2018

Development Of Bimetallic Catalysts For Dry Reforming Of Methane And Hydrogenation Of Succinic Acid

Jayson Michael Keels  
University of South Carolina

Follow this and additional works at: https://scholarcommons.sc.edu/etd

Part of the Chemical Engineering Commons

Recommended Citation  

This Open Access Dissertation is brought to you by Scholar Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact dillarda@mailbox.sc.edu.
DEVELOPMENT OF BIMETALLIC CATALYSTS FOR DRY REFORMING OF METHANE AND HYDROGENATION OF SUCCINIC ACID

by

Jayson Michael Keels

Bachelor of Science
University of South Carolina, 2014

Submitted in Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy in
Chemical Engineering
College of Engineering and Computing
University of South Carolina
2018

Accepted by:

John R. Regalbuto, Major Professor
John R. Monnier, Major Professor
Jochen Lauterbach, Committee Member
Donna A. Chen, Committee Member
John W. Weidner, Committee Member
Cheryl L. Addy, Vice Provost and Dean of the Graduate School
DEDICATION

To my amazing wife, Anna.

I could not have gone through this program without your unwavering love, patience, and support. Thank you for pretending to care about nanoparticles and dry reforming of methane.

I love you dearly.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisors Dr. Regalbuto and Dr. Monnier for giving me the opportunity to work in their groups and develop a very diverse and unique set of skills. I would like to thank Dr. Regalbuto for teaching me how to become a better scientist and independent thinker. He is a great role model in life, family, faith, and work. I would like to thank Dr. Monnier for all the invaluable lessons on the practical aspects of research and catalysis. His inspiring stories and his training have given me a major head start for an industrial career in process development.

I would like to thank my committee members Dr. Chris Williams, Dr. Frank Chen, Dr. Jochen Lauterbach and Dr. Donna Chen for their insight into my research and their review of my work.

I would also like to acknowledge the collaborators with whom I have worked over these years. Dr. Jadid Samad from our own group trained me on strong electrostatic adsorption methodology. Dr. Frank Chen and Dr. Libin Lei from Department of Mechanical Engineering here at USC gave me the chance to work with them on solid oxide fuel cells. Dr. Changhai Liang and Dr. Xiao Chen from Dalian University of Technology welcomed me into their lab for three months for the work on hydrogenation of succinic acid. For that same project, Dr. Stavros Karakalos from our department provided XPS expertise. Special thanks to Ben Egelske for his help and major contributions to the dry reforming project.
Also, Dr. Alan Nicholls from University of Illinois at Chicago provided STEM imaging for that project. It was a pleasure to work with Dr. Weijian Diao on epoxidation of ethylene.

Finally, I would like to thank my family for their encouragement and support. I am especially thankful for my parents, Mike and Kim Keels, who have done so much to get me to where I am today. From an early age, they instilled in me the importance of education and perseverance, which I cannot thank them enough for. Also, I cannot express enough gratitude for my wife, Anna, who inspires me to be a better person and to work hard. She has been very understanding throughout this program and has always been there for me. I could not have done it without her. Also, I must acknowledge our precious daughter, Addison. She has brought so much joy to our lives and has made writing this dissertation so much easier.

*This is the day that the LORD has made; let us rejoice and be glad in it.*

- Psalm 118:24


**ABSTRACT**

Advances in natural gas recovery have greatly impacted the global economy; the abundant supply of gas has revealed new opportunities and challenges in a wide range of markets within the fuels and chemicals industries. One such opportunity exists with the overabundance of gas from remote wells that is flared or emitted because of the high costs associated with transportation of a chemical with such a high molar volume. A possible solution is an on-site process to convert gas to higher value chemicals that are liquid at standard conditions, and can more easily be transported. As a first step, CO$_2$ from the process may be utilized to convert CH$_4$, the main component of natural gas, to synthesis gas through dry reforming of methane (DRM). Synthesis gas, a mixture of H$_2$ and CO, may then be converted to liquid chemicals through a number of different reactions. In this study, we prepared a series of Pt-promoted Ni bimetallic catalysts by electroless deposition (ED) and evaluated them for DRM. An enhancement in activity was observed with the addition of an intermediate loading of Pt, which is associated with the formation of a NiPt alloy phase. However, the overall stability decreases with increasing Pt loading because of the high rate of carbon formation. Post-reaction characterization reveals phase separation of the alloy at high temperatures.

Another opportunity arises out of cheap natural gas as petrochemical producers shift from oil-based naphtha cracking to natural gas cracking for ethylene production.
Since gas cracking produces none of the heavier hydrocarbon co-products that naphtha cracking does, the result is a growing gap in the supply of C₄ building block chemicals. One possible alternative is to utilize biomass-based compounds, such as succinic acid (SAC), which is a C₄-diacid. To reach many of the end markets that succinic acid is used as feed, it is necessary to hydrogenate it to downstream high-performance chemicals such as γ-butyrolactone (GBL), 1,4-butanediol (BDO), and tetrahydrofuran (THF). In this work, we evaluated a series of Ir-Re/C bimetallic catalysts prepared by strong electrostatic adsorption (SEA) for aqueous phase hydrogenation of SAC. Activity measurements show remarkable synergistic effects, forming a volcano-shaped plot over a range of bulk Re mole fractions with a peak at a fraction of 0.4 – 0.5, which corresponds to a 20-fold enhancement of activity over either monometallic catalyst. This intermediate catalyst composition exhibiting optimum activity strongly suggests a bifunctional effect. Through a consecutive reaction pathway with GBL as an intermediate, the main product is THF with 60 – 75% selectivity. Butanol formation is minimized with decreasing Re mole fraction.
# Table of Contents

Dedication .......................................................................................................................... iii

Acknowledgements ........................................................................................................ iv

Abstract ............................................................................................................................ vi

List of Tables ...................................................................................................................... x

List of Figures ...................................................................................................................... xi

Chapter 1 Background and Introduction ......................................................................... 1
  1.1 Shale Boom ................................................................................................................ 2
  1.2 Natural Gas Utilization: Dry Reforming of Methane .............................................. 3
  1.3 C₄ Hydrocarbon Supply: Hydrogenation of Succinic Acid .................................... 4
  1.4 Dissertation Layout .................................................................................................. 5

Chapter 2 Design of Bimetallic Catalysts ....................................................................... 6
  2.1 Overview of Catalyst Development ......................................................................... 7
  2.2 Bimetallic Catalysts .................................................................................................. 7
  2.3 Catalyst Preparation Methods ................................................................................ 9

Chapter 3 Dry Reforming of Methane with Pt-Promoted Ni Catalysts Prepared by
Electroless Deposition ..................................................................................................... 25
  3.1 Abstract .................................................................................................................... 26
  3.2 Introduction ................................................................................................................ 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Experimental</td>
<td>35</td>
</tr>
<tr>
<td>3.4</td>
<td>Results and Discussion</td>
<td>39</td>
</tr>
<tr>
<td>3.5</td>
<td>Conclusion</td>
<td>60</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Aqueous-Phase Hydrogenation of Succinic Acid Using Bimetallic Ir-Re/C</td>
<td>62</td>
</tr>
<tr>
<td>4.1</td>
<td>Abstract</td>
<td>63</td>
</tr>
<tr>
<td>4.2</td>
<td>Introduction</td>
<td>63</td>
</tr>
<tr>
<td>4.3</td>
<td>Experimental Section</td>
<td>66</td>
</tr>
<tr>
<td>4.4</td>
<td>Results and Discussion</td>
<td>69</td>
</tr>
<tr>
<td>4.5</td>
<td>Conclusions</td>
<td>85</td>
</tr>
<tr>
<td>4.6</td>
<td>Acknowledgements</td>
<td>85</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Summary and Conclusions</td>
<td>86</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>Appendix A</td>
<td>Supplementary Information for Dry Reforming of Methane</td>
<td>105</td>
</tr>
<tr>
<td>Appendix B</td>
<td>Supplementary Information for Hydrogenation of Succinic Acid</td>
<td>109</td>
</tr>
<tr>
<td>Appendix C</td>
<td>Permission to Reprint</td>
<td>111</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 2.1: Common metal salts for electroless deposition. ................................................. 21

Table 3.1: Summary of Ni-Pt/Al₂O₃ catalysts. ........................................................................ 40

Table 3.2: Summary of kinetic evaluation. ............................................................................. 44

Table 3.3: Summary of deactivation in DRM at 700°C. .......................................................... 49

Table 3.4: Summary of particle sizes estimated by XRD, sizes in nm. ................................. 59

Table 4.1: Catalyst compositions, Re surface coverage on Ir calculated from chemisorption, reaction rates. .................................................................................................. 70

Table B.1: Ir particle size comparison for 1.5% Ir/C, all sizes in nm. ................................. 110
LIST OF FIGURES

Figure 1.1: U.S. production of oil and natural gas. ................................................................. 2

Figure 2.1: Illustration of bimetallic impregnation methods.................................................. 11

Figure 2.2: Strong electrostatic adsorption mechanism......................................................... 12

Figure 2.3: Close packed monolayer of PtCl$_6^{2-}$ with hydration sheath as a result of strong
electrostatic adsorption........................................................................................................... 12

Figure 2.4: pH shift at high surface loading (50,000 m$^2$/L) for
PZC determination of γ-Al$_2$O$_3$. ......................................................................................... 14

Figure 2.5: (a) pH shift with and without metal (control); (b) metal uptake survey of
H$_2$PtCl$_6$ on Al$_2$O$_3$. Surface loading = 500 m$^2$/L.............................................................. 15

Figure 2.6: Schematic of selective adsorption onto oxides with different PZCs [28].
Reprinted with permission........................................................................................................ 16

Figure 2.7: Mechanism of electroless deposition..................................................................... 19

Figure 2.8: Catalytic activity of metals for anodic oxidation. .................................................. 22

Figure 3.1: Thermodynamic equilibrium conversion for DRM calculated by minimization
of Gibbs free energy with DWSIM process simulator software. Varying partial pressures
of CH$_4$ with equimolar amounts of CO$_2$. ........................................................................... 28

Figure 3.2: DRM near equilibrium conversion of 5 wt% Ni/Al$_2$O$_3$.
CH$_4$/CO$_2$/He = 1/1/1, GHSV = 1300 h$^{-1}$......................................................................... 33

Figure 3.3: (a) Image of catalyst bed after ~40 h of reaction near equilibrium conversion
and (b) representative XRD patterns. Illustrates significant
coke-formation gradient across catalyst bed. ......................................................................... 33
Figure 3.4: DRM at ~50% of equilibrium conversion of 5 wt% Ni/Al₂O₃. CH₄/CO₂/He = 1/1/1, GHSV = 80,000 – 90,000 h⁻¹. .................................................................................................................. 34

Figure 3.5: Schematic of reactor system used for DRM. .......................................................... 39

Figure 3.6: ED results for varying theoretical Pt coverages on Ni. DMAB/EN/Pt = 5/4/1, 70°C. .................................................................................................................. 41

Figure 3.7: Kinetic evaluation of Ni@0.075Pt. CH₄/CO₂/He = 1/1/2, P = 1 atm, 120 – 200 sccm. .................................................................................................................. 42

Figure 3.8: (a) Arrhenius plots of Ni-Pt catalysts and (b) rates vs. Pt/Ni atomic ratio, CH₄/CO₂/He = 1/1/2, P = 1 atm. .................................................................................................. 43

Figure 3.9: Compensation plot for Ni-Pt catalysts. ................................................................ 45

Figure 3.10: H₂/CO product ratio as a function of CH₄ conversion. CH₄/CO₂/He = 1/1/2, P = 1 atm. ............................................................................................................. 45

Figure 3.11: DRM stability at 700°C, CH₄/CO₂/He = 1/1/2. Flowrates adjusted after 20 h to increase CH₄ conversion to ~40%. ............................................................................ 46

Figure 3.12: DRM deactivation rates based on pseudo-steady state conditions. 700°C, CH₄/CO₂/He = 1/1/2, P = 1 atm. ................................................................................................. 48

Figure 3.13: TPO-coke burn-off after reaction. 20 sccm of 10% O₂/He, ramp rate = 10°C. Normalized mass spec signal for CO₂ (m/z=44). ................................................................. 49

Figure 3.14: Representative STEM image of (a) Ni@0.7Pt and (b) Ni@1.0Pt after ~100 h of reaction time. 550 – 650°C, CH₄/CO₂/He = 1/1/2. .................................................. 50

Figure 3.15: TPR of Ni-Pt catalysts after oxidation at 300°C. Ramp rate = 10°C/min. .......................................................... 51

Figure 3.16: XRD patterns of Ni-Pt samples (a) after preparation (200°C heat treatment) and (b) after 20 h time online (700°C, CH₄/CO₂/He = 1/1/2, P = 1 atm). ....................... 53

Figure 3.17: Ni-Pt binary phase diagram [72]. ............................................................... 54

Figure 3.18: STEM HAADF micrographs and XEDS maps of fresh (a) – (d) Ni@0.7Pt and (e) – (h) Ni@1.0Pt. After 200°C heat treatment under H₂. ........................................ 55
Figure 3.19: Deconvolution of metal peaks after Al$_2$O$_3$ subtraction from Ni@0.7Pt (a) after heat treatment at 200°C under H$_2$ and (b) after 20 h time online at 700°C, CH$_4$/CO$_2$/He = 1,1,2, P = 1 atm. ........................................................................................................... 56

Figure 3.20: STEM HAADF micrographs and XEDS maps of Ni@0.7Pt after ~100 h time on line at 700°C, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm. ........................................................................................................... 57

Figure 3.21: (a) Representative STEM micrograph and (b) particle size distribution of 5% Ni/Al$_2$O$_3$. ........................................................................................................................................... 60

Figure 4.1: (a) pH shift of impregnation solution for metal uptake surveys of (b) single metals using IrCl$_6^{2-}$ and ReO$_4^-$ and (c) co-impregnation using both metals on activated carbon (surface area = 1400 m$^2$/g), surface loading = 1000 m$^2$/L, control/metal-free (black squares), IrCl$_6^{2-}$ (red circles), ReO$_4^-$ (blue triangle), IrCl$_6^{2-}$/ReO$_4^-$ (green diamonds). ........................................................................................................... 72

Figure 4.2. H$_2$-TPR of catalysts after exposure to air at 25 °C showing normalized mass spec signal of H$_2$O (m/e = 18), temperature ramp rate = 5 °C, “AC” corresponds to the carbon support alone........................................................................................................... 73

Figure 4.3: (a) XRD of catalysts after reduction, scan speed = 1°/min, (b) deconvolution of 1.5% Ir/C after background subtraction with fitted peaks, “AC” corresponds to the carbon support alone........................................................................................................... 75

Figure 4.4: Re coverage on Ir determined by H$_2$-chemisorption........................................................................... 76

Figure 4.5: (a) Representative STEM micrograph and (b) particle size distribution of 1.5% Ir/C, D$_p$ = 1.7 ± 0.04 nm........................................................................................................... 77

Figure 4.6: Re 4f spectra of (a) IrRe/C and (b) 1.5% Re/C, Ir 4f spectra of (c) IrRe/C and (d) 1.5% Ir/C before and after in-situ reduction at 300 °C. ........................................................................... 78

Figure 4.7: (a) Succinic acid concentrations versus reaction time, (b) linearization of concentration versus time showing first order dependence, 1.5% Ir/C (black circles), IrRe$_{0.3}$/C (gray stars), IrRe$_{0.5}$/C (orange plus), IrRe$_{0.6}$/C (pink diamond), IrRe/C (blue triangle down), IrRe$_2$ (green triangle up), 1.5% Re/C (red squares)........................................................................... 80

Figure 4.8: Normalized reaction rates at 10% conversion of SAC versus bulk Re loading, compared to 50-50 physical mixture of 1.5% Ir/C and 1.5% Re/C. ........................................................................... 81
Figure 4.9: (a) GBL and (b) THF concentrations versus reaction time, 1.5% Ir/C (black circles), IrRe$_{0.3}$/C (gray stars), IrRe$_{0.5}$/C (orange plus), IrRe$_{0.6}$/C (pink diamond), IrRe/C (blue triangle down), IrRe$_2$ (green triangle up), 1.5% Re/C (red squares). .......................... 83

Figure 4.10: Product distribution after 10 h of reaction time. .......................................................... 84

Figure A.1: Deconvoluted XRD patterns of Ni@0.075Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm................................................................. 105

Figure A.2: Deconvoluted XRD patterns of Ni@0.4Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm. ...... 106

Figure A.3: Deconvoluted XRD patterns of Ni@0.7Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm. ...... 106

Figure A.4: Deconvoluted XRD patterns of Ni@1.0Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm. ...... 107

Figure A.5: Deconvoluted XRD patterns of 3%Pt/Al$_2$O$_3$ (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm................................................................. 107

Figure A.6: STEM HAADF micrographs and XEDS maps of Ni@0.4Pt before (a)-(d) and after (e)-(h) reaction for ~100 h time on line 500-600°C, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm................................................................. 108

Figure B.1: pH shift of activated carbon in solution for PZC determination, surface loading = 50,000 m$^2$ L$^{-1}$........................................................................................................................................ 109

Figure B.2: H$_2$-chemisorption on 1.5% Re/C at varying temperatures, catalyst was reduced at 300 °C for 2 h, degassed under Ar flow for 4 h, cooled to chemisorption temperature, exposed to pulses of 10% H$_2$/Ar, then degassed and repeated at varying temperatures. .............................................................................. 110
CHAPTER 1

BACKGROUND AND INTRODUCTION
1.1 Shale Boom

Over the past decade, oil and natural gas production in the United States have exhibited tremendous growth as a result of increased production of unconventional recourses. This growth is largely attributed to the technological advancements in hydraulic fracturing and horizontal drilling for oil and gas extraction from shale reserves [1-4], thus it is often referred to as the shale boom. Figure 1.1 depicts annual oil and natural gas production in the U.S. from 2000 to 2025, which clearly illustrates that the total increase is attributed to tight oil and shale gas, both products of unconventional recovery methods. In 2005, shale oil and gas only accounted for 10.7% and 8.6% of total production, but jumped to an astonishing 56.5% and 56.6% respectively in 2015.

![Figure 1.1: U.S. production of oil and natural gas.](image)

The U.S. shale boom has had a significant impact on both domestic and global economies. For example, while there are currently only 3 other countries (Canada, Argentina, and China) producing natural gas from shale, a number of countries are in the process of developing such technology and infrastructure to attempt to replicate the
economic growth [1, 2]. Moreover, in 2013, the U.S. surpassed Saudi Arabia as the largest petroleum producer in the world and has been the top natural gas producer since 2009 [5]. 2017 marks the first time since at least the 1950’s that the U.S. is a net exporter of gas and is expected to be a net exporter of oil by 2020 [2, 3, 6]. This has spurred great interest for investment not only in the oil and natural gas industries, but also in chemicals and petrochemicals industries [1, 2]. As of 2016, $164B of investments have been made or committed to build shale-driven chemical projects in the U.S., most of which are grassroots [2]. Overall, the abundant supply of natural gas has revealed many opportunities to develop chemical processes for both new technologies and for improvements on old ones.

1.2 Natural Gas Utilization: Dry Reforming of Methane

One opportunity that the shale revolution has presented is the overabundance of gas from remote oil reserves. The advancements in oil extraction have allowed the deployment of such technologies to remote locations where it is uneconomical to transport the associated gas [7]. This leads companies to flare the gas, which could otherwise be utilized. Elvidge et al. have estimated that gas flaring represents 3.5% of the global natural gas consumption and 19.8% of U.S. consumption [8]. Efficient utilization of this gas would not only provide a significant contribution to the nation’s energy portfolio, but would also provide a significant environmental benefit, as emissions would be avoided. The solution to this problem could also be applied to gas reserves in remote
locations, which remain untapped because of the same reason of high transportation costs [7].

A possibility to exploit this unutilized resource is to employ gas-to-liquids (GTL) processes to upgrade methane to higher value fuels and chemicals. The liquid products could then be used on site or shipped to market. GTL processes involve a series of chemical conversions that typically start with methane reforming. The work in Chapter 3 focuses on the development of a bimetallic catalyst for dry reforming of methane (DRM), which utilizes CO₂ as a co-feed with CH₄. We explored the effects that Pt-promotion of Ni catalysts have on activity, selectivity, and stability.

1.3 C₄ Hydrocarbon Supply: Hydrogenation of Succinic Acid

Another opportunity arises because of the shift to produce petrochemicals from natural gas instead of from oil. Traditionally, C₄ platform chemicals have been derived as a co-product of naphtha cracking for production of ethylene, which is the largest petrochemical feedstock. However, cheap natural gas is attracting petrochemical producers to shift their ethylene plant feedstock from naphtha to natural gas, which produces almost none of the longer chain hydrocarbon co-products [9]. This shift, coupled with the increasing demand of C₄ products due to the growing middle class in emerging economies, will ultimately create a supply gap in these C₄ building blocks.

A possible alternative to fill the C₄ supply gap is to utilize biomass. One particular bio-chemical that has been identified as commercially viable is succinic acid (SAC), which is a C₄-diacid [10]. In order to reach the end markets for which succinic acid is used, it is
necessary to hydrogenate it to downstream chemicals such as tetrahydrofuran (THF). The work in Chapter 4 focuses on the development of a bimetallic catalyst for aqueous phase hydrogenation of SAC. Here, we explored the performance of Ir-Re catalysts with varying compositions.

1.4 Dissertation Layout

Both dry reforming of methane and hydrogenation of succinic acid represent opportunities for the development of new processes as a result of the shale boom. Both works focus specifically on the development of supported bimetallic catalysts using novel preparation techniques, which will be discussed in more detail in the following section.
CHAPTER 2

DESIGN OF BIMETALLIC CATALYSTS
2.1 Overview of Catalyst Development

The development of catalytic processes, both grassroots and retrofit, typically start with the design and preparation of the catalyst. In particular, the development of heterogeneous catalysts is of interest as they account for over 90% of the chemicals and fuels produced worldwide [11]. Heterogeneous catalysts typically consist of transition metal nanoparticles that are anchored to a critically porous, inert material, usually an oxide or carbon. Characteristics of a catalyst such as type of metal, metal loading, metal particle size, type of support, porosity, and surface area are all factors that need consideration when designing a catalyst. Moreover, there are several methods of preparation and each one can have a significant impact on the resulting performance. Catalytic activity, selectivity, and stability are the primary response variables used to evaluate the performance of a catalyst.

2.2 Bimetallic Catalysts

In recent decades, there have been tremendous improvements to the preparation of supported monometallic catalysts, however bimetallic catalysts frequently can offer even further enhancements in performance. These enhancements may be attributed to the interaction between the two metals as a result of all or any combination of three effects: electronic effect, ensemble effect, and bifunctional effect [12-14]. Electronic effects occur when there is e\textsuperscript{-} transfer from one metal to the other. Alteration of the e\textsuperscript{-} density at the surface can have significant effects on adsorption/desorption of the
reaction species. An example of this is the effect of Re on Cs-Ag catalysts for the selective oxidation of ethylene to produce ethylene oxide [15]. The presence of Re has been demonstrated to increase the Ag 3d binding energy, which makes the active Ag site more e\textsuperscript{-} deficient. This in turn facilitates the electrophilic addition of dissociatively adsorbed O species to the C = C double bond, ultimately enhancing selectivity. Ensemble effect refers to the alteration of the size of active site by addition of a secondary metal to allow desired reactions while inhibiting undesired reactions. In certain situations, reaction selectivity is a strong function of ensemble size where non-selective reactions occur on large ensembles and desired reactions occur on smaller ensembles. In this case, it is beneficial to break-up large ensembles of the active species with islands of a secondary metal, which is sometimes inert. An example of this is the partial coverage of Pd catalysts by inert metal such as Au, Ag, or Cu for hydrogenation of acetylene [16, 17]. Pd alone is highly active for this reaction, however large Pd ensembles adsorb both reactant and products too strongly, leading to low selectivity. A second metal to break up the Pd ensembles has been demonstrated to significantly enhance selectivity. Finally, a bifunctional effect occurs when two different metals are active for two different reactions or reaction events. Bifunctional catalysts offer many potential opportunities as they can be versatile and applied to a wide range of reactions. However, in many cases, close proximity of the two metals with equal amounts of surface exposure is crucial since the mechanism of a bifunctional system typically involves a reaction intermediate that must interact with both metals in parallel. For example, Rodriguez et al. demonstrated the optimization of activity for glycerol dehydrogenation over Au-Pd catalysts [14]. Activity was maximized
with intermediate surface coverages of Au on Pd due to activation of the reaction intermediate (Au function) and the subsequent dehydrogenation (Pd function).

2.3 Catalyst Preparation Methods

As previously mentioned, the method of catalyst preparation can have a significant impact on the performance. It is important to understand the performance requirements for the catalyst when considering the preparation method to use. Thus, catalyst development is often an iterative process. Although there are plenty of exceptions, one of the most common goals of bimetallic catalyst preparation is to achieve high dispersion with the two metals in close contact. High dispersion maximizes metal utilization while metal proximity maximizes promotional effects. Here, we will discuss methods of preparation used in this work.

2.3.1 Impregnation

Impregnation is by far the simplest and most common method of preparation for both monometallic and bimetallic catalysts. Impregnation is accomplished by contact of metal precursor solutions with a porous support. Subsequently, the finished catalyst is formed after drying, calcination and/or reduction. There are two types of impregnation: incipient wetness impregnation (or dry impregnation, DI) and wet impregnation (WI). DI is a method used widely in industry where the impregnation solution is prepared with a volume that is equal to the pore volume of the support. When contacted, the impregnation solution containing metal ions fills the pores of the support through
convection and capillary action. This method is beneficial because it is simple to employ, it results in precise metal loading, and it does not require separation of the catalyst from excess solution. However, this method does not ensure interaction between the metal precursor and the support, which often leads to large particles with a broad size distribution. On the other hand, WI is performed with a large excess of solution. This results in improved mixing and more even distribution of metal ions throughout the catalyst. However, interaction between the metal ions and the support are still not ensured. Further, the catalyst must be filtered from the excess solution, so un-adsorbed metal ions will be carried out with the filtrate.

Impregnation, both DI and WI, is widely employed for bimetallic catalyst preparation using two different procedural methods: co-impregnation and sequential impregnation. As illustrated in Figure 2.1, co-impregnation is a single-step process in which the impregnation solution contains both metal precursors when contacted with the support. Conversely, sequential impregnation is a two-step process where the impregnation of one metal is followed by the impregnation of the second metal. After the first impregnation, the catalyst is dried and calcined/reduced to prevent dissolution of the precursor during the second impregnation step. The main disadvantages of preparing bimetallic catalysts with these procedures is that there is no control over the composition of the particles. This means that both bimetallic and monometallic particles will be formed and there will not necessarily be strong interactions between the two metals.
Thus, any promotional effect that may exist between two metals may not be realized when these preparation methods are employed.

2.3.2 Strong Electrostatic Adsorption

A related method that has significantly more control over metal-support and metal-metal interaction is strong electrostatic adsorption (SEA) [18, 19]. SEA is differentiated from simple impregnation because it accounts for the charge of the support surface as a function of pH. The underlying principle is that oxide support materials contain naturally occurring terminal hydroxyl species in solution that protonate or deprotonate, depending on the acidity of the solution. This also applies to carbon supports since carbon surfaces are typically terminated by an assortment of functional groups that can also be protonated or deprotonated. Every material has a characteristic point of zero charge (PZC), which is a pH at which the functional groups are neutral. As illustrated in Figure 2.2, when the pH is less than the PZC, the functional groups will
protonate, which results in a positively charged surface that can readily adsorb anionic metal complexes, such as [PtCl$_6$]$^{2-}$. Conversely, when the pH is less than the PZC, the functional groups will deprotonate, which results in a negatively charged surface that can readily adsorb cationic metal complexes, such as [(NH$_3$)$_4$Pt]$^{2+}$. At an optimal pH, the strong electrostatic interaction will result in a close packed monolayer of metal complexes with retained hydration sheaths that create spacing of the complexes, as depicted in Figure 2.3. When dried and reduced, the dispersion of the metal is preserved and very small (typically 1-2 nm) particles are formed.
SEA is very advantageous as it is highly reproducible, simple, and it produces highly dispersed metal particles. One of the drawbacks is that only one monolayer of metal precursor is adsorbed at once, so if a higher weight loading is required, then multiple cycles of SEA must be performed. Another disadvantage is that the optimal pH must be determined, which requires a number of additional experiments as explained here.

The optimal pH is typically far away from the PZC of the support. That is, if the PZC is in the acidic region, then the electrostatic interaction should be maximized with a metal cation in the basic region. Thus, in order to choose a cationic metal precursor versus an anionic one, it is necessary to determine the PZC of the support. Noh and Schwarz demonstrated that the PZC may be determined via the measurement of solution pH after contact with sufficiently large amounts of support surface [20]. This is because the PZC is the pH at which the concentration of protons in solution has equilibrated with the concentration of protons on the surface. Therefore, as the amount of surface in solution is increased, the pH will approach the PZC. Regalbuto has refined this idea and has developed a comprehensive experimental protocol for PZC determination [18, 21-23]. According to Regalbuto’s approach, which is shown in Figure 2.4, multiple solutions are prepared with varying pH values before being contacted with the support. The equilibrium pH is plotted as a function of initial pH and the PZC reveals itself as a plateau. An important metric that is used for comparison across experiments is surface loading, which is the amount of support surface per volume of precursor solution and is calculated by the equation below.
Surface Loading \( \left( \frac{m^2}{L} \right) = \frac{\text{support surface area} \left( \frac{m^2}{g} \right) \times \text{mass of support (g)}}{\text{volume of precursor solution (L)}} \)

Typically, a surface loading of at least 50,000 m\(^2\)/L may be employed to accurately determine the PZC. In Figure 2.4, the PZC of γ-Al\(_2\)O\(_3\) was determined to be 8.1, which is slightly basic. Therefore, in this case, a metal anionic precursor, such as PtCl\(_6^{2-}\), is favorable.

![Figure 2.4: pH shift at high surface loading (50,000 m\(^2\)/L) for PZC determination of γ-Al\(_2\)O\(_3\).](image)

The next step is to determine the pH of optimal electrostatic interaction, which is achieved via measurement of metal uptake across a range of equilibrium pH values, such as in Figure 2.5. In the PtCl\(_6^{2-}\)/Al\(_2\)O\(_3\) example, multiple solutions containing H\(_2\)PtCl\(_6\) are pH-adjusted before contact with Al\(_2\)O\(_3\) support. The pH and metal concentrations of the solution are measured before and after the addition of the support. Here, the metal uptake is calculated by the difference in concentrations before and after the addition of the support; the units are given as µmol of metal adsorbed per m\(^2\) of support. The uptake
survey shows that there is hardly any Pt uptake near the PZC of Al$_2$O$_3$, which is expected since there should not be any electrostatic interaction. As the equilibrium pH moves away from the PZC, the uptake increases until a pH of 4 is reached, beyond which it begins to fall off. This is due to the ionic strength defect – inhibition of metal complex adsorption due to the over-abundance of ions in solution [18, 24]. For enhanced control, uptake surveys are typically done with a low surface loading – between 500 and 1,000 m$^2$/L – to minimize the pH shift from the support. However, high surface loadings may be used if the control pH shift curve (without metal) is consulted to estimate the equilibrium pH. In fact, the same principles and methods may be applied to a dry impregnation version of SEA, called charged enhance dry impregnation (CEDI) [18, 25, 26].

Similar to simple impregnation, SEA may also be applied to bimetallic catalysts via either co-SEA or sequential SEA [27]. For co-SEA, a preparation solution that contains both metal precursors is pH-adjusted, then contacted with the support. The result is very small, highly dispersed particles that consist of a well-mixed alloy of the two metals [19, 27]. Sequential SEA can be employed to produce core-shell particles given that the core metal

Figure 2.5: (a) pH shift with and without metal (control); (b) metal uptake survey of H$_2$PtCl$_6$ on Al$_2$O$_3$. Surface loading = 500 m$^2$/L.
has a very different PZC in its oxidized state than the support material [18, 27, 28]. This is accomplished by adsorption of the core metal via SEA, which is followed by drying and calcination to form a supported metal oxide. The shell metal can then be selectively adsorbed onto the core metal oxide when the pH is between the PZC of the support and the core metal oxide. A hypothetical example of this is a Co@Pt/SiO₂ catalyst, where Pt is selectively deposited onto Co₃O₄, which is previously supported on SiO₂. SiO₂ has a PZC of ~4 [18], while Co₃O₄ has a PZC of ~8 [28], as depicted in Figure 2.6. A Pt anionic complex will electrostatically adsorb to Co₃O₄ below a pH of 8, but it will also adsorb to SiO₂ below a pH of 4. Therefore, if the equilibrium pH is maintained

![Figure 2.6: Schematic of selective adsorption onto oxides with different PZCs [28]. Reprinted with permission.](image-url)
between 4 and 8, the Pt anion will be repulsed by the SiO$_2$ and attracted to the Co$_3$O$_4$ surface. The resulting catalyst can then be dried and reduced to form Co@Pt bimetallic particles.

In summary, SEA is simple and produces highly dispersed and well distributed particles. In the case of bimetallic catalysts, the particles are evenly distributed with the metals in close contact. However, additional experiments are needed to determine the optimal preparation variables.

2.3.3 Electroless Deposition

Electroless deposition (ED) is a process in which a metal salt in an aqueous solution is reduced and deposited onto a pre-existing metal by chemical means. Here, chemical means, refers to a driving force that is a result of either a difference in reduction potentials of two metals, or a water-soluble chemical reducing agent. ED is differentiated from electroplating because it does not require the use of an external electrical current [29]. This process is commonly known as electroless plating and has widespread use throughout industry in the manufacturing of printed circuits, semiconductors, batteries, medical devices, and corrosion resistant materials [29, 30]. One major advantage to ED, is that it allows selective deposition of thin metal films onto catalyzed surfaces [29]. Because of this, it is uniquely applicable for synthesis of bimetallic core-shell catalysts. Electroless deposition may be divided into three different categories: displacement deposition, contact deposition, and catalytic/autocatalytic deposition.
Displacement deposition, also known as galvanic displacement, is a process in which the reduction of a secondary metal precursor in solution is driven by the lower reduction potential of a primary base metal on a surface. The result is the oxidation and dissolution of the base metal and consecutive deposition of the secondary metal. Since the exposure of the base metal is required to drive the reaction, the amount of deposited secondary metal is limited to one monolayer coverage on the base metal. Further, the application of this process to the synthesis bimetallic catalyst systems is limited to those where the secondary metal has a higher reduction potential than the primary base metal [29].

Contact deposition is identical to conventional electroplating except that the electrical current is derived from the reaction between the two metals instead of an external current source. With this method, the substrate metal is a cathode while the metal to be deposited is the anode. When contacted, the anode is oxidized and dissolves in solution. Consequently, the dissolved metal is deposited onto the cathode. The amount of deposition with this method is also limited because the solution becomes unstable as the concentration of the dissolved metal increases. Thus, the practical application of this method is limited [29].

Catalytic/autocatalytic deposition is the most common electroless deposition process and is the one that will be used in this report. Catalytic deposition employs a chemical reducing agent (typically water soluble, organic) to reduce a secondary metal precursor, which is then deposited onto the primary base metal, as illustrated in Figure 2.7. As the name implies, this method requires a catalytically active surface to activate
the reducing agent. This activation forms adsorbed hydride species that serve as the reduction site for the secondary metal precursor. Once the secondary metal is deposited, it may also activate the reducing agent and serve as a reduction site on which more secondary metal is deposited; thus, it is termed autocatalytic deposition. Electroless deposition must always begin with catalytic deposition, but at some point, both catalytic and autocatalytic deposition occur simultaneously or successively, depending on the materials and conditions. Under certain conditions, only catalytic deposition occurs,

Figure 2.7: Mechanism of electroless deposition.

which results in a single monolayer coverage – or up to one monolayer – of the secondary metal on the primary metal. Conversely, if autocatalytic deposition occurs, there is no limit to the number of monolayer deposited. The main advantage to electroless deposition is the ability to precisely control the surface composition of the bimetallic particles, which is critical for accurate correlation with catalyst performance. However, one disadvantage is that the development of an ED bath for the specific application is required, which can be quite involved.
The most important characteristics of an ED developer bath is that it must be kinetically stable to prevent thermal decomposition of the metal precursor, as well as thermodynamically unstable to ensure that the deposition goes to completion. A bath is typically a pH-controlled, aqueous solution that consists of a metal salt and a reducing agent. In many cases, a chelating (complexing) agent that complexes with the metal ion is required to maintain kinetic stability. Optionally, temperature is controlled for desired kinetics. A supported monometallic catalyst is used as the substrate for deposition. Before addition of the catalyst, stability of the metal concentration in solution must be confirmed to ensure that the deposition is only a result of the catalytic surface. Additionally, adsorption of the metal complex onto the catalyst support must be avoided by application of the principles of SEA as discussed previously. Specifically, a pH must be selected the metal ion is electrostatically repulsed from the support surface based on the PZC of the support and the charge of the metal ion. This may not be so trivial since pH also greatly affects the kinetic control of ED. Monnier et al. have successfully developed baths for preparation of bimetallic catalysts containing a wide range of metals such as Ag, Pt, Ru, Rh, Au, Cu, Ni, Co, and Ir [31-37].

The metal ion source is typically any water-soluble metal salt such as chlorides, sulfates, cyanides, acetates, etc. Table 2.1 lists metal salts that are commonly used as metal ion sources for electroless deposition. The choice of metal salt is usually determined by the stability in solution. The metal complex must be stable enough not to undergo reduction and deposition without a catalyst present, but it must not be too stable.
so that it does reduce when the catalyst is added. Other than stability, environmental effects also need consideration. Such is the case with Ag and Au deposition where cyanide salts are used [29]. Finally, effects of the counter ions and other components of the salt on the catalytic properties should be addressed. For instance, sulfates may be difficult to remove from the surface and may poison the catalyst. Other components such as Cl\(^-\), K\(^+\), and Na\(^+\) could also influence reactivity.

Table 2.1: Common metal salts for electroless deposition.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>NiSO(_4), NiCl(_2), Ni(H(_2)PO(_2))(_2), Ni(CH(_3)COO)(_2)</td>
</tr>
<tr>
<td>Co</td>
<td>CoSO(_4), CoCl(_2)</td>
</tr>
<tr>
<td>Au</td>
<td>KAu(CN)(_2), KAuCl(_4), Na(_3)Au(SO(_3))(_2)</td>
</tr>
<tr>
<td>Ag</td>
<td>AgNO(_3), NaAg(CN)(_2)</td>
</tr>
<tr>
<td>Pd</td>
<td>PdCl(_2), Pd(NH(_3))(_4)Cl</td>
</tr>
<tr>
<td>Pt</td>
<td>Na(_2)Pt(OH)(_6), (NH(_3))(_2)Pt(NO(_2))(_2), Na(_2)PtCl(_6)</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO(_4), KCu(CN)(_2)</td>
</tr>
</tbody>
</table>

The ED bath also contains a reducing agent which serves as the source of electrons for reduction of the metal ion complex. The most important requirement for the reducing agent is that it must have a favorable oxidation potential with respect to the metal being reduced. That is, the reducing agent should have a more negative red-ox potential for the thermodynamics to be favorable. Commonly used reducing agents include dimethylamine borane (DMAB), sodium hypophosphite (NaPO\(_2\)H\(_2\)), formaldehyde (HCHO), and hydrazine (N\(_2\)H\(_4\)) [38, 39]. Strong reducing agents such as NaBH\(_4\) are typically avoided as they are too strong and lead to thermal reduction in the absence of catalytic activation. Ohno tested the catalytic activity of reduction for various metals with a
combination of reducing agents [38]; a comparison of the anodic oxidation potentials of reducing agents for different metal electrodes is shown in Figure 2.8. Autocatalytic deposition will occur if the reducing agent is more easily activated on the secondary metal than the primary metal. Conversely, if the reducing agent is more easily activated on the primary metal, catalytic deposition will dominate until either the secondary metal ion is exhausted or the primary metal surface is fully covered. In most cases catalytic deposition is desired to achieve a uniform bimetallic catalyst, so a reducing agent must be chosen accordingly. For example, DMAB would be a good candidate as a reducing agent for deposition of Ag on Pt because it has a more negative oxidation potential on Pt than it has on Ag. For deposition of Pt on Ag, either NaH$_2$PO$_2$ or HCHO should be used.

Sometimes, a complexing agent is required to improve the kinetic stability of the metal ion to prevent unwanted deposition. Complexing agents donate electrons and coordinate with metal ions, which lowers the “free” metal ion concentration [40]. This prevents

Figure 2.8: Catalytic activity of metals for anodic oxidation.
speciation of the metal ions to form hydroxides, which leads to precipitation. In addition, the complexing agent may act as a pH buffer. Complexing agents are typically organic acids or their salts such as succinate, acetate, citrate, pyrophosphate etc. Ethylene diamine is also a very common complexing agent.

Other factors that greatly affect the stability and deposition are operating conditions such as pH, temperature, and agitation. As mentioned before, the pH of the bath is controlled throughout the process; this is done by continuous addition of acid/base to the bath during deposition. It is necessary to control the pH because it has a significant effect on the oxidation potential of the reducing agent, thus it will affect the kinetics of the deposition and the stability of the bath [29, 40]. In addition, if the pH becomes too basic, the excess OH⁻ ions can lead to precipitation of insoluble hydroxides.

Obviously, temperature is another variable that affects deposition rate, as it follows the Arrhenius law. Temperature effects have previously been studied for Ni deposition with various baths [40]. In some cases, as certain threshold temperature is required for deposition to occur. In other cases, high temperatures will cause instability. Since controlled deposition is desired for bimetallic catalyst preparation, a period of 15 – 60 min for complete deposition serves as a good rule of thumb [41].

Lastly, it is important to have very good mixing to ensure even deposition throughout the catalyst. The rate of deposition increases with agitation if the reaction has external mass transfer limitations. That is, if diffusion is slower than deposition, higher stirring rates will minimize mass transfer limitations and increase the overall reaction rate. However, high stirring rates will cause attrition which is problematic for filtration and later
catalytic testing in plug flow reactors. Instead, it is typically desired to alter temperature, while still maintaining good mixing, to affect the rate of deposition since temperature has a much more significant effect anyway [41].
CHAPTER 3

DRY REFORMING OF METHANE WITH PT-PROMOTED NI CATALYSTS PREPARED BY

ELECTROLESS DEPOSITION
3.1 Abstract

A series of Pt-promoted Ni catalysts was prepared by electroless deposition and evaluated for dry reforming of methane. At temperatures between 500 – 600°C, Pt exhibited a promotional effect, which was optimized at low loadings. However, kinetic data reveal a compensational effect with an isokinetic temperature at ~624°C, meaning the promotional effect is reversed at higher temperatures. Selectivities were not significantly affected by Pt incorporation as products were near equilibrium ratios. On the other hand, stability was adversely affected by Pt incorporation. Characterization reveals that Pt increases the rate of CH₄ decomposition, which leads to accumulation of coke in the form of carbon whiskers. Alloy formation readily occurs upon preparation, but then separation occurs during reaction to form very large Pt-rich ensembles.

3.2 Introduction

Gas-to-liquid (GTL) processes have drawn much attention in recent years as the demand for diversified and distributed sources of energy increases. Advancements in oil recovery have unlocked reserves in remote locations, which makes transportation of associated gas uneconomical because of methane’s high molar volume; often, the associated gas goes unused and is either flared or emitted to the atmosphere [7, 42]. Similarly, natural gas reserves in remote locations are often left untapped for the same reason. On-site GTL processes provide a possible solution by upgrading cheap and
voluminous CH$_4$ to higher value fuels and chemicals that are liquid at standard conditions and can more easily be transported.

Most GTL processes require the CH$_4$ to be reformed to syngas, a mixture of H$_2$ and CO, as an intermediate step to a wide range of products and processes [7]. One such process, and the most prominent, is Fischer-Tropsch synthesis to produce longer chain hydrocarbons for use as jet fuel, diesel, naphtha, lubricants, or waxes [7]. Reforming of methane has traditionally been accomplished using steam reforming (Equation 1), however, water may not always be readily available in the remote locations in which unconventional oil and gas reserves are found [43]. In these cases, it would be beneficial to utilize CO$_2$, which is abundant on oil and gas fields, in dry reforming of methane (DRM), shown in Equation 2. Not only does this process have the benefit of utilizing the two most potent greenhouse gas emitters, CH$_4$ and CO$_2$, but it also produces syngas with a lower H$_2$/CO ratio than steam reforming, which is beneficial to use as feed for Fischer-Tropsch synthesis [43, 44].

3.2.1 Thermodynamics of DRM

Overall, DRM is highly endothermic with a heat of reaction of 247 kJ/mol and requires very high temperatures, as indicated in the equilibrium curves in Figure 3.1. Equilibrium conversions were calculated at varying partial pressures of CH$_4$ with equimolar amounts of CO$_2$ by minimization of Gibbs free energy with process simulator software DWSIM. According to Equation 2, DRM should produce syngas with a H$_2$/CO ratio near unity, however there are a number of inevitable side reactions that occur under
typical operating conditions, shown in Equation 2 - Equation 5. Between 500 – 700 °C, reverse water gas shift consumes \( \text{H}_2 \) to form water, which lowers the \( \text{H}_2/\text{CO} \) ratio in the product [42]. To avoid this, typical operating temperatures are above 700 – 800 °C [42, 45, 46], which could prove to be problematic to catalyst stability. Alternatively, water may be added to the feed along with \( \text{CO}_2 \) to tune the desired syngas ratio. However, the most problematic side reactions involved are those that form carbon deposits, which result in fouling of the catalyst or reactor plugging. Both \( \text{CH}_4 \) decomposition and Boudouard reaction occur at temperatures below 700 °C – 800°C, whereas only \( \text{CH}_4 \) decomposition is more prominent above 800°C [42, 45].

Figure 3.1: Thermodynamic equilibrium conversion for DRM calculated by minimization of Gibbs free energy with DWSIM process simulator software. Varying partial pressures of \( \text{CH}_4 \) with equimolar amounts of \( \text{CO}_2 \).
Steam Reforming \[ CH_4 + H_2O \rightleftharpoons 3H_2 + CO \] \[ \Delta H_{rxn} = 260 \frac{kJ}{mol} \] Equation 1

Dry Reforming \[ CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \] \[ \Delta H_{rxn} = 247 \frac{kJ}{mol} \] Equation 2

Reverse Water Gas Shift \[ CO_2 + H_2 \rightleftharpoons CO + H_2O \] \[ \Delta H_{rxn} = 41.2 \frac{kJ}{mol} \] Equation 3

Methane Decomposition \[ CH_4 \rightleftharpoons C(s) + 2H_2 \] \[ \Delta H_{rxn} = 75.0 \frac{kJ}{mol} \] Equation 4

Boudouard Reaction \[ 2CO \rightleftharpoons C(s) + CO_2 \] \[ \Delta H_{rxn} = -171 \frac{kJ}{mol} \] Equation 5

3.2.2 DRM Catalyst Coking

Nickel is the most commonly used catalyst for methane reforming because of its high activity and low cost. In fact, nickel has comparable, or better, activity to many noble metals and is more resistant to sintering at high temperatures [47]. However, the biggest challenge to commercializing a process using Ni as the catalyst is that Ni is especially susceptible to deactivation by coking [45, 47, 48]. Carbon is highly soluble in the Ni lattice, which allows migration through subsurface layers and terraces to step edge facets where accumulation is favorable [48]. In many cases, Ni has been shown to accumulate graphitic layers between the Ni particle and support surface, which lifts the particle off the support surface and forms carbon whiskers. This type of carbon does not cover up the active sights, but the whiskers will continue to grow until the reactor is clogged or the catalyst is destroyed [47].
Inhibition of carbon accumulation has been extensively studied over the last few decades. Methods for inhibiting the kinetics of carbon accumulation on Ni catalysts have focused on metal loading, type and structure of support, secondary metal, preparation method, and reaction conditions [42, 47]. Ni particle size is one notable characteristic that significantly affects carbon formation. It is known that CH₄ decomposition is kinetically favorable on large Ni ensembles, while CH₄ reforming may occur on much smaller ensembles [49-52]. The critical size under which CH₄ decomposition is unfavorable is still under debate as reported values range from 2 – 10 nm [52]. Nevertheless, preparation of small Ni particles would be favorable to prevent carbon formation.

The observation of the ensemble effect was first discovered by Rostrup-Nielsen with the development of the SPARG (“sulfur passivated reforming”) Process [53]. The SPARG Process utilizes H₂S as a co-feed in small concentrations to effectively control the ensemble size through sulfur poisoning of the Ni surface, which kinetically inhibits CH₄ decomposition. In later studies, Rostrup-Nielsen et al. demonstrated that carbon nucleation occurs on the step sites of Ni particles [48, 54]. Using density functional theory (DFT), they suggested that dopants other than sulfur, such as K and Au, may also be suitable promoters as they preferentially bind to the step sites [54].

Several studies have also claimed that noble metals such as Pt or Rh are suitable promoters for Ni catalysts for three primary reasons [42, 47, 55-61]. First, the noble metal may act as the agent to break up the ensemble sizes as discussed above. Second, carbon has a low solubility in noble metals which promotes gasification and inhibits accumulation. This is also said to prevent carbon migration through subsurface layers and
to step sites where whisker formation is prevalent. Third, the reducibility of NiO is enhanced through H₂ and CO spillover from adjacent noble metal species. Hou et al. have demonstrated that an Al₂O₃-supported Ni catalyst has enhanced activity and more resistance to carbon formation when promoted with a small amount of Rh [57]. As expected, this increase in activity was attributed to enhanced reducibility. The results indicate that there is an optimum Rh/Ni ratio to maximize conversion, but there is a monotonic trend of reducing carbon deposition with increasing Rh content. That is, a small amount of Rh enhances activity and significantly reduces coke formation, but too much Rh will decrease overall activity, due to the nature of Rh/Al₂O₃. A number of studies have shown similar effects with Pt as a promoter to Ni/Al₂O₃ catalysts. de Miguel et al. demonstrated that Pt significantly enhances the reducibility of NiO using temperature programmed reduction [61]. They also showed that the Pt-containing catalyst formed less carbon based on transmission electron microscopy (TEM) images. García-Diéquez et al. varied the Pt/Ni ratio and illustrated that carbon formation decreases with increasing Pt content [58]. All Pt-containing catalysts exhibited higher initial activity than the Ni-only catalyst. Gould et al. utilized atomic layer deposition (ALD) to prepare very small bimetallic Ni-Pt particles that exhibited an enhancement of stability [55].

Many of these studies use bulk synthesis techniques that result in formation of both bimetallic and monometallic particles. However, there are a few exceptions in more recent studies. Li et al. selectively deposited Pt on Ni nanoparticles by reduction of a Pt precursor using surface nickel hydrides [62]. They concluded that increasing Pt coverage results in an increase in activity over the range of compositions tested. The authors
demonstrated that the catalyst surface undergoes restructuring to form a Ni-Pt alloy shell over a Ni-rich core.

### 3.2.3 Stability Testing Methodology

Many stability tests of DRM catalysts reported in the literature were performed at high CH\(_4\) conversions approaching thermodynamic limitations. When a catalyst is run at such condition, it is not possible to observe the true dynamics of catalyst deactivation because of the excess of catalyst. That is, there may be so much catalyst that only a fraction of the bed provides enough activity for the reaction mixture to reach equilibrium; the mixture then travels through the rest of the bed unreactive and essentially leaves the unused portion as “fresh” catalyst. When the former portion of the bed deactivates, the latter “fresh” portion will maintain an artificially high conversion.

To demonstrate the importance of testing catalyst stability far from equilibrium limitations, we tested a 5 wt% Ni catalyst supported on \(\gamma\)-Al\(_2\)O\(_3\) at conditions that result in near-equilibrium conversions, which is shown in Figure 3.2. The gas hourly space velocity (GHSV) was kept sufficiently low (GHSV = 1300 h\(^{-1}\)) to obtain high conversions. As shown in the figure, experimental CH\(_4\) conversions approach, and even reach, calculated equilibrium conversion. Moreover, conversions appear to be stable up to 40 h time on line, which is longer than many stability experiments found in the literature. From these data, it is easy to conclude that this catalyst is stable. However, examination of the catalyst bed after reaction, shown in Figure 3.3, reveals there are very distinct regions: a light region and a dark region. To confirm the suspicion of varying amounts of coke, x-ray
diffraction (XRD) was performed on each region to observe the graphite peak at 28° 2θ, shown in Figure 3.3. In fact, the graphite peak of the sample from the dark region has a

Figure 3.2: DRM near equilibrium conversion of 5 wt% Ni/Al₂O₃. CH₄/CO₂/He = 1/1/1, GHSV = 1300 h⁻¹.

Figure 3.3: (a) Image of catalyst bed after ~40 h of reaction near equilibrium conversion and (b) representative XRD patterns. Illustrates significant coke-formation gradient across catalyst bed.
significantly higher relative intensity than that of the light region.

To further highlight the fallacy that this catalyst is stable, a fresh sample from the same original batch of Ni/Al$_2$O$_3$ was tested under conditions that result in much lower conversion, shown in Figure 3.4. A CH$_4$ conversion that is around 50% of equilibrium was targeted by altering the GHSV (80,000 – 90,000 h$^{-1}$), which is high enough to “stress test” the catalyst, but low enough to see the dynamics of deactivation. In fact, the data reveal that this catalyst is never stable and linearly deactivates for most of the time on line. This preliminary study illustrates the importance of operating away from thermodynamic limitations so that the kinetics of deactivation may be observed.

![Figure 3.4: DRM at ~50% of equilibrium conversion of 5 wt% Ni/Al$_2$O$_3$. CH$_4$/CO$_2$/He = 1/1/1, GHSV = 80,000 – 90,000 h$^{-1}$.](image)
3.2.4 Objectives

The primary focus of this study was to evaluate the activity and stability of a series of Ni-Pt bimetallic catalysts for DRM. Extensive measures were taken to utilize reaction conditions that provide a realistic and accurate comparison of catalyst deactivation. Catalysts were prepared by electroless deposition (ED) of varying amounts of Pt onto Ni catalyst. X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and temperature programmed reduction (TPR) were employed to investigate the metal-metal interaction and the nature of the catalyst. After reaction, the mode of deactivation was assessed with data from XRD, STEM, and temperature programmed oxidation (TPO).

3.3 Experimental

3.3.1 Catalyst Preparation

5 wt% Ni and 3 wt% Pt monometallic catalysts were prepared by dry impregnation of Ni(NO$_3$)$_2$ (Alfa Aesar) and H$_2$PtCl$_6$ (Sigma Aldrich) onto γ-Al$_2$O$_3$ (SBa 200, Sasol, 189 m$^2$ g$^{-1}$ specific surface area, 0.76 m$^3$ g$^{-1}$ pore volume) respectively. Samples were dried in air at room temperature overnight, dried in flowing He at 100°C for 12 h, and reduced at 600°C for Ni and 300°C for Pt under a flow of 30% H$_2$/He for 2 h. A series of Ni core, Pt shell bimetallic catalysts with varying amounts of theoretical Pt monolayers, which are listed in Table 3.1, were prepared by ED (discussed in Chapter 2). The Ni-Pt catalysts are referred to as Ni@nPt where $n$ is the number of theoretical monolayers which is based on the amount and size of the Ni nanoparticles. In this case, the previously prepared 5
wt% Ni/Al₂O₃ catalyst served as the base metal catalyst, and Pt was the secondary shell material. The ED bath, which was previously developed [34], consisted of H₂PtCl₆ as the Pt precursor, dimethyamine borane (DMAB) as the reducing agent, and ethylene diamine (EN) as a chelating agent. The DMAB/EN/Pt molar ratio was held constant at 5/4/1 while varying the initial absolute Pt concentration in order to achieve the desired theoretical Pt coverage. Theoretical coverages are based on the number of surface Ni atoms in the base catalyst, which is estimated by the particle diameters determined from XRD. The ED bath was heated to 70°C under constant stirring before the Ni/Al₂O₃ catalyst was added. NaOH was continuously added to maintain a pH value of ~11. Aliquots were taken from the bath periodically to measure the Pt concentration using inductively coupled plasma optical emission spectroscopy (ICP, Perkin Elmer Optima 2000 DV). After complete deposition, catalysts were filtered and washed with ~1 L/g catalyst with DI water to remove byproducts and unreacted components from the ED reaction. All bimetallic catalysts were dried at room temperature in air overnight, then heat treated under 30% H₂/He at 200°C for 2 h.

3.3.2 Catalyst Characterization

To qualitatively determine the degree of bimetallic interaction between Ni and Pt, temperature programmed reduction (TPR) was performed on all catalysts with a Micromeritics Autochem II 2920. First, samples were oxidized at 300°C for 2 h under a flow of 10% O₂/He, then cooled to room temperature in flowing Ar. The flow was then switched to 20 sccm of 10% H₂/Ar and outlet gases were monitored with an in-line
thermal conductivity detector (TCD). The TCD signal was allowed to stabilize before the temperature of the sample was ramped to 800°C at a rate of 10°C/min.

A Rigaku Miniflex Series II equipped with a D/teX silicon strip detector and Cu Kα₁ radiation was used for x-ray diffraction (XRD) measurements. Scans were performed over a 2θ range of 10 – 80° with a scan speed of 1°/min and a sampling width of 0.02°. In support of XRD data, scanning transmission electron microscopy (STEM) was used to obtain high angle annular dark field (HAADF) images of selected catalysts using a cold field emission, probe-aberration-corrected, 200 kV JEOL JEM-ARM200CF. The microscope is fitted with JEOL and Gatan detectors for acquiring HAADF images. X-ray energy dispersive spectroscopy (XEDS) was also employed for elemental mapping of Pt and Ni using an Oxford Instruments X-Max100TLE SDD detector, which was also fitted to the JEM-ARM200CF.

After reaction, temperature programmed oxidation (TPO) burn-off of carbon deposits was performed to determine amount and type of coke formation on all catalysts. For each analysis, a sample was loaded into a 1/4-inch quartz tube (4 mm ID) supported on a quartz wool plug and placed inside a high wattage, split-tube furnace. The sample was then heated from 25 to 800 °C with a ramp rate of 10 °C min⁻¹ under a 20 SCCM flow of 10% O₂/He. The exit stream gas composition was monitored with a quadrupole mass spectrometer (Inficon Transpector 2 Mass Spectrometer). Relative amounts of coke were determined by integrating the normalized signal for CO₂ (m/e = 44), which was calibrated after each run.
3.3.3 Evaluation for Dry Reforming of Methane

The stability and activity of all catalysts were evaluated for DRM in a home-built, packed bed micro reactor system with a fully automated analytical system, shown in Figure 3.5. The analytical system consists of an HP 5890 Series II gas chromatograph (GC) equipped with two TCDs. One TCD uses an argon carrier and a Carboxen 1010 PLOT (Supelco) column, which is used to detect H₂. The other TCD uses a helium carrier and a PoraPLOT Q (Agilent) column, which is used to detect CO, CO₂, CH₄, and H₂O. A series of switching valves allow sampling from either the feed or product streams and injection into either column.

For a typical run, about 10 mg of catalyst (~120 mesh) diluted in 60 mg of crushed quartz (120 mesh) was loaded into a ¼-inch quartz tube reactor (4 mm ID) supported by a quartz wool plug. The amount of quartz diluent was enough to make the bed height ~2 times greater than the inner diameter of the tube in order to suppress effects of channeling. The reactor tube was then placed into a high temperature split tube furnace. Catalysts were activated under a flow of H₂ at 600 or 700°C before being heated/cooled to reaction temperature under He flow. The feed composition typically consisted of a CH₄/CO₂/He ratio of 1/1/2 while total flowrates varied from 80 SCCM to 200 SCCM. Catalysts were allowed to reach steady state, or “pseudo-steady state”, before reaction conditions were varied. For the activity evaluations, after 15 h (TOS), temperatures were varied from 550 – 600°C to develop Arrhenius-type plots. Each temperature was maintained for at least 3 h to ensure steady state. In contrast to the stability tests, CH₄ conversions for the activity tests were kept below 15% by increasing the total flowrates.
at higher temperatures. In the case of the stability tests, flowrates were altered after 20 h time on stream (TOS) to achieve a CH$_4$ conversion of about 40%, which is critical for determining the kinetics of deactivation as indicated earlier in this chapter.

3.4 Results and Discussion

3.4.1 Preparation

A series of catalysts were prepared by using ED to deposit varying loadings of Pt onto Ni supported on Al$_2$O$_3$ which is shown in Table 3.1. Prior to Pt deposition on Ni, the developer bath was tested for thermal stability by measuring Pt concentration as a function of time after the addition of the reducing agent (without Ni catalyst). There were

![Figure 3.5: Schematic of reactor system used for DRM.](image-url)
no signs of thermal decomposition as the Pt concentration was stable up to 60 min, consistent with previous reports [34]. In a separate experiment, to ensure that the Pt precursor does not adsorb to the support surface, Pt concentration in solution was measured after the addition of the Al₂O₃. As expected, no adsorption was observed since PtCl₆²⁻ is an anion and the pH of solution was maintained about the PZC of Al₂O₃ (~8.1).

For the deposition experiments, Pt concentration was measured as a function of time and recorded in Figure 3.6. The time-dependent concentration profiles show that all the Pt loadings were achieved within the first 30 min, however, there is an induction period for the first 15 min. This “shelf” is most likely due to the presence of NiO on the surface of the base catalyst that is inactive for DMAB decomposition. Therefore, during the first 15 min, the DMAB seems to reduce the NiO before the active Ni is exposed and able to carry out the Pt reduction. Pt deposition terminates when concentration falls below 5-6 ppm even with the addition of more DMAB. This has been seen by others and implies that there is a threshold of Pt concentration for this reaction to occur [34].

Table 3.1: Summary of Ni-Pt/Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst Name</th>
<th>Theoretical monodisperse coverage, θₚt, on Ni</th>
<th>Ni wt loading (%)</th>
<th>Pt wt loading (%)</th>
<th>Bulk Pt/Ni atomic ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% Pt</td>
<td>-</td>
<td>0.00</td>
<td>3.00</td>
<td>-</td>
</tr>
<tr>
<td>5% Ni</td>
<td>0.00</td>
<td>5.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.075Pt">Ni@0.075Pt</a></td>
<td>0.07</td>
<td>4.99</td>
<td>0.20</td>
<td>0.012</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.4Pt">Ni@0.4Pt</a></td>
<td>0.40</td>
<td>4.94</td>
<td>1.10</td>
<td>0.07</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.7Pt">Ni@0.7Pt</a></td>
<td>0.69</td>
<td>4.91</td>
<td>1.90</td>
<td>0.12</td>
</tr>
<tr>
<td>Ni@1Pt</td>
<td>1.02</td>
<td>4.86</td>
<td>2.75</td>
<td>0.17</td>
</tr>
</tbody>
</table>
3.4.2 DRM Kinetic Evaluation

The catalysts were evaluated for their kinetic performance for DRM at low CH$_4$ conversion. After activation under H$_2$ flow at 700°C, the catalyst temperature was lowered to 550°C before the reaction feed was sent to the reactor. Figure 3.7 illustrates the typical operating protocol and run data for kinetic evaluation. Typically, the initial stabilization period took up to 15 – 20 hr TOS. Subsequently, temperatures were altered to form Arrhenius plots; flowrates were also adjusted to avoid CH$_4$ conversions above ~12%. This is in contrast to the conditions described earlier in this chapter for evaluating
kinetics of deactivation, which targeted a conversion of ~40%. This particular run also illustrates the effect of temperature on deactivation where the temperature was increased to 625°C at around 45 h, activity immediately began to decrease linearly. In efforts to preserve the activity, temperature was lowered back to 575°C at 62 h, which resulted in stable performance once again. However, activity was permanently lost as indicated by the lower reaction rate compared to the previous segment at the same temperature: 7.2 versus 13.0 mmol CH₄ mg⁻¹ metal⁻¹ h⁻¹. Because of this, we were unable to obtain stable activity data above 600°C.

CH₄ consumption rates were calculated at temperatures between 525°C and 600°C across the series of catalysts and Arrhenius-type plots were formed to calculate

Figure 3.7: Kinetic evaluation of Ni@0.075Pt. CH₄/CO₂/He = 1/1/2, P = 1 atm, 120 – 200 sccm.
apparent activation energies, shown in Figure 3.8(a) and summarized in Table 3.2. The 5 wt% Ni catalyst had an activation energy of 122 kJ/mol, which is in-line with other reported values [43]. Interestingly, the bimetallic catalysts have a lower activation energy, ranging between 86 – 100 kJ/mol, which suggests that Pt has a promotional effect. In fact,

Figure 3.8: (a) Arrhenius plots of Ni-Pt catalysts and (b) rates vs. Pt/Ni atomic ratio, CH₄/CO₂/He = 1/1/2, P = 1 atm.
there is an apparent optimum Pt loading where the activation energy is minimized, meaning the effect of temperature on activity is minimized with an intermediate loading of Pt. To illustrate this more clearly, Figure 3.8(b) displays the CH$_4$ consumption rates versus Pt/Ni atomic ratio at varying temperatures. As the plot indicates, the catalysts with low Pt loadings have 50 – 100% higher activity than the Ni-only catalyst at low operating temperatures. As discussed previously, Hou et al. observed a similar trend with a series of Rh-promoted Ni catalysts [57].

Although low Pt loadings seem to be more active than Ni alone, there appears to be a kinetic compensation effect as indicated by the linear relationship between the activation energy and the natural logarithm of the pre-exponential factor [63-65]. This relationship, as shown in Figure 3.9, may be expressed mathematically as:

\[ \ln(A) = \alpha + \frac{E_a}{R\theta} \]  

Equation 6

where $\alpha$ is a constant and $\theta$ is the isokinetic temperature. When this equation is fitted to the series of catalysts, we find that $\alpha = 3.25$ and $\theta = 624^\circ C$. This means that the promotional effect seen at lower temperatures will reverse at temperatures above 624$^\circ C$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt/Ni atomic ratio</th>
<th>Activation Energy (kJ/mol)</th>
<th>Reaction rate (mmol CH$<em>4$/h-g$</em>{metal}$)*</th>
<th>H2/CO*</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ni</td>
<td>0.00</td>
<td>122</td>
<td>7.1</td>
<td>0.37</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.075Pt">Ni@0.075Pt</a></td>
<td>0.012</td>
<td>100</td>
<td>10.0</td>
<td>0.38</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.4Pt">Ni@0.4Pt</a></td>
<td>0.07</td>
<td>86.2</td>
<td>10.8</td>
<td>0.39</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.7Pt">Ni@0.7Pt</a></td>
<td>0.12</td>
<td>95.8</td>
<td>7.8</td>
<td>0.37</td>
</tr>
<tr>
<td><a href="mailto:Ni@1.0Pt">Ni@1.0Pt</a></td>
<td>0.17</td>
<td>97.3</td>
<td>5.4</td>
<td>0.40</td>
</tr>
</tbody>
</table>

* Steady state at 550$^\circ C$, CH$_4$/CO$_2$/He = 1/1/2.
This helps explain the promotional effect of Pt that was seen by others at these lower temperatures [55, 62]. However, as we will discuss later, the promotional effect is clearly reversed at high temperatures, consistent with a compensational effect. This illustrates

Figure 3.9: Compensation plot for Ni-Pt catalysts.

Figure 3.10: $H_2/CO$ product ratio as a function of $CH_4$ conversion. $CH_4/CO_2/He = 1/1/2$, $P = 1$ atm.
the importance of studying steady-state performance at multiple temperatures.

The H\textsubscript{2}/CO product ratio of all catalysts were very similar and increased mutually with CH\textsubscript{4} conversion, as shown in Figure 3.10. In fact, the values for H\textsubscript{2}/CO were all in very good agreement to thermodynamic equilibrium. This implies that selectivity is driven by thermodynamics and is not affected by the composition of the catalyst in this case.

3.4.3 DRM Catalyst Deactivation

Long-term stability tests were performed at 700°C with the same feed of CH\textsubscript{4}/CO\textsubscript{2}/He equal to 1/1/2, shown in Figure 3.11. The Pt-only catalyst deactivates very quickly within the first 2 h of time on line. de Miguel et al. reported an 80% loss in activity after the first 6 h with a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst, which they attributed to sintering [61]. In our

![Graph showing DRM stability at 700°C, CH\textsubscript{4}/CO\textsubscript{2}/He = 1/1/2. Flowrates adjusted after 20 h to increase CH\textsubscript{4} conversion to ~40%.](image)

Figure 3.11: DRM stability at 700°C, CH\textsubscript{4}/CO\textsubscript{2}/He = 1/1/2. Flowrates adjusted after 20 h to increase CH\textsubscript{4} conversion to ~40%.
case, we believe that the deactivation is due to both sintering and carbon deposition, as we will discuss later. Conversely, all other samples were allowed to run for 20h to reach a “pseudo-steady state”, where the rates of deactivation are linear. It is interesting to note the differences in conversions for each sample at 15 – 20h time on line. At this stage, all flowrates were 200 sccm, thus the conversions provide a rough comparison of rates. The trend that we observed in the Arrhenius experiments before is now reversed. That is, the Ni-only sample has the highest conversion and the low Ni loading samples have the lowest conversion, which is consistent with the compensation effect previously discussed. The catalysts are at 700°C for these tests, which is above the isokinetic temperature of 624°C.

After reaching pseudo-steady state, conversions were brought back to around 40% by decreasing the flowrates accordingly so that they all have roughly the same starting point. 40% conversion was used as the target because this corresponds to roughly 50% of thermodynamic equilibrium conversion. As mentioned earlier, this conversion is low enough to observe the kinetics of deactivation, but it is high enough to “stress test” the catalysts. Interestingly, the Ni-only catalyst appears to be slightly more stable than the bimetallic catalysts. Figure 3.12 shows a comparison of the deactivation rates based on the slopes of the pseudo-steady state regions of the stability plots. In fact, the Ni-only catalyst has the slowest rate of deactivation, 121 mmol CH₄ h⁻² g⁻¹ metal⁻¹, while increasing Pt loading serves to increase the rate of deactivation. The rate of deactivation for Ni@1.0Pt is 263 mmol CH₄ h⁻² g⁻¹ metal⁻¹, which is more than double that of the Ni-only catalyst. This
trend seems intuitive since the Pt-only catalyst was shown to deactivate immediately, presumably because of carbon deposition.

To confirm that the deactivation was due to coking, TPO was employed for selected catalysts after extended periods of reaction time; results are shown in Figure 3.13. Since the reactors were cooled down slowly under a flow of He, all hydrocarbons on the catalysts were desorbed, leaving only solid carbon species. Therefore, the single TPO peak at 550°C that is present in all catalysts may be attributed to some form of solid carbon. In fact, this temperature is within the range that is characteristic of carbon whiskers [66]. STEM images in Figure 3.14 confirm the presence of carbon whiskers. This type of carbon formation is commonly found in dry reforming of methane [48, 55, 66]. Further, it is interesting to note the Pt-only catalyst exhibits the same type of carbon formation as the Ni-based catalysts, which has also been reported by others [66].
The signals for CO\textsubscript{2} were calibrated and integrated to estimate amount of coke and are summarized in Table 3.3. Indeed, the reason for deactivation seems to be carbon formation as the calculated deactivation rate based on the slopes in activity are correlated with the amount of carbon determined by TPO. Lucrédio et al. also observed a similar

Table 3.3: Summary of deactivation in DRM at 700\textdegree C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt/Ni atomic ratio</th>
<th>Deactivation rate (mmol CH\textsubscript{4} h\textsuperscript{-1} g\textsubscript{metal}\textsuperscript{-1})\textsuperscript{b}</th>
<th>Coke formation (mmol C/g\textsubscript{cat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ni</td>
<td>0.00</td>
<td>121.2</td>
<td>3.54 (150\textsuperscript{c})</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.075Pt">Ni@0.075Pt</a></td>
<td>0.012</td>
<td>145.8</td>
<td>4.22 (150)</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.4Pt">Ni@0.4Pt</a></td>
<td>0.07</td>
<td>205.2</td>
<td>-</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.7Pt">Ni@0.7Pt</a></td>
<td>0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><a href="mailto:Ni@1.0Pt">Ni@1.0Pt</a></td>
<td>0.17</td>
<td>262.8</td>
<td>6.99 (110)</td>
</tr>
<tr>
<td>3% Pt</td>
<td>\infty</td>
<td>-</td>
<td>7.21 (20)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} After reaction at 700\textdegree C for 20 h.
\textsuperscript{b} Deactivation rate in pseudo-steady state region as shown in Figure 3.11.
\textsuperscript{c} Time on line (h).
trend of increased carbon deposition with Rh-promoted Ni catalysts as compared to Ni-only catalysts [67]. They attributed this to the thermodynamic favorability of CH$_4$ decomposition on Rh. Similarly, Pt is a well-known dehydrogenation catalyst [68, 69], which could help explain the increase in carbon content. In fact, Pt is commonly used as the catalyst for naphtha reforming, which is an industrial process that depends on the continuous removal of coke deposits [70]. In our case, since Pt is the underlying cause of increased carbon deposition, this implies that the rate of CH$_4$ dissociation is greater than the rate of gasification by CO$_2$ and/or H$_2$O. There are a number of reasons why this catalyst system exhibits this behavior in contrast to what others have reported for Pt-promoted Ni systems [55, 61, 62]. For example, much of the previous work was done at lower temperatures, and as we demonstrated in Figure 3.7, temperature has a major impact on stability. Also, as previously discussed, particle size can have a great influence on rates of CH$_4$ dissociation.

Figure 3.14: Representative STEM image of (a) Ni@0.7Pt and (b) Ni@1.0Pt after ~100 h of reaction time. 550 – 650°C, CH$_4$/CO$_2$/He = 1/1/2.
3.4.4 Particle size and morphology

To determine the degree of bimetallic interaction, TPR was performed on the catalysts after oxidation at 300°C, which is shown in Figure 3.15. The Pt-only catalyst does not exhibit any reduction peak since PtO\text{x} is easily reduced at room temperature before the temperature program is started. Conversely, the Ni-only catalyst shows a main reduction peak at 290°C with a broad shoulder centered at 370°C and a smaller peak at \sim200°C. The main reduction peak gradually shifts to a lower temperature with increasing Pt loading as a result of H\textsubscript{2}-spillover. However, even with the highest Pt loading, the peak only shifts by 30°C. This is possibly an indication of autocatalytic deposition, where Pt was chemically reduced and deposited onto itself. This means that a small amount of Pt assists reduction of Ni as expected, but the addition of more Pt does not necessarily result in
greater contact with the Ni. A small peak develops at 50°C with the addition of Pt, which we speculate is a result of the reduction of a Pt-rich alloy. As we will discuss later, the bimetallic samples contain a Pt-rich phase, which we would expect to have a reduction temperature closer to that of the Pt-only catalyst. Also with the addition of Pt, a reduction peak emerges at 540°C, which can be attributed to Pt-assisted reduction of nickel aluminates [71].

XRD was performed on the series of fresh catalysts to determine metal phases and particle sizes, shown in Figure 3.16. These patterns were taken after preparation, which included a heat treatment under H₂ for 2 h and after 20h of time on line at 700°C. As expected, Ni-containing catalysts have a Ni⁰ phase which is clearly defined from the Ni(200) peak centered at 52° 2θ. Although less evident, the Ni(111) peak centered at 45° may also be seen as a shoulder on the left side of the Al₂O₃ peak. Interestingly, there is a very clearly defined series of peaks at 41.7° and 48.5° 2θ, which increase with Pt loading. This pattern corresponds to a NiPt alloy with a 1:1 atomic ratio. Given the temperature used to prepare the catalysts, the formation of an alloy is consistent with the binary phase diagram of Ni and Pt mixtures, shown in Figure 3.17. According to the phase diagram, the NiPt phase exists when the atomic composition is 45 – 55% Pt at 200°C, which agrees closely with the majority of the bimetallic samples examined by XEDS; Figure 3.18 illustrates an example of a particle with 58% Pt. However, the amount of Pt was controlled to only reach up to 1 theoretical monolayer on the Ni particles, which corresponds to a bulk metal composition of up to 14.5% Pt (from Table 3.1, Pt/Ni = 0.17 => 14.5% Pt). In order for the atomic composition of Pt to be as high as 45%, it would need to be unevenly
distributed, with higher concentration in certain areas than others. This implies that either (1) catalytic deposition occurred during ED synthesis and the Pt shells agglomerated to form Pt-rich alloy ensembles within the Ni particles; or (2) autocatalytic
deposition occurred where Pt was deposited onto Pt, which resulted in some particles with a higher concentration of Pt than others. To obtain a better understanding of the structure, the XRD signal from the Al₂O₃ support was subtracted from all patterns to obtain a deconvoluted pattern, such as the one shown for Ni@0.7Pt in Figure 3.19 (all others in Appendix A). Deconvolution reveals a series of peaks centered at 40.3 and 45.7°C, which corresponds to a Pt-rich alloy phase. As mentioned previously, the majority of the bimetallic particles examined by XEDS were in agreement with the NiPt phase, however, there were a few spots analyzed with up to 76% Pt. This is also in agreement with XRD as the NiPt is the prominent bimetallic phase. The formation of this Pt-rich alloy further suggests an autocatalytic deposition mechanism. Despite the fact there were higher concentrations of Pt in certain areas, the maps reveal that Ni is present wherever

Figure 3.17: Ni-Pt binary phase diagram [72].
Figure 3.18: STEM HAADF micrographs and XEDS maps of fresh (a) – (d) Ni@0.7Pt and (e) – (h) Ni@1.0Pt. After 200°C heat treatment under H₂.
there is Pt. This confirms the ED mechanism, because Ni is required to initiate the chemical reduction and subsequent deposition of Pt.

![Figure 3.19: Deconvolution of metal peaks after Al₂O₃ subtraction from Ni@0.7Pt (a) after heat treatment at 200°C under H₂ and (b) after 20 h time online at 700°C, CH₄/CO₂/He = 1,1,2, P = 1 atm.](image)

After 20 h of reaction time, the XRD patterns of the spent catalysts in Figure 3.16(b) show an apparent separation of the NiPt phase as indicated by the appearance of a 1 or 2 Ni-rich peaks and the growth of the Pt-rich peak. It is evident that the extent of separation increases with Pt loading as the NiPt peak originally located at 41.7° 2θ gradually shifts to the right with increasing Pt loading. The Ni-rich peaks can be deconvoluted into two separate peaks, as in Figure 3.19(b): one Ni-rich peak between 42.5°C and 43.5°C, and one NiPt peak at ~41.7°C. However, the NiPt peak with a 1:1 ratio is much less prominent for all catalysts than it was in the fresh samples. This is confirmed by XEDS with atomic compositions reaching up to 88% Pt as illustrated in Figure 3.20. This separation of the alloy is again consistent with the phase diagram at the operating temperature of 700°C.
Figure 3.20: STEM HAADF micrographs and XEDS maps of Ni@0.7Pt after ~100 h time on line at 700°C, CH₄/CO₂/He = 1/1/2, P = 1 atm.
The deconvoluted XRD patterns were used to estimate the particle sizes of the Pt, Pt-rich, NiPt, Ni-rich, and Ni components of all the catalysts, which are summarized in Table 3.4. The particle diameters were calculated using the average full width at half maximum (FWHM) of the two respective peaks in the Scherrer equation. The Ni particle size was \( \sim 4.5 - 5.0 \) nm for all Ni-containing catalysts. A consistent Ni size was expected for all the samples since they all came from the same original 5 wt% Ni/Al\(_2\)O\(_3\) batch. For comparison, the particle size distribution of the 5 wt% Ni/Al\(_2\)O\(_3\) catalyst obtained from STEM, shown in Figure 3.21, was used to calculate the number-weighted average (\( d_n = \sum n_i d_i / \sum n_i \)) and the volume-weighted average (\( d_v = \sum n_i d_i^3 / \sum n_i d_i^3 \)). Both the number-weighted average, 6.1 nm, and the volume-weighted average, 7.5 nm, are slightly higher than the estimate from XRD. This discrepancy is likely due to twinning, where multiple particles are agglomerated, but with individual grain boundaries. XRD would detect the agglomerates as separate particles, whereas visual analysis of STEM micrographs may not. In this case, the grain boundaries are not discernible in the micrographs, however, there are many irregular shaped and elongated particles present, which suggests the existence of twinning. Based on XRD, after 20 h of reaction time, the Ni particles only grew by \( 0.5 - 2.0 \) nm, expect for Ni@0.075Pt, which sintered to 9.2 nm.

The Pt-rich and the NiPt alloy phases for the high loading catalysts had slightly larger particles sizes than the base Ni catalysts before the reaction, which is also evident in the XEDS images in Figure 3.18. Schaal et al. demonstrated that Pt sintering occurs as a result of strong interactions with reducing agents, including DMAB, in liquid phase solutions [73]. After reaction, the NiPt size did not significantly change for any of the
Table 3.4: Summary of particle sizes estimated by XRD, sizes in nm.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt</th>
<th>Pt-rich alloy</th>
<th>NiPt</th>
<th>Ni-rich alloy</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh$^a$</td>
<td>Spent$^b$</td>
<td>Fresh</td>
<td>Spent</td>
<td>Fresh</td>
</tr>
<tr>
<td>5% Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.075Pt">Ni@0.075Pt</a></td>
<td>ND</td>
<td>ND</td>
<td>8.2</td>
<td>8.8</td>
<td>3.8</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.4Pt">Ni@0.4Pt</a></td>
<td>ND</td>
<td>ND</td>
<td>9.1</td>
<td>9.9</td>
<td>5.7</td>
</tr>
<tr>
<td><a href="mailto:Ni@0.7Pt">Ni@0.7Pt</a></td>
<td>ND</td>
<td>ND</td>
<td>6.6</td>
<td>17.2</td>
<td>6.1</td>
</tr>
<tr>
<td><a href="mailto:Ni@1.0Pt">Ni@1.0Pt</a></td>
<td>ND</td>
<td>ND</td>
<td>5.5</td>
<td>19.7</td>
<td>5.7</td>
</tr>
<tr>
<td>3% Pt</td>
<td>9.3</td>
<td>17.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

ND Not detected.

$^a$ After preparation and heat treatment at 200°C under H$_2$.

$^b$ After 20 h time online at 700°C, CH$_4$/CO$_2$/He = 1/1/2, P = 1 atm.

$^c$ Ranges between 40.2 – 40.5° 2θ.

$^d$ Ranges between 42.5 – 43.5° 2θ.
catalysts based on XRD measurements. However, after reaction, the sizes of the Pt-rich phases in these two catalysts tripled to 17.2 and 19.7 nm respectively, which demonstrates the tendency of Pt to sinter. In fact, the STEM micrographs, such as those in Figure 3.20, reveal formation of massive agglomerates of Pt-rich particles. Interestingly, these images also reveal that the Ni particles have retained their small size, in agreement with XRD. Conversely, the low Pt-loading catalysts, Ni@0.075 and Ni@0.4Pt, had Pt-rich sizes of 8.2 and 9.1 nm before reaction and 8.8 and 9.9 nm after reaction respectively. However, there was much less Pt in these samples, thus there is likely much more error in deconvoluting these phases.

![Figure 3.21: (a) Representative STEM micrograph and (b) particle size distribution of 5% Ni/Al₂O₃.](image)

### 3.5 Conclusion

A series of Ni-Pt catalysts supported on Al₂O₃ were prepared by the electroless deposition method and evaluated for dry reforming of methane. A kinetic study reveals that the activation energy is minimized with an intermediate loading of Pt. Indeed, Pt
exhibits a promotional effect on activity at lower temperatures. Further, selectivity is
driven by thermodynamics and is not affected by Pt loading. Interestingly, stability at
700°C is adversely affected by the incorporation of Pt as indicated by the increase in
deactivation rates with increasing Pt loading. TPO and STEM reveal that coke formation
is the leading cause of deactivation as carbon formation also increases with Pt loading.
This may be attributed to the higher CH₄ dissociation rate on Pt. TPR, XRD, and STEM
suggest the occurrence of autocatalytic deposition during ED preparation, which results
in higher concentrations of Pt in some particles than others. However, the particles that
contain Pt have an even distribution of the two metals because Ni-Pt alloy formation is
very favorable at the initial heat treatment temperature of 200°C. Post-reaction
characterization reveals that the Pt separates from the alloy, due to the high reaction
temperature, and forms massive Pt-rich agglomerates. The Pt-rich agglomerates then
accelerate coke formation and lead to faster rates of deactivation.
CHAPTER 4

AQUEOUS-PHASE HYDROGENATION OF SUCCINIC ACID USING BIMETALLIC IR-RE/C

CATALYSTS PREPARED BY STRONG ELECTROSTATIC ADSORPTION

4.1 Abstract

Aqueous phase hydrogenation of succinic acid (SAC) was investigated using a series of Ir-Re/C bimetallic catalysts prepared by strong electrostatic adsorption (SEA). Activity measurements show remarkable synergistic effects, forming a volcano-shaped plot over a range of bulk Re mole fractions with a peak at a fraction of 0.4 – 0.5, which corresponds to a 20-fold enhancement of activity over either monometallic catalyst. This intermediate catalyst composition exhibiting optimum activity strongly suggests a bifunctional effect. Through a consecutive reaction pathway with γ-butyrolactone (GBL) as an intermediate, the main product is tetrahydrofuran (THF) with 60 – 75% selectivity. Butanol formation is minimized with decreasing Re mole fraction.

4.2 Introduction

Many important building block chemicals, including C₄ compounds, are produced as co-products from naphtha cracking in the production of ethylene. However, because of the abundance of natural gas, ethylene is increasingly being produced by gas cracking which provides almost none of these heavier co-products [9]. Thus, it is imperative to explore alternative sources to meet the demand of these longer chain, platform chemicals. One alternative is biomass-derived C₄-diacids, such as succinic acid (SAC), which has been named by the Department of Energy (DOE) as one of the top 12 candidates for most economically-viable building block chemicals from biomass [10].
To reach the most promising end markets where SAC is used as feed, it is necessary to hydrogenate it to high-performance chemicals such as γ-butyrolactone (GBL), 1,4-butanediol (BDO), and tetrahydrofuran (THF), shown in Scheme 4.1. This route is competitive with the well-established hydrogenation processes of maleic acid (MAC) such as those developed by Davy-McKee and DuPont [74-78]. In fact, succinic acid is a reaction intermediate in both of these commercial processes; thus, the chemistries are nearly identical [79-81]. Much of the relevant patent literature discusses processes using catalysts based on the early works of Adkins [82, 83] and Broadbent [84], who used copper chromite and Re black, respectively, to hydrogenate various acids and esters,
including MAC and SAC [74-78, 85-90]. For example, the Davy-McKee process uses a copper chromite catalyst to selectivity produce BDO [74], while DuPont has successfully used many bimetallic catalysts containing Re, such as Pd/Re and Ru/Re, both of which are selective to THF [75, 83]. Budge has also found that adding Ag to a Pd/Re/C catalyst enhanced activity and shifted selectivity towards BDO compared to the non-Ag containing catalyst [89].

Until recently, much of the research on hydrogenation of MAC and SAC was only found in patent literature; therefore, little has been done to investigate the fundamentals of the reaction. Regardless, even the proprietary work has shown that bimetallic catalysts exhibit remarkable synergistic effects, especially those containing one oxophilic metal and one platinum group metal (PGM). Deshpande et al. have reported significant enhancement of activity and high selectivity to THF when a Co catalyst is doped with small amounts Ru [91]. We have shown in earlier work synergistic effects on activity between Pd and Re by varying the ratios of the two metals to give a peak in turnover frequency (TOF) at low Re compositions [92]. In a similar study, we demonstrated a similar synergy between Ru and Re [93] where TOF passes through a maximum between a Ru/Re ratio of 1. Through a kinetic study, we determined that Ru was responsible for carboxyl hydrogenolysis, while Re promoted carboxyl hydrogenation. Re is thought to be a good promoter in hydrogenation of oxygenated hydrocarbons because of the strong binding energy between Re and oxygen species [94]. Manyar et al. have suggested that Re promotion for Pt catalysts in the hydrogenation of carboxylic acids is due to the increased
oxophilicity of the surface caused by Re, facilitating the interaction with the lone electron pair of the carbonyl group [95].

For the above reason, we have extended the effect of Re promoters to supported Ir, since Ir is also active for various hydrogenation reactions [96-100]. Results of Nakagawa have also shown promise of Ir-Re catalysts for the hydrogenolysis of glycerol [101]. The authors proposed a bifunctional mechanism where glycerol is adsorbed to the low valent ReO$_x$ species, followed by the hydrogenation of the -OH group at the 2-position by hydrogen adsorbed on an adjacent Ir site. In this study we have prepared a series of Ir, Re, and Ir-Re catalysts using strong electrostatic adsorption (SEA) and evaluated them for the aqueous phase hydrogenation of succinic acid. The results demonstrate significant synergistic interactions between Ir and Re which may be attributed to a bifunctional effect. The metals are apparently located in proximal contact with each other which leads to remarkable improvement in activity of the bimetallic catalyst relative to a physical mixture of the two monometallic catalysts.

4.3 Experimental Section

4.3.1 Catalyst Preparation

All Ir, Re, and Ir-Re catalysts were supported on activated carbon using SEA, which has been explained thoroughly elsewhere [18, 102]. In short, the functional groups on the carbon surface may be utilized by protonation or deprotonation with adjustments of pH to create a strong surface charge. The charged surface is then contacted with an
oppositely charged metal ion, creating a strong electrostatic interaction. K$_2$IrCl$_6$ (99.99% Mack Chem) and NH$_4$ReO$_4$ (99% Sigma Aldrich) were used as the Ir and Re precursors, respectively. The activated carbon granules (derived from coconut-shell, 1400 m$^2$ g$^{-1}$ specific surface area and 0.7 m$^3$ g$^{-1}$ pore volume) were crushed and sieved to 100 mesh before catalyst synthesis. In order to determine the pH at which the strongest surface interaction occurs, surveys were conducted to measure metal salt uptakes using inductively coupled plasma (Perkin Elmer Optima 2000 DV) at various pH values, using a surface loading of 1000 m$^2$ L$^{-1}$, which is the amount of support surface per volume of solution. An uptake survey was performed for each metal, then for both metals together. Catalyst samples of more than 1.0 g each, which are listed in Table 4.1, were then prepared at an optimized pH value of 2. After electrostatic adsorption, the samples were filtered, dried in air overnight at ambient temperature, dried in air at 110 °C for 4 h, and then reduced in 30% H$_2$/Ar for 2 h. After reduction, the samples were stored at ambient conditions.

4.3.2 Catalyst Characterization

Temperature programmed reduction (TPR), x-ray diffraction (XRD), H$_2$ chemisorption, and scanning transmission electron microscopy (STEM) were used to determine metal dispersions and relative locations of Re and Ir to each other. X-ray photoemission spectroscopy (XPS) was conducted to determine the existence of any electronic interactions between Ir and Re. TPR was performed by loading 50 mg of sample into a 1/4-inch quartz tube (4 mm ID) supported on a quartz wool plug and placing the
tube inside a high wattage, split-tube furnace. Prior to analysis, UHP argon was flowed over the sample and heated at 100 °C for 1 h to remove moisture. The sample was cooled to room temperature and the flow was switched to 20 SCCM of 10% H₂/Ar. The sample was then heated from 25 to 800 °C with a ramp rate of 5 °C min⁻¹ while monitoring the exit stream with a quadrupole mass spectrometer (Inficon Transpector 2 Mass Spectrometer). A Rigaku Miniflex Series II equipped with a D/teX silicon strip detector and Cu Kα₁ radiation was used for XRD measurements, and a Micromeritics Autochem II 2920 was used for H₂ chemisorption. Before chemisorption, all samples were reduced in 10% H₂/Ar at 300 °C for 2 h, degassed at 300 °C in flowing argon for 4 h, then cooled to 45 °C. Pulses of 10% H₂/Ar were passed over the sample and the amount of H₂ uptake was measured using a thermal conductivity detector (TCD) to determine active site concentrations. An aberration corrected JEOL JEM2100F was used for STEM imaging. XPS analysis was conducted on selected samples both as prepared and after an in-situ reduction at 300 °C in a flow of H₂ for 2 h using a Kratos Axis Ultra DLD equipped with a monochromated Al Kα x-ray source, hemispherical analyzer, and an in-situ catalysis treatment cell.

4.3.3 Hydrogenation of Succinic Acid

The hydrogenation of succinic acid was carried out in a 50 mL Hastelloy autoclave with a magnetic stirrer and temperature controller. The procedure is similar to previous reports [92, 93]. Prior to the reaction, the catalysts were pretreated in a flow of 30% H₂/Ar at 300 °C for 2 h and allowed to cool to ambient temperature. In a typical reaction, the
autoclave was loaded with 5 wt% SAC in water (1.0 g of SAC, 19.0 g of H₂O). The reduced catalysts were then transferred to the autoclave under an Ar blanket. The reactor was sealed and pressurized/purged five times with H₂ to remove all air, then pressurized to 8 MPa H₂ pressure and closed-off. It was then heated to 240 °C, which increased the pressure to ca. 15 MPa. The reaction was typically run for 10 h with constant stirring at an impeller speed of 800 rpm; liquid aliquots were taken periodically using a dip tube. SAC concentrations were measured using a Waters 1525 high pressure liquid chromatograph equipped with an ultraviolet detector and a C18 column (Welch, Ultimate LP-C18). A 5 mM aqueous solution of phosphoric acid was used as the mobile phase and the absorbed wavelength was 204 nm. All other reaction components were measured using a Tianmei 7890F gas chromatograph equipped with an Agilent HP-FFAP capillary column.

4.4 Results and Discussion

4.4.1 Catalyst Synthesis

In order to find optimum conditions for SEA interaction, metal uptake surveys were performed over a wide range of pH values by contacting the carbon support with pH adjusted solutions. Values of pH and metal ion concentrations were measured before and after carbon addition and are displayed in Figure 4.1. It is intuitive that metal ions should not affect the pH shift of the solution for a purely electrostatic mechanism because the pH shift is a result of only proton exchange between the functional groups on the
Table 4.1: Catalyst compositions, Re surface coverage on Ir calculated from chemisorption, reaction rates.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Ir wt%</th>
<th>Re wt%</th>
<th>Bulk mole fraction, Re/(Ir+Re)</th>
<th>XRD (D_p), Ir diameter (nm)</th>
<th>Chemisorption (\theta_{Re}), Re coverage on Ir</th>
<th>Reaction Rate @ 10% conv. (mol L(^{-1}) h(^{-1}) g(_{metal})^{-1})</th>
<th>(k), rxn rate const. (hr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5%Re/C</td>
<td>0.00</td>
<td>1.50</td>
<td>1.00</td>
<td>-</td>
<td>n/a</td>
<td>9.87</td>
<td>0.08</td>
</tr>
<tr>
<td>IrRe(_2)/C</td>
<td>0.90</td>
<td>1.80</td>
<td>0.67</td>
<td>3.10</td>
<td>37.5</td>
<td>0.79</td>
<td>55.8</td>
</tr>
<tr>
<td>IrRe/C</td>
<td>1.90</td>
<td>1.60</td>
<td>0.47</td>
<td>3.00</td>
<td>80.3</td>
<td>0.54</td>
<td>169.9</td>
</tr>
<tr>
<td>IrRe(_0.6)/C</td>
<td>2.20</td>
<td>1.80</td>
<td>0.46</td>
<td>3.20</td>
<td>75.7</td>
<td>0.57</td>
<td>154.1</td>
</tr>
<tr>
<td>IrRe(_0.5)/C</td>
<td>0.95</td>
<td>0.55</td>
<td>0.37</td>
<td>2.20</td>
<td>434.7</td>
<td>-</td>
<td>212.8</td>
</tr>
<tr>
<td>IrRe(_0.3)/C</td>
<td>1.20</td>
<td>0.30</td>
<td>0.21</td>
<td>1.90</td>
<td>348.0</td>
<td>-</td>
<td>90.5</td>
</tr>
<tr>
<td>1.5%Ir/C</td>
<td>1.60</td>
<td>0.00</td>
<td>0.00</td>
<td>3.20</td>
<td>174.8</td>
<td>0.00</td>
<td>1.33</td>
</tr>
<tr>
<td>Mix*</td>
<td>0.75</td>
<td>0.75</td>
<td>0.51</td>
<td>-</td>
<td>-</td>
<td>12.8</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* 50-50 physical mixture of 1.5% Re/C and 1.5% Ir/C
carbon surface and the proton source/acceptor in solution. This in turn, creates a physical attraction between the metal ion and the carbon surface. As a control experiment, a pH shift survey was performed without any metal ions in solution and compared to those done with metal ions, shown in Figure 4.1(a). For ReO$_4^-$ uptake, the pH shift curve closely follows that of the control experiment, both of which have minimal pH shift, as indicated by the proximity to the 45-degree line. However, in the case of IrCl$_6^{2-}$, there is significant shift to a lower pH in the range of initial pH’s of 4 to 11. The difference from the control curve suggests there is a mechanism other than electrostatic adsorption occurring. Our group has previously demonstrated that oxidized carbon is a major proton donor, leading to a large pH shift similar to the one presented here [102]. In the same study, we also demonstrate that PtCl$_6^{2-}$ undergoes a reductive mechanism when in contact with carbon for long times. Therefore, a possible explanation for the pH-shift in the current study could be the presence of a reductive mechanism where IrCl$_6^{2-}$ is reduced by the carbon surface, which itself is oxidized. IrCl$_6^{2-}$ is known to be a relatively strong oxidizing agent with a reduction potential of 0.867 V [103] and has even been shown to undergo a redox mechanism with carbon nanotubes [104].

Figure 4.1(b) displays the uptake surveys for each IrCl$_6^{2-}$ and ReO$_4^-$ from two separate tests. Since the point of zero charge (PZC) of the activated carbon is about 7 (Figure B.1), it would follow that metal anions should adsorb under acidic conditions. This is exactly what the uptake data show; metal uptake increases as pH is decreased, reaching a maximum of 0.23 and 0.24 µmol m$^{-2}$ for IrCl$_6^{2-}$ and ReO$_4^-$, respectively. Zhu has also reported similar maximum uptake of ReO$_4^-$ on Vulcan XC-72 carbon black [105]. A co-SEA
uptake survey was performed using a solution containing both IrCl$_6^{2-}$ and ReO$_4^-$, which is represented in Figure 4.1(c). The IrCl$_6^{2-}$ uptake was about half of what it was in the case of the monometallic sample, whereas the ReO$_4^-$ uptake was slightly more than half. Thus, the total metal uptake for the bimetallic case is higher than the combined metal uptake of both monometallic surveys. Based on the uptake results, a pH of 2 was chosen for sample preparation.

Figure 4.1: (a) pH shift of impregnation solution for metal uptake surveys of (b) single metals using IrCl$_6^{2-}$ and ReO$_4^-$ and (c) co-impregnation using both metals on activated carbon (surface area = 1400 m$^2$/g), surface loading = 1000 m$^2$/L, control/metal-free (black squares), IrCl$_6^{2-}$ (red circles), ReO$_4^-$ (blue triangle), IrCl$_6^{2-}$/ReO$_4^-$ (green diamonds).
4.4.2 Composition and Physicochemical Properties

Hydrogen TPR was employed to investigate the degree of bimetallic interaction, which is shown in Figure 4.2. Prior to TPR, the samples were exposed to air at 25 °C for a period of time to form Ir and Re oxides, which was confirmed by XPS and discussed later. Therefore, the main reduction peaks are attributed to the reduction of these oxides. The main reduction peak for 1.5% Re/C appears at 310 °C, which is a much higher temperature than that for 1.5% Ir/C, which occurs at 105 °C. The bimetallic samples have a single peak between the two temperatures of the monometallic Ir and Re samples, although the peak location is much closer to that for the 1.5% Ir/C. In fact, the broad peak for the IrRe₂/C sample can be resolved into two peaks, one centered at ~105 °C and the other near 190 °C.

Figure 4.2. H₂-TPR of catalysts after exposure to air at 25 °C showing normalized mass spec signal of H₂O (m/e = 18), temperature ramp rate = 5 °C, “AC” corresponds to the carbon support alone.
℃. The pronounced trend of gradually decreasing reduction temperature with increasing Ir/Re atomic ratios strongly indicates a high degree of bimetallic interaction. The close contact between the two metals permits Ir-assisted reduction of Re by H spillover; dissociative adsorption of H₂ occurs on Ir followed by diffusion of adsorbed H to adjacent Re sites. This same trend has been reported before for Ru-Re/C and Pd-Re/C [92, 93]. It is also well known that Re oxide has a very low surface free energy and Ir has a very high surface energy, thus it is thermodynamically favored for the Re oxide to diffuse onto the surface of Ir in order to reduce the overall surface free energy [15, 106, 107]. This helps explain the close interaction of the two metals. In addition to the reduction peaks of the oxidized Ir and Re, all samples have a broad peak above 400 ℃ which can be attributed to methanation of the carbon support.

XRD patterns of all SEA-prepared samples are displayed in Figure 4.3(a). All patterns closely resemble that of the activated carbon support with very subtle Ir⁰ features. However, these peaks may be deconvoluted by subtracting the contribution from the support. As an example, the baseline-subtracted pattern for 1.5% Ir/C is shown in Figure 4.3(b). After subtraction of the support, Ir⁰ is still the only phase present with prominent peaks at 42° and 47° for Ir(111) and Ir(200), respectively. The Scherrer equation was used on these peaks to obtain a volume average particle size and the results are shown Table 4.1. All samples had XRD particle sizes between 1.9 and 3.2 nm, which confirms the control of the metal particle sizes using the SEA preparation methodology. The absence of any Re phase suggests that Re is highly dispersed, which agrees well with the literature [92, 93, 108]. Further, comparison of the patterns of the bimetallics to that
of the monometallic Ir sample shows there are no observable shifts in the Ir peaks, suggesting there is no Ir-Re alloy formation [108].

Figure 4.3: (a) XRD of catalysts after reduction, scan speed = 1°/min, (b) deconvolution of 1.5% Ir/C after background subtraction with fitted peaks, “AC” corresponds to the carbon support alone.

Since Re is thermodynamically favored to exist as a shell on the Ir core, H$_2$-chemisorption was employed to determine the surface coverage of Re on Ir. Two
assumptions were necessary in order to do this. First, we assumed there is no H spillover from Ir to Re at the chemisorption temperature of 40 °C. The TPR results in Figure 4.2 suggest that H spillover does occur but appears to require temperatures > 40 °C and dissociative chemisorption of H\textsubscript{2} on metallic Re is activated and does not occur to a significant degree at temperatures below 150 °C, as shown in Figure B.2. Secondly, we assumed the available Ir surface area for Re to cover is consistent for all samples and is equal to that for 1.5% Ir/C. This is a reasonable assumption because XRD suggests Ir sizes are consistent for all samples. Table 4.1 and Figure 4.4 show the results of chemisorption. Calculating the particle size from the chemisorption data for 1.5% Ir/C yields 1.5 nm, which is about half the size determined by XRD. This may be explained by the particle size distribution determined by STEM, shown in Figure 4.5. The distribution is right-skewed; thus, the XRD is likely detecting the larger particles that make up the larger diameter tail.

![Figure 4.4: Re coverage on Ir determined by H\textsubscript{2}-chemisorption.](image-url)
As a comparison, the STEM data were used to calculate the number, surface, and volume average particle sizes, summarized in Table B.1. As expected, the volume average, 2.3 nm, agrees more closely with XRD, whereas the number and surface averages, 1.7 and 2.1 respectively, agree better with chemisorption results. As shown in Figure 4.4, the calculated Re surface coverage on Ir is consistently 15 – 20% greater than the bulk Re loadings for all samples with a Re mole fraction > 0.5. A possible explanation for the higher coverage is the low surface free energy and mobility of oxidized Re species permitting a higher coverage on the Ir surface [15]. However, samples with a Re fraction < 0.5, adsorbed more H₂ than their Ir-only reference, possibly indicating enhanced H spillover for the Ir-rich surfaces.

In order to explore possible electronic interactions between Ir and Re, XPS studies were conducted on 1.5% Ir/C, 1.5% Re/C, and IrRe/C samples, which are summarized in Figure 4.6. Measurements were taken of the “as prepared” samples and again after an in-
situ reduction with 100% H₂ at 300 °C for 2 h using a catalysis cell attached to the XPS chamber. All “as prepared” samples had undergone prior reduction treatments before exposure to air at ambient conditions. The Re 4f spectra of 1.5% Re/C and IrRe/C catalysts are shown in Figure 4.6(a). The Re 4f<sub>7/2</sub> binding energy (BE) values for both “as prepared” catalysts are 44.8 eV. According to the NIST database, ReO₃ has a BE of 45.0 eV, confirming that both samples are in an oxidized state [109]. This is not surprising given that Re is very oxophilic. After in-situ reduction, the Re 4f<sub>7/2</sub> BE for the 1.5% Re/C catalyst shifted to 40.6 eV, whereas for the IrRe catalyst, the BE was 41.1 eV. According to the database, Re⁰ has a BE between 40.3 and 40.9 eV, which agrees well with the 1.5% Re/C catalyst. However, for IrRe/C, the presence of Ir shifts the BE of Re by 0.5 eV to 41.1 eV, which corresponds to an oxidation state of +1.8, indicating an electronic interaction between Ir and Re. Amada et al. have published similar results using in situ extended x-ray absorption fine

![Figure 4.6: Re 4f spectra of (a) IrRe/C and (b) 1.5% Re/C, Ir 4f spectra of (c) IrRe/C and (d) 1.5% Ir/C before and after in-situ reduction at 300 °C.](image)
structures (EXAFS) during H₂ TPR of Ir-ReOₓ/SiO₂ [108]. They demonstrated that the valence of Re changes from +7 to +2 between reduction temperatures of 130 – 200 °C and remains at +2 even at reduction temperatures up to 630 °C. Similar studies have shown the presence of low valence Re species in the presence of noble metals [110-112].

The Ir 4f peaks of 1.5% Ir/C and IrRe/C are displayed in Figure 4.6(b). Before reduction, the Ir 4f7/2 peak of both the 1.5% Ir/C and IrRe/C catalysts had binding energy peaks at 61.7 eV, which is consistent with IrO₂. According to XRD, only the Ir⁰ phase is present in the bulk, which suggests that IrO₂ is only present on the surface of the particles. After reduction of 1.5% Ir/C, XPS shows a peak at 61.1 eV with a shoulder at 61.7 eV. According to the NIST database, Ir⁰ has a BE of 61.0 eV, which implies there is mostly Ir⁰ with some residual IrO₂ [109]. Conversely, the IrRe/C catalyst does not exhibit the presence of any IrO₂ and the BE of the Ir 4f7/2 is at 60.9 eV which is lower than that of the monometallic Ir sample which strongly implies the source of the +0.5 eV BE shift for the Re 4f7/2 is e⁻ transfer from Re to the 4f7/2 Ir energy level. In short, the XPS data confirm the strong bimetallic interaction between the Re and Ir components of the bimetallic surface.

4.4.3 Hydrogenation of Succinic Acid

The series of catalysts were evaluated for the aqueous phase hydrogenation of succinic acid. The concentrations of succinic acid as a function of reaction time for all catalysts are shown in Figure 4.7(a). These data were linearized based on the integrated form of the first order reaction rate equation, displayed in Figure 4.7(b) and used to calculate the first order reaction rate constants summarized in Table 4.1. There is a
significant synergistic effect between Re and Ir since the monometallic catalysts displayed very low activity with 1.5% Ir/C and 1.5% Re/C reaching only about 9% and 60% conversion of SAC, respectively, after 10 h on-line. Conversely, the bimetallic catalysts reached full conversion of SAC after only 1 – 6 h. Because of the varying concentrations of Ir and Re, it is better to compare pseudo-initial activities at 10% conversion of SAC by normalizing to the total amounts of metal. From Figure 4.8, there is a very evident volcano-shaped trend where the normalized reaction rate reaches a maximum at a bulk

Figure 4.7: (a) Succinic acid concentrations versus reaction time, (b) linearization of concentration versus time showing first order dependence, 1.5% Ir/C (black circles), IrRe$_{0.3}$/C (gray stars), IrRe$_{0.5}$/C (orange plus), IrRe$_{0.6}$/C (pink diamond), IrRe/C (blue triangle down), IrRe$_2$ (green triangle up), 1.5% Re/C (red squares).
Re mole fraction of ~ 0.4 moles Re/(moles Ir + moles Re). At this composition, the normalized reaction rate is approximately 160 times greater than that of 1.5% Ir/C and 20 times greater than that of 1.5% Re/C. To confirm that this marked enhancement in activity is due to the bimetallic interactions of Ir and Re, we ran a reaction using a 50-50 physical mixture of 1.5% Ir/C and 1.5% Re/C. The physical mixture displayed low activity similar to the average of the two monometallic catalysts as shown in Figure 4.8. Rodriguez et al. have suggested that synergistic effects like the current example could be the result of an ensemble effect, an electronic effect, or a bifunctional effect [113]. As previously mentioned, others have found that Re typically functions best as an oxophile and preferentially adsorbs oxygenated species; other metals such as Ir are much more effective as hydrogenation catalysts [93, 95, 101]. This implies that catalysts having a

![Figure 4.8: Normalized reaction rates at 10% conversion of SAC versus bulk Re loading, compared to 50-50 physical mixture of 1.5% Ir/C and 1.5% Re/C.](image)
bimetallic surface, such as the Ir-Re surfaces of these catalysts, exhibit a bifunctional
effect. Di et al. found that TOF for hydrogenation of SAC is highest for catalysts containing
equal amounts of Ru and Re, which suggests that both sites are involved in the rate
determining step, again evidence for a bifunctional effect. In our case, the maximum
activity occurs at a bulk Re mole fraction of 0.4 – 0.5 suggesting a similar bifunctional
effect with bimetallic Ir-Re site pairs as the active sites. The maximum, statistical
concentration of such occurs at 0.5 surface coverage of Re on Ir.

Because the hydrogenation of SAC follows a consecutive reaction pathway as
shown in Scheme 4.1, it is informative to examine the transient concentrations of GBL,
which are shown in Figure 4.9(a) [91, 93]. For the monometallic catalysts, GBL
concentrations slowly increase throughout the entire reaction time and make up about
82 – 84% of all products, as shown in the product distribution of Figure 4.10; however,
they are almost completely inactive for the C – O bond scission of GBL. Conversely, C—O
bond rupture is facilitated for all the bimetallic catalysts. All bimetallic catalysts reach a
peak in GBL concentration between 1 and 2 h of reaction time. Interestingly, the rates of
hydrogenation of GBL increase with higher Re content of the bimetallic catalysts, as
indicated by the lower heights of the GBL peaks and the shorter length of time it takes for
GBL to react away. This same trend was seen by Shao for Pd-Re/C catalysts [92].

Hydrogenation of GBL may require more surface Re sites, but still needs the bifunctional
effect of the noble metal because Re alone results in termination of the reaction at GBL.
Even though bimetallic compositions with a large amount of Re are faster for
hydrogenation of GBL, the intermediate compositions are still kinetically favored for THF
production as indicated by the concentration profiles in Figure 4.9(b). THF makes up 60 – 75% of the products for all bimetallic samples, and n-butanol accounts for the remainder. Butanol formation increases with increasing Re content, consistent with the acid-
catalyzed ring opening mechanism proposed by the groups of Davis, Dumesic, and Neurock [114-116]. They have suggested hydroxylated Re atoms serve as acid sites for C – O hydrogenolysis of cyclic ethers to form a stabilized and ring-opened, oxocarbenium ion, which is then hydrogenated by the noble metal. In our case, the monotonic trend of further ring opening with higher Re loading suggests that the C – O hydrogenolysis is the rate determining reaction. This is followed by the rapid hydrogenation of the intermediate by Ir. Thus, control of both surface Re and Ir concentrations are required to balance the rates of hydrogenation of SAC with the consecutive, non-selective ring opening of THF and rapid hydrogenation to n-butanol. In addition, reaction parameters can very likely be further tailored to minimize butanol production [80] and increase production of the more valuable THF molecule.

Figure 4.10: Product distribution after 10 h of reaction time.
4.5 Conclusions

The effect of Ir-Re/C bimetallic catalyst composition on performance in aqueous phase hydrogenation of SAC was investigated. A series of Ir, Re, and Ir-Re catalysts supported on activated carbon were prepared using strong electrostatic adsorption (SEA). Characterization data show that bimetallic catalysts consist of highly dispersed Ir particles (~1.5 nm), which are in close contact and partially covered by Re. Activity measurements for hydrogenation of SAC result in a volcano-shaped plot over the whole range of catalyst compositions, with the maximum at an intermediate composition, indicating a bifunctional effect. THF selectivity for all bimetallic samples ranged from 60 – 75%, which was formed through a consecutive pathway with GBL as an intermediate. Further hydrogenation occurred to produce 20 – 30% butanol, but was minimized with decreasing Re mole fraction.

4.6 Acknowledgements

This work was supported by the National Science Foundation (no. 1250052) and the National Natural Science Foundation of China (no. 21573031).
CHAPTER 5

SUMMARY AND CONCLUSIONS
In summary, the U.S. shale gas revolution has brought tremendous growth in the energy and petrochemicals industries. The abundant supply of hydrocarbons has revealed opportunities to develop catalytic processes that are directly and indirectly related to upstream and downstream production. This work focused on the development of bimetallic catalysts using novel preparation techniques.

One opportunity that exists because of the shale boom is to employ GTL processes to utilize gas that is associated with oil wells in remote locations. The development of these technologies would also increase the commercial appeal of remote gas wells. Many GTL processes require synthesis gas, which is produced by reforming of methane. In certain situations, it is attractive to utilize CO\textsubscript{2} as the oxidant in reforming of methane. This also has the benefit of utilizing the two most potent greenhouse gases.

For this work, the performance of a series of Pt-promoted Ni catalysts were evaluated for dry reforming of methane. Kinetic data reveal a promotional effect of Pt at temperatures between 525 – 600°C, which is optimized with a small loading of Pt. However, there is an apparent compensational effect as indicated by the relationship between activation energies and pre-exponential factors. This results in a reversal of the promotional effect at high temperatures (>624°C). Selectivity is not affected by incorporation of Pt as products are near equilibrium ratios. A Pt-only catalyst is shown to deactivate very quickly at 700°C due to high CH\textsubscript{4} decomposition rates and subsequent coke deposition. Following suit, Pt addition to Ni increases the rate of carbon deposition. Characterization data suggest that coke is in the form of carbon whiskers for all samples. During ED preparation, autocatalytic deposition was prominent, which resulted in
particles with high Pt content. However, particles that contained Pt were well mixed Ni-Pt alloys because of the favorability of alloy formation at the preparation heat treatment temperature of 200°C. After reaction at 700°C, characterization reveals the alloy separated and very large Pt-rich agglomerates were formed. This explains the increased rate of deactivation as Pt was shown to accelerate CH₄ decomposition. This study highlights the importance of testing long-term stability under conditions that avoid thermodynamic limitations and expose the dynamics of deactivation. Moreover, it is also important to study the steady state performance of catalysts at varying temperatures. As we found here, what seems to be a more active catalyst at one temperature is not necessarily more accurate at another temperature.

Another opportunity that has been revealed by the shale boom through an indirect relationship is the utilization of biomass to fill the growing supply gap in C₄ building block chemicals for downstream production. This is a result of the shift to employ natural gas as the feed to petrochemical plants, which produces almost no longer chain hydrocarbon co-products. Succinic acid has been identified as one of the most commercially viable building block chemicals derived from biomass. The most useful derivatives of SAC are produced via hydrogenation.

For this work, a series of Ir-Re/C catalysts with varying composition were prepared by co-SEA and evaluated for aqueous phase hydrogenation of SAC. Characterization data reveal that bimetallic catalysts consist of very small Ir particles (~1.5 nm), which are partially covered by Re because of the difference in surface free energies. Reaction results reveal a significant synergistic effect between Ir and Re as the most active bimetallic
catalyst exhibits an activity that is 20 times greater than either of the monometallic catalysts. The most active catalyst has an Ir/Re atomic surface ratio near unity, which indicates that the synergy is mainly due to a bifunctional effect. This is consistent with mechanisms for similar systems in literature where the oxygenated functional group preferentially binds to the oxophilic Re surface, followed by hydrogenation by adsorbed hydride species on the noble metal, in this case Ir [101]. Selectivity towards THF ranged from 60 – 75% for all bimetallic catalysts through a consecutive pathway with GBL as an intermediate. Further hydrogenation to n-butanol increases with increasing Re content, consistent with the acid-catalyzed ring opening mechanism previously reported [114]. Hydroxylated Re atoms in an aqueous environment provide acid sites for this mechanism to occur.
REFERENCES


[60] H. Wu, G. Pantaleo, V. La Parola, A.M. Venezia, X. Collard, C. Aprile, L.F. Liotta, Bi- and trimetallic Ni catalysts over Al2O3 and Al2O3-MOx (M= Ce or Mg) oxides for methane dry reforming: Au and Pt additive effects, Applied Catalysis B: Environmental, 156 (2014) 350-361.


Figure A.1: Deconvoluted XRD patterns of Ni@0.075Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH₄/CO₂/He = 1/1/2, P = 1 atm.
Figure A.2: Deconvoluted XRD patterns of Ni@0.4Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH₄/CO₂/He = 1/1/2, P = 1 atm.

Figure A.3: Deconvoluted XRD patterns of Ni@0.7Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH₄/CO₂/He = 1/1/2, P = 1 atm.
Figure A.4: Deconvoluted XRD patterns of Ni@1.0Pt (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH₄/CO₂/He = 1/1/2, P = 1 atm.

Figure A.5: Deconvoluted XRD patterns of 3%Pt/Al₂O₃ (a) after preparation heat treatment of 200°C and (b) after reaction at 700°C for 20 h, CH₄/CO₂/He = 1/1/2, P = 1 atm.
Figure A.6: STEM HAADF micrographs and XEDS maps of Ni@0.4Pt before (a)-(d) and after (e)-(h) reaction for ~100 h time on line 500-600°C, CH₄/CO₂/He = 1/1/2, P = 1 atm.
Figure B.1: pH shift of activated carbon in solution for PZC determination, surface loading = 50,000 m² L⁻¹.
Table B.1: Ir particle size comparison for 1.5% Ir/C, all sizes in nm.

<table>
<thead>
<tr>
<th></th>
<th>XRD</th>
<th>Chemisorption</th>
<th>STEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number average</td>
<td>3.2</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Surface average</td>
<td>1.7</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Volume average</td>
<td></td>
<td></td>
<td>2.3</td>
</tr>
</tbody>
</table>
APPENDIX C

PERMISSION TO REPRINT
Aqueous-phase hydrogenation of succinic acid using bimetallic Ir-Re/C catalysts prepared by strong electrostatic adsorption

Author: Jayson M. Kees, Xiao Chen, Stavros G. Karakalos, et al

Publication: ACS Catalysis
Publisher: American Chemical Society
Date: Jun 1, 2018
Copyright © 2018, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.