>
<td>wt% Fe</td>
</tr>
<tr>
<td>NC State catalysts made in-house</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Environex catalyst slurry</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Note: The 5% Pt catalysts were tested last. During these runs Kyle Bishop was unable to get consistent readings from the balance. This likely led to the diversity of the results. The 2% Pt and 0.5% Pt catalysts were more representative of the NCSU catalysts.
Appendix F  Matlab Code for Characterization Analysis

% 02-26-04 PTC
% clear all variables in workspace and set numerical format

clear;format short g

% have user get csv file

[fname pname] = uigetfile(...
    {'*.csv','Comma Separated Value (CSV) files (*.csv)'},...
    'Choose a file');

fullname = [pname fname];
xdata_name = 'Time (sec)';
% y01data_name = 'CO #1 Data';
y02data_name = 'CO #2 Data';
Tdata_name = 'Temperature Data';

% read in columns 1, 2, & 3 into matlab variables (ignoring the first 3 lines)

[SampleTimeTemp co_02Temp TinTemp] =
textread(fullname,'%n%n%n%*[^
]','delimiter','.',',','headerlines',3);

done = 0;
i = 1;
while ~done
    i = i + 1;
    if (i == length(SampleTimeTemp)) | (SampleTimeTemp(i+1) < SampleTimeTemp(i))
        done = 1;
    end
end

SampleTime = SampleTimeTemp(1:i);

% co_01 = co_01Temp(1:i);
co_02 = co_02Temp(1:i);
Tin = TinTemp(1:i);

% Average temperature data
Tavg = mean(Tin);

% Eliminate all negative values (True or false)
ElimNegVals = 0; %if set to 0 then we will not elim neg vals
if ElimNegVals
    % co_01 = co_01.*(co_01>0);
    co_02 = co_02.*(co_02>0);
end
%% create baseline at zero for plot
zero = zeros(1,i);

%% plot the data in one graph ( 'b--' = blue dashed line, 'g-' = green solid line, 'r-' = red dashed line)
plot(SampleTime,co_02,'g-',SampleTime,zero,'r-','LineWidth',2);
legend(y02data_name,0);
xlabel(xdata_name);
ylabel('Concentration (ppm)');
title('CO concentration in ppm');

%% set X-axis ticks to 300 and turns on Grid
set(gca,'XTick', [0:300:5400],'XGrid','on','GridLineStyle','-.');

%% Trapezoid Method (for comparison to the spline method)

%% TrapInt_Data01 = trapz(SampleTime,co_01);
TrapInt_Data02 = trapz(SampleTime,co_02);

%% display trap int results for all data in file
fprintf('
Total Area for range of data (by trapazoid method)
')
fprintf('%s = %g
',y01data_name,TrapInt_Data01);
fprintf('%s = %g

',y02data_name,TrapInt_Data02);
fprintf('%s = %g

','Average Reactor Temperature',Tavg);
% User Input

fprintf('Enter in range of integration\n')

min_val = input('input lower value: ');

max_val = input('input upper value: ');

% Spline method (ultimately uses Trapizoid Method)

StepSize = 0.001;

% make sure user inputed value are within data range (if not, redefine)

min_time = min(SampleTime);

if min_val > min_time
    min_time = min_val;
end

max_time = max(SampleTime);

if max_val < max_time
    max_time = max_val;
end

% Setup new (evenly spaced) domain for spline interpolation

x_data = [min_time:StepSize:max_time];
% do spline interpolation
% y01_data = spline(SampleTime,co_01,x_data);
y02_data = spline(SampleTime,co_02,x_data);

% do trap int under interp/spline data
% SplineInt_Data01 = trapz(x_data,y01_data);
SplineInt_Data02 = trapz(x_data,y02_data);

% display results
fprintf('
Total Area for selected range (by spline/trapazoid method)\n')

% fprintf('%s = %g\n',y01data_name,SplineInt_Data01);
fprintf('%s = %g\n',y02data_name,SplineInt_Data02);