ETHANOL STEAM REFORMING OVER COBALT BASED CATALYSTS:

ROLES OF ZINC OXIDE

By

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ETHANOL STEAM REFORMING OVER COBALT BASED CATALYSTS:
ROLES OF ZINC OXIDE

Abstract

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The effects of zinc oxide (ZnO) addition to cobalt based catalysts was investigated over multiple supports. In each case the impacts on cobalt oxidation state and ESR activity were studied. In the case of cobalt supported on carbon (Co/C) it was found that ZnO addition inhibited reduction of cobalt oxides by H₂ and created surface sites for H₂O activation. At 250 °C cobalt reduction was minimal, in situ XANES demonstrated that ZnO addition significantly facilitated oxidation of Co⁰ under vapor phase reforming conditions, which was further demonstrated by lower C₁ product yield. During vapor phase reforming at 450 °C the redox of cobalt, driven by steam oxidation and H₂ reduction, trended to an equilibrium of Co⁰/Co²⁺. ZnO showed no significant effect on cobalt oxidation, inferred from the minor changes of C₁ product yield. Surface sites created by ZnO addition enhanced water activation and oxidation of surface carbon species, increasing CO₂ selectivity. In the case of cobalt supported on zirconia (Co/ZrO₂) it was found that the addition of ZnO to cobalt supported on ZrO₂ decreased the activity for H₂O dissociation, leading to a lower degree of cobalt oxidation. The decreased H₂O dissociation was also found to affect the reaction pathway, evidenced by a shift in liquid product selectivity away from acetone and towards acetaldehyde. The changes in H₂O dissociation activity were further supported by in situ Raman spectroscopy, H₂O-TPO, and pulsed H₂O oxidation coupled with H₂-
TPR. Finally, for the case of cobalt supported on ceria (Co/CeO$_2$) it was found that the addition of ZnO facilitates the oxidation of metallic Co$^0$ via enhanced oxygen mobility of the CeO$_2$ support which decreases the activity of Co/CeO$_2$ in C–C bond cleavage of ethanol. 3 wt % ZnO promoted Co/CeO$_2$ exhibits minimum CO and CH$_4$ selectivity and maximum CO$_2$ selectivity. Overall, it was found that ZnO addition can affect the activity for H$_2$O dissociation and the oxidation stability of Co$^0$. This creates a new control facet for more intelligent design of future cobalt based catalysts for ESR.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>CHAPTER ONE: GENERAL INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1. HYDROGEN PRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. BIO-HYDROGEN</td>
<td>2</td>
</tr>
<tr>
<td>2.1 Ethanol Steam Reforming (ESR)</td>
<td>2</td>
</tr>
<tr>
<td>2.2 ESR Over Co</td>
<td>3</td>
</tr>
<tr>
<td>3. DISSERTATION OUTLINE</td>
<td>7</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>9</td>
</tr>
<tr>
<td>CHAPTER TWO: THE EFFECT OF ZNO ADDITION ON CO/C CATALYST FOR VAPOR AND AQUEOUS PHASE REFORMING OF ETHANOL</td>
<td>14</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>15</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>16</td>
</tr>
<tr>
<td>2. RESULTS AND DISCUSSION</td>
<td>18</td>
</tr>
<tr>
<td>2.1 Effect of ZnO on Physical Properties</td>
<td>18</td>
</tr>
<tr>
<td>2.2 Effect of ZnO on Reduction and Oxidation Properties</td>
<td>20</td>
</tr>
</tbody>
</table>
2.3 Effect of ZnO on ethanol reforming activity ................................................................. 23
2.3.1 ESR at 450 °C ........................................................................................................... 23
2.3.2 Vapor phase and aqueous phase ethanol reforming at 250 °C ............................... 27
3. CONCLUSION .................................................................................................................. 29
ACKNOWLEDGEMENTS ................................................................................................. 29
REFERENCES ..................................................................................................................... 31

CHAPTER THREE: THE EFFECT OF ZNO ADDITION ON H2O ACTIVATION OVER CO/ZRO2 CATALYST .................................................................................................................. 46

ABSTRACT .......................................................................................................................... 47

1. INTRODUCTION ............................................................................................................. 48

2. RESULTS AND DISCUSSION ......................................................................................... 49
   2.1 Catalyst characterization ............................................................................................ 49
      2.1.1 Effect of ZnO on physical properties ............................................................... 49
      2.1.2 Effect of ZnO on H2O Dissociation ................................................................. 51
      2.2 Effect of ZnO on Ethanol Steam Reforming ......................................................... 56

3. CONCLUSION .................................................................................................................. 58
ACKNOWLEDGEMENTS ................................................................................................. 59
REFERENCES ..................................................................................................................... 60
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broader Impact</td>
<td>113</td>
</tr>
<tr>
<td>BACKGROUND</td>
<td>114</td>
</tr>
<tr>
<td>RESULTS FROM PRIOR WORK</td>
<td>117</td>
</tr>
<tr>
<td>PROJECT PLAN</td>
<td>118</td>
</tr>
<tr>
<td>Catalyst Synthesis</td>
<td>119</td>
</tr>
<tr>
<td>Physical/Chemical Characterization</td>
<td>119</td>
</tr>
<tr>
<td>H$_2$O Dissociation Activity</td>
<td>120</td>
</tr>
<tr>
<td>Kinetic Testing</td>
<td>122</td>
</tr>
<tr>
<td>Objective 1: Cobalt Particle Size Effect</td>
<td>123</td>
</tr>
<tr>
<td>Objective 2: Low H$_2$O Dissociation Activity</td>
<td>124</td>
</tr>
<tr>
<td>Objective 3: High H$_2$O Dissociation Activity</td>
<td>124</td>
</tr>
<tr>
<td>PRELIMINARY RESULTS</td>
<td>124</td>
</tr>
<tr>
<td>MANAGEMENT PLAN</td>
<td>124</td>
</tr>
<tr>
<td>EVALUATION ASSESSMENT</td>
<td>124</td>
</tr>
<tr>
<td>DISSEMINATION</td>
<td>125</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>125</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>126</td>
</tr>
<tr>
<td>APPENDIX a: SUPPORTING INFORMATION</td>
<td>136</td>
</tr>
<tr>
<td>APPENDIX B: EXPERIMENTAL METHODS</td>
<td>144</td>
</tr>
<tr>
<td>1. CHAPTER TWO EXPERIMENTAL METHODS</td>
<td>144</td>
</tr>
</tbody>
</table>
1.1 Catalyst Synthesis ................................................................. 144
1.2 Catalyst Characterization .................................................. 144
1.3 Catalyst Activity Evaluation .............................................. 147

2. CHAPTER THREE EXPERIMENTAL METHODS ........................... 148
2.1 Catalyst Synthesis ............................................................. 148
2.2 Catalyst Characterization .................................................. 149
2.3 Catalyst Activity Evaluation .............................................. 151
2.4 In situ Raman characterization of cobalt oxidation by H₂O .......... 152

3. CHAPTER FOUR EXPERIMENTAL METHODS .............................. 152
3.1 Catalyst Synthesis ............................................................. 152
3.2 Nitrogen adsorption-desorption ........................................ 153
3.3 CO Chemisorption ............................................................. 153
3.4 X-ray Diffraction (XRD) ..................................................... 153
3.5 Temperature Programmed Reduction/Oxidation/Desorption (TPR/TPO/TPD) .......... 154
3.6 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis of adsorbed pyridine (IR-Py) ................................................................. 155
3.7 Transmission Electron Microscope (TEM) ............................. 155
3.8 Activity Test ...................................................................... 155

APPENDIX C: EXPERIMENTAL PROTOCOLS .................................... 158
AUTOCHEM 2920/CHEMISORPTION ANALYZER OPERATIONS .............. 158
LIST OF TABLES

CHAPTER TWO: THE EFFECT OF ZNO ADDITION ON CO/C CATALYST FOR VAPOR AND AQUEOUS PHASE REFORMING OF ETHANOL

Table 1 – Physical properties of catalysts........................................................................................................35

CHAPTER THREE: THE EFFECT OF ZNO ADDITION ON H2O ACTIVATION OVER CO/ZRO2 CATALYST

Table 1 – Physical properties of catalysts........................................................................................................66
Table 2 – Comparison of H2O dissociation over different supports...............................................................71

CHAPTER FOUR: ETHANOL STEAM REFORMING ON CO/CEO2: THE EFFECT OF ZNO PROMOTER

Table 1 – Physical-chemical properties of catalysts.........................................................................................96

CHAPTER SIX: FUTURE WORK – NSF PROPOSAL

Table 1 – Timeline of experiments................................................................................................................135
LIST OF FIGURES

CHAPTER TWO: THE EFFECT OF ZNO ADDITION ON CO/C CATALYST FOR VAPOR AND AQUEOUS PHASE REFORMING OF ETHANOL

Figure 1 – XRD patterns .................................................................................................................36

Figure 2 A – TEM images ................................................................................................................37

Figure 2 B – TEM images ................................................................................................................38

Figure 3 A – TPR profiles ................................................................................................................39

Figure 3 B – TPO profiles ................................................................................................................40

Figure 4 A – XANES spectra 10Co/C ...............................................................................................41

Figure 4 B – XANES spectra 10Co5ZnO/C ......................................................................................42

Figure 5 – ESR activity at 450 °C ......................................................................................................43

Figure 6 – ESR activity at 250 °C ......................................................................................................44

Schematic 1 – Catalyst system for ESR over Co/C .........................................................................45

CHAPTER THREE: THE EFFECT OF ZNO ADDITION ON H2O ACTIVATION OVER CO/ZRO2 CATALYST

Figure 1 – XRD patterns .................................................................................................................67

Figure 2 A – TEM particle size distribution 10Co/ZrO2 .................................................................68

Figure 2 B – TEM particle size distribution 10Co1Zn/ZrO2 ...........................................................69
Figure 2 C – TEM particle size distribution 10Co/ZnO .........................................................70

Figure 3 A – Raman spectra 10Co/ZrO$_2$ ..................................................................................72

Figure 3 B – Raman spectra 10Co1Zn/ZrO$_2$ ...............................................................................73

Figure 4 A – Raman spectra 10Co/ZnO .......................................................................................74

Figure 4 B – Raman spectra Co$_3$O$_4$ ..........................................................................................75

Figure 5 A – Pulsed H$_2$O oxidation ............................................................................................76

Figure 5 B – Pulsed H$_2$O oxidation H$_2$-TPR .............................................................................77

Figure 6 – H$_2$O TPO profiles .......................................................................................................78

Figure 7 – ESR at 450 °C ................................................................................................................79

CHAPTER FOUR: ETHANOL STEAM REFORMING ON CO/CEO$_2$: THE EFFECT OF ZNO PROMOTER

Figure 1 – XRD patterns ...............................................................................................................97

Figure 2 – High resolution XRD patterns ....................................................................................98

Figure 3 – TEM images ................................................................................................................99

Figure 4 – TPR profiles .................................................................................................................100

Figure 5 – TPO profiles ................................................................................................................101

Figure 6 – Pyridine DRIFTs spectra .............................................................................................102

Figure 7 – CO$_2$ TPD profiles .......................................................................................................103

Figure 8 – C-C cleavage conversion .............................................................................................104

Figure 9 – ESR C$_1$ selectivity .....................................................................................................105
Scheme 1 – Schematic of oxidation over 10Co3ZnO/CeO2.................................................................106
Figure 10 – ESR light alkane selectivity..........................................................................................107

CHAPTER FIVE: CONCLUDING REMARKS

Scheme 1 – Schematic of ESR over cobalt based catalyst .............................................................111

CHAPTER SIX: FUTURE WORK – NSF PROPOSAL

Figure 1 A – ESR over Co/ZrO2 ...................................................................................................130
Figure 1 B – ESR over Co/CNF ....................................................................................................131
Figure 2 A – XANES spectra of 10Co/C......................................................................................132
Figure 2 B – XANES spectra of 10Co5ZnO/C.............................................................................133
Figure 3 – ESR selectivity over Co catalysts............................................................................134
DEDICATION

This work is dedicated to my friends and family for their all of their love and support.

A special dedication to Suzanne Marie de Lemos.
CHAPTER ONE:
GENERAL INTRODUCTION

This dissertation is divided up into six chapters, with chapter one being a general introduction to integrate the presentation of individual manuscripts. Chapters two, three, and four are published manuscripts. Each manuscript has been published in the peer-reviewed journals Catalysis Today and Topics in Catalysis. In each manuscript Stephen Davidson contributed the experimental work, data analysis, and manuscript writing. The manuscripts are co-authored with Junming Sun, Yongchun Hong, Ayman M. Karim, and Abhaya K. Datye, who contributed technical expertise. Professor Yong Wang is the corresponding author for all publications. Chapter five provides overall conclusions from all work and chapter six proposes potential future work for the project. Appendix A contains some additional supporting information that was not published in peer reviewed journals. Experimental methods from published papers have been moved to appendix B. Appendix C contains experimental protocols used and appendix D contains calibration curves for GC analysis and for TCD and QMS analysis.

1. HYDROGEN PRODUCTION

Hydrogen is a widely used chemical commodity. The market for hydrogen was estimated at ~254 billion m³ and $103.5 billion [1, 2]. Uses of hydrogen range from chemical synthesis of ammonia and methanol to metal and petroleum processing [3]. More recently, hydrogen has also gained attention as a clean energy carrier with use of proton exchange membrane (PEM) fuel cells.

Despite the wide range of uses for hydrogen, the majority is produced and consumed on site; this is because hydrogen poses several challenges that other commodity chemicals do not.
Hydrogen boasts one of the highest energy densities on a per mass basis (~142 MJ/kg), however, it has an extremely low energy density by volume (~8 MJ/L for liquid H\textsubscript{2}) [4]. In addition, because of the high diffusivity and embrittlement of metal, specialized materials are needed for construction of the piping [4]. Alternatively, hydrogen can be compressed or liquefied and then shipped. Both, however, are costly operations and liquefaction also requires cryogenic storage materials, adding additional costs for shipping. To avoid this, the majority of hydrogen is produced via natural gas. ~49% of global hydrogen production is done via steam reforming of methane (SRM) [3, 5]. SRM is typically done at high temperatures (700 – 1000 °C) and high pressure (> 5 atm) over a Ni/Al\textsubscript{2}O\textsubscript{3} catalyst [3, 5]. Natural gas avoids many of the transportation and storage problems associated with H\textsubscript{2}; it is able to be transported via pipeline and does not require specialized materials for storage. While natural gas works well on industrial scales at fixed locations, there is a need for smaller and more modular hydrogen production, especially for usage with fuel cells.

2. BIO-HYDROGEN

2.1 Ethanol Steam Reforming (ESR)

In recent decades, bio-derived compounds, such as ethanol, have received a great deal of attention as potential feed stocks for steam reforming [3, 6]. Ethanol has several advantages as it is easy to transport and store, has a relatively low toxicity, and fermentation broth can be used with little to no further separations [7]. In addition, ethanol is the simplest molecule with both C-C and C-O bonds, making it an excellent model compound for extrapolation to other oxygenates. A wide range of catalysts have already been investigated for ethanol steam reforming (ESR) from noble to base metals [6]. Of the noble metals Pt and Rh have shown some of the highest activity for C-C bond cleavage [6, 8, 9]. However, Pt and Rh have also shown high selectivity to

2
methane both through ethanol decomposition and through competitive methanation reaction, which severely limits H₂ yield [8, 9]. Of the base metals investigated, Ni and Co have shown the highest activity. Ni has shown relatively high activity for C-C cleavage, however, it too suffers from high CH₄ selectivity. Much of the recent work on ESR over Ni based catalysts have been focused on minimizing selectivity to CH₄. Co has shown similar C-C cleavage to Ni and relatively lower selectivity to CH₄.

2.2 ESR Over Co

A great deal of work has already been done in the area of ESR over Co based catalysts. The activity of cobalt for ethanol steam reforming has been investigated over a variety of supports ranging from acidic/basic Al₂O₃, TiO₂, ZrO₂, MgO, ZnO and CeO₂ to relatively inert C, SiO₂, and so forth [10-14]. A general agreement is that metallic cobalt acts as the most active site for C-C/C-H bond cleavage, while the support plays a key role in the ESR reaction network leading to the different product distribution and catalyst stability. Especially at lower Co loading, the catalysts and its performance are dominated by support chemistry. For example, Llorca et al. studied 1 wt% cobalt on a series of supports; ethylene, a dehydration product, was predominant with acidic supports (e.g., Al₂O₃) [14]. Even at high loading (8.6 wt% Co/Al₂O₃), Batista et al. found that Al₂O₃ favored ethanol dehydration to ethylene, which then polymerized and formed carbon filament on the cobalt [11]. In contrast, ethanol dehydrogenation was enhanced on basic supports (e.g., MgO) [14]; the facile dehydrogenation has been credited for the low amount of coking on the Co/MgO catalyst [15]. Sufficiently basic and/or reducible supports have been shown to be active for aldol condensation (e.g., ethanol dehydrogenates to acetaldehyde which proceeds via aldol condensation to acetone) [16-20]. This reaction pathway has been cited as the main cause for the deactivation of those supported cobalt catalysts, as carbonaceous species
cover and block the catalyst surface [20, 21]. Supports with high oxygen mobility (i.e., CeO2 and CeO2 doped ZrO2) have been shown to mitigate coke formation and increase EtOH conversion activity [21].

Song et al. investigated cobalt supported on CeO2. It was found that the oxygen mobility of the catalyst resulted in the gasification/oxidation of carbon residues during ESR, which helped maintain the surface active sites and simultaneously mitigated coking/deactivation of the catalysts [21]. Lin et al. observed the additional benefit of CeO2 stabilized the hcp Co0 phase, which was shown to have higher activity for ESR than the fcc phase [22]. In addition to the dehydration and condensation side reactions, the selectivity to C1 products (i.e., COx and CH4) was also found to be significantly affected by support. Haga et al. investigated Co supported over Al2O3, C, MgO, SiO2 and ZrO2 and found that methanation took place and contributed to part of the methane formation on Co/SiO2, Co/MgO and Co/ZrO2, while ethanol decomposition was the predominant source of methane formed over Co/C and Co/Al2O3. [10] It has been suggested by other works that the difference in methanation activity may be more closely tied to the oxidation state of cobalt, and thus the stability of the cobalt oxidation state over different supports [23, 24].

The different methanation activity on different support was not clearly understood until in situ characterization techniques (e.g., XPS and XANES) were applied to investigate the real-time cobalt oxidation state in ESR. Hyman and Martono et al. performed an extensive investigation over model cobalt catalysts in ultra-high vacuum (UHV) [23, 25]. After comparing cobalt in unsupported and supported forms and different degrees of surface oxidation, they concluded that fully reduced cobalt is most active for decomposition and decarboxylation reactions, while the CoO or Co2+ state favors dehydrogenation of ethanol to acetaldehyde. However, cobalt surfaces only partially oxidized to CoO showed the highest activity for conversion of ethanol to
acetaldehyde, suggesting the roles of adjacent metallic Co for converting acetaldehyde and freeing CoO surface for ethanol. Although the support influences the activity of these model catalysts, it was the cobalt activity that was predominantly observed. In another word, CoO adjacent to Co⁰ may be the most active domain for ethanol steam reforming, allowing for rapid conversion of ethanol to acetaldehyde and subsequent conversion of the acetaldehyde to regenerate the surface sites. However, there remains disagreement over the role of Co²⁺ and Co⁰ in the overall ethanol conversion. Karim et al. studied the activity of the different oxidation states of cobalt, using the calcination temperature to manipulate the degree of Co³⁺ that was stabilized by MgO. It was found that overall ethanol conversion and yield of C₁ products increase with Co⁰/Co²⁺, indicating Co⁰ is more active for ESR. It was also found that as the ratio of Co⁰/Co²⁺ decreases (i.e., Co²⁺ became more predominant) the selectivity to CH₄ markedly increases. This shift in selectivity was attributed to an increase in the methanation activity catalyzed by Co²⁺. Lin et al. also conducted an investigation on the formation of cobalt oxides under steam reforming conditions. Despite the initial composition of metallic and oxidized cobalt being set via pretreatment conditions, the ratio of metallic to oxidized cobalt was more influenced by the feed composition under steam reforming conditions. Specifically, as H₂O content increased, the amount of Co³⁺ increased; exposure to ethanol alone was not found to oxidize Co⁰. A series of in situ techniques (e.g., XRD, XPS, and XANES) have also been used to investigate oxidation state of cobalt supported on CeO₂. Similar to Lin et al.’s results, Bayram et al. found that the ratio of Co⁰/Co²⁺ trended towards the same ratio, given sufficient temperature (> 400 °C), regardless of if the catalyst was left in the fresh oxide state or underwent H₂ reduction pretreatment before the reforming process. Catalyst activity data further supported this observation, as reaction temperature increased the activity and product distribution
of pre-reduced and unreduced Co/CeO$_2$ became more similar, for 500 °C reaction temperature
the activity and product distribution are almost identical [27]. Similarly, Kim and Lee found that
both pre-reduced and the fresh/unreduced Co/ZnO catalyst developed stable Co$^0$ during ESR.
However, higher temperatures (600 °C) were needed to reduce the fresh/unreduced catalyst
during ESR and negligible ESR activity was observed until Co$^0$ was formed as evidenced by in situ EXAFS [28]. Passos et al. performed a detailed in situ and operando study of Co/Al$_2$O$_3$ for ESR, investigating the effect of both calcination treatment and reaction temperature on the cobalt oxidation state [29]. It was found that increasing calcination temperature from 450 °C to 600 °C increased the formation of CoAl$_2$O$_4$ (from 18% to 27%) but the amount of Co$^0$ after reduction remained similar (62% for 450 °C, 63% for 600 °C). Under ESR conditions over a temperature range from 400 °C to 580 °C as temperature increased so too did the Co$^0$/Co$^{2+}$ ratio (CoAl$_2$O$_4$ remained relatively constant); however, carbonaceous deposition also increased as the Co$^0$/Co$^{2+}$ ratio increased. From these observations the authors postulated that CoO also plays a key role in mitigating carbonaceous deposition. Co/Al$_2$O$_3$ calcined at 600 °C, generating the largest amount of CoAl$_2$O$_4$, showed higher overall ethanol conversion, but lower selectivity to H$_2$ and CO$_2$ and increased selectivity to C$_2$H$_4$ and CO [29]. Avila-Neto et al. found that not only a stable Co$^0$/Co$^{2+}$ ratio, but also a stable spatial distribution of Co$^{2+}$ and Co$^0$ along the catalyst bed; with Co$^{2+}$ being primarily at the inlet [30]. From the recent body of work investigating ESR over cobalt catalysts there has been consensus that Co$^0$ is the active phase for C-C cleavage and that a stable ratio of Co$^0$/Co$^{2+}$ will form during ESR [26-30], however, there is presently no clear agreement on the role of Co$^{2+}$ and the dehydrogenation of ethanol to acetaldehyde. Studies have also observed additional effects of Co$^{2+}$ ranging from facilitating CH$_4$ formation to mitigating coke formation [24, 29].
In addition to the feed composition and reaction temperature, a study by Lebarbier et al. revealed that the oxidation of cobalt by steam is also related to the support. Oxidation was found to be facile on 8wt%Co/ZrO$_2$ at 450 °C in steam, while with zinc promoter (i.e., 8wt%Co0.8wt%ZnO/ZrO$_2$), cobalt could be stabilized in the Co$^0$ state, evidenced by in situ XPS characterizations. This observation correlated well to the increased ethanol conversion and lower methane selectivity, indicated by Karim et al. [24, 31].

In addition, the role of water activation is now known to play several critical roles in the ESR system. Water plays the role of oxidizer in steam reforming systems, aiding with the removal of carbon from the surface and also affecting the equilibrium of cobalt oxidation state. Recent work by Sun et al. has shown that water activation is key for conversion of acetaldehyde to acetone [32]. It was shown that for cobalt supported on graphitized carbon ethanol would convert to acetaldehyde and the acetaldehyde would then continue to go through a steam reforming process and no acetone was detected [33]. For cobalt supported on ZrO$_2$, however, the acetaldehyde was quickly converted to acetone and acetone then underwent further steam reforming [32].

3. DISSERTATION OUTLINE

Despite the wide range of work already done in the area of ESR over cobalt-based catalysts, there is still a need to a systematic investigation of the roles of water activation in ESR. To this end three supports were selected. Activated carbon was selected as it has negligible activity for water activation and provides a good reference for very low metal-support interactions. ZrO$_2$ was selected as it has a high activity for water activation. CeO$_2$ was also chosen for high water activation and high oxygen mobility. ZnO was selected as a dopant because of its intermediate water activation, higher than activated carbon but lower than ZrO$_2$. 
and CeO$_2$. Chapter Two will focus on ESR over Co supported on activated carbon. Chapter
Three will focus on Co supported on ZrO$_2$. Chapter Four will focus on Co supported on CeO$_2$. 
REFERENCES


CHAPTER TWO:
THE EFFECT OF ZNO ADDITION ON CO/C CATALYST FOR
VAPOR AND AQUEOUS PHASE REFORMING OF ETHANOL

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ABSTRACT

The effect of ZnO addition on the oxidation behavior of Co along with catalytic performance in vapor and aqueous phase reforming of ethanol were investigated on Co supported on carbon black (XC-72R). Carbon was selected to minimize the support interactions. Effect of ZnO addition during both vapor and aqueous phase reforming were compared at 250 °C. ZnO addition inhibited the reduction of cobalt oxides by H₂ and created surface sites for H₂O activation. During vapor phase reforming at 450 °C the redox of cobalt, driven by steam oxidation and H₂ reduction, trended to an equilibrium of Co⁰/Co²⁺. ZnO showed no significant effect on cobalt oxidation, inferred from the minor changes of C₁ product yield. Surface sites created by ZnO addition enhanced water activation and oxidation of surface carbon species, increasing CO₂ selectivity. At 250 °C cobalt reduction was minimal, in situ XANES demonstrated that ZnO addition significantly facilitated oxidation of Co⁰ under vapor phase reforming conditions, demonstrated by lower C₁ product yield. Sites introduced by ZnO addition improved the COₓ selectivity at 250 °C. Both Co/C and Co-ZnO/C rapidly oxidized under aqueous phase reaction conditions at 250 °C, showing negligible activity in aqueous phase reforming. This work suggests that ZnO affects the activation of H₂O for Co catalysts in ethanol reforming.
1. INTRODUCTION

Steam reforming is a well-established industrial process for hydrogen production; currently natural gas steam reforming accounts for ~49% of worldwide hydrogen production [1]. Over the last decades, steam reforming of renewable feed stocks, especially alcohols such as bio-ethanol, have gained a great deal of attention [2-5]. In addition to steam reforming, aqueous phase reforming of bio-derived liquids has also been gaining attention [6]. Reforming in the aqueous phase has several advantages over steam reforming, including reduced energy usage from not needing to vaporize reactants and more complete oxidation of products, increasing CO$_2$ selectivity [7]. Investigations thus far have focused primarily on noble metals with very little focus on cobalt or other base metals [6, 8, 9].

Of the numerous catalysts that have been investigated for ethanol steam reforming (ESR) supported cobalt catalysts have emerged as some of the most promising ones. While noble metal catalysts have shown the highest activity for ethanol conversion, they have also shown high selectivity to CH$_4$ at reaction temperatures below 500 °C [10]. Supported Co catalysts have shown relatively high C-C cleavage activity and low CH$_4$ selectivity [4, 11-13]. Recent studies have shown that both the nature of support and cobalt oxidation state greatly affect the ESR reaction mechanism [4, 12, 14]. For example, cobalt supported on basic or reducible metal oxides (e.g., ZnO and CeO$_2$) have shown high stability and selectivity towards CO$_2$ and H$_2$ [12, 13, 15, 16]. Acidic supports, such as Al$_2$O$_3$, displayed high selectivity to C$_2$H$_4$ [17], while non-reducible supports (e.g., SiO$_2$) deactivated from significant coke formation [12]. Song et al. found catalyst stability could be related to oxygen mobility of the support, i.e., catalyst stability increases with oxygen mobility [18]. For Co supported on MgO, Karim et al. demonstrated that as the ratio of Co$^{2+}$/Co$^0$ increased, the CH$_4$ selectivity increased and conversion of ethanol
decreased [14]. A series of model catalyst investigations demonstrated that a combination of Co\textsuperscript{0} and Co\textsuperscript{2+} yields the highest conversion of ethanol to H\textsubscript{2} and CO\textsubscript{x} products and that Co\textsuperscript{0} is the active site for C-C cleavage [19, 20]. Recent \textit{in situ} X-ray absorption studies have also started correlating catalyst performance to cobalt oxidation state [21, 22]. Similar to the conclusion from the model catalyst study both Co\textsuperscript{0} and Co\textsuperscript{2+} were observed during ESR and higher C-C cleavage was observed when more Co\textsuperscript{0} was present [21]. The nature of the support has also been shown to influence the oxidation state of cobalt. Lebarbier et al. found that ZnO addition to Co supported on ZrO\textsubscript{2} stabilized Co\textsuperscript{0} against steam oxidation, yielding higher ethanol conversion and lower CH\textsubscript{4} selectivity [23]. When ZnO addition was extended to Co supported on CeO\textsubscript{2}, however, it was found that ZnO interacted strongly with the CeO\textsubscript{2}, which enhanced the oxygen mobility of the CeO\textsubscript{2} and facilitated the oxidation of Co\textsuperscript{0} [24]. The enhanced oxygen mobility increased the oxidation of surface carbon species as evidenced by 10% increase in CO\textsubscript{2} selectivity, but the facile oxidation of Co\textsuperscript{0} decreased C-C cleavage [24].

In addition to affecting the oxidation state of Co, the support plays an important role in the activation of H\textsubscript{2}O. While H\textsubscript{2}O activation can occur over Co, it has been shown to be dependent on the Co particle size [25, 26]. For Co supported on a metal oxide, the metal oxide plays a dominant role for activation of H\textsubscript{2}O [27, 28]. This suggests when Lebarbier et al. observed that ZnO stabilized Co\textsuperscript{0} in the Co/ZrO\textsubscript{2}, ZnO may have directly interacted with Co\textsuperscript{0} or it may have affected H\textsubscript{2}O activation on the ZrO\textsubscript{2} support [23].

Carbon is well known for its relatively inert chemistry in several reaction systems and low activity for H\textsubscript{2}O activation, as well as high hydrothermal stability [29]. To better understand the effect of ZnO on Co for ESR while minimizing the complications by support, carbon is chosen as the support material. In this work, carbon black (XC-72R) is selected as support
material, to minimize strong support-metal interactions. The effect of ZnO addition to Co/C on its redox property as well as catalytic performance is investigated for both the vapor and aqueous phase reforming of ethanol.

2. RESULTS AND DISCUSSION

2.1 Effect of ZnO on Physical Properties

The results of physical property analysis are shown in Table 1. The XC-72R support was found to have a surface area of 236 m²/g. Addition of 10 wt% Co to XC-72R (10Co/C) decreased the BET surface area to 160 m²/g. The further addition of 5 wt% ZnO to XC-72R (10Co5ZnO/C) showed a negligible effect of total surface area (~159 m²/g).

XRD pattern of XC-72R (Figure 1-a) showed no well-defined peaks. Only a very broad peak centered at 43.4°, a shallow and broad peak at 79°, and the tail of a peak below 30° were observed. XRD pattern of 10Co/C displayed well-defined peaks at 31.2, 36.7, 38.4, 44.6, 55.6, 59.4, and 65.2° along with minor features at 74.0, 77.3, and 78.3 (Figure 1-b) corresponding to the (220), (311), (222), (400), (422), (511), (440), (620), (533), and (622) diffractions of Co₃O₄ (JCPDS PDF card 00-009-0418). The area near 42.8° displayed a broad hump that the bare XC-72R does not, suggesting the formation of a small amount of CoO, whose peaks are located at 36.5°, 42.4, 61.5, 73.7, and 77.6° (JCPDS PDF card 00-009-0402). After addition of ZnO, the XRD pattern for 10Co5ZnO/C (Figure 1-c) still showed diffraction peaks characteristic of Co₃O₄ with an exception that the peak at 36.7° became less symmetric, due to the diffraction of ZnO at 36.2° (JCPDS PDF card 00-036-1451). Additionally, ZnO appeared to increase the amount of CoO, inferred from the increase and refinement of the peak at 42.8 and 61.5. The lack of ZnO features indicated that ZnO was either highly dispersed or incorporated into a solid oxide mixture ZnCoO₄ (JCPDS PDF card 00-023-1390), which has a nearly identical diffraction
pattern to Co₃O₄. ZnO features became apparent and well defined following reduction (Figure 1-e).

Following reduction and passivation, XRD of 10Co/C (Figure 1-d) revealed that the majority of the Co₃O₄ diffraction features disappeared. New peaks appeared at 44.3, 51.4, and 75.8°, which matched with the primary Co⁰ fcc peaks for (111), (200), and (220) diffractions (JCPDS PDF card 0-015-0806). Minor peaks at 41.6, 47.3 and 75.9 indicated that a small amount of hcp Co phase was formed on the reduced 10Co/C catalysts (JCPDS PDF card 00-005-0727). In addition, the broad peak at 36.8° suggest the presence of a thin layer of Co₃O₄ on the reduced sample, which was formed during the passivation process. Similarly, fcc phase Co⁰ was formed on 10Co5ZnO/C after reduction and passivation (Figure 1e). New peaks appeared at 31.8, 34.4, 47.5, 56.6, 62.8, 66.4, 67.9, 69.0, and 72.5° which are attributed to the (101), (100), (002), (102), (110), (103), (200), (112), (201), and (004) diffractions of ZnO, respectively. It should be mentioned, no clear formation of ZnO was observed on the fresh 10Co5ZnO/C, which suggests that ZnO and Co₃O₄ are well mixed in oxide form, while ZnO and metallic Co segregate after reduction. Analyzing the ZnO peaks using the Scherrer equation revealed the ZnO crystallites were ~14.7 nm. Additionally, little or no hcp Co⁰ was observed on 10Co5ZnO/C, however, the large number of peak overlaps between hcp Co⁰ and ZnO make it difficult to rule out the presence of hcp Co⁰.

TEM of 10Co/C (Figure 2) revealed that the Co particles were well dispersed. The particle size estimated from TEM and calculated from XRD are summarized in Table 1. The distribution of particles observed was roughly normal; though the variance was relatively high (23.2), the skewness and peakedness were both less than 1 (0.31 and 0.91 respectively), indicating a fairly symmetric distribution. TEM also revealed that the Co particles did not evenly
disperse over the XC-72R support, but instead collected together in high density clusters. In addition, changes in the morphology of the XC-72R were observed around the clusters of Co particles, likely due to gasification of the support material by H₂ activation over Co evidenced by CH₄ generation during TPR experiments. TEM images of 10Co5ZnO/C showed that the addition of ZnO affected particle distribution. While the mean value remained roughly equivalent (10Co/C – 9.1 nm, 10Co5ZnO/C – 10.1 nm) the variance, skewness, and peakedness all increased significantly to 59.8, 0.79, and 2.24 respectively.

2.2 Effect of ZnO on Reduction and Oxidation Properties

The results of TPR investigations are shown in Figure 3 plot A. XC-72R showed no reduction peak (data not shown). 10Co/C (Figure 3A-α) displayed two main H₂ consumption peaks at 240 °C and 395 °C corresponding to the reduction of Co³⁺ to Co²⁺ and Co²⁺ to Co⁰, respectively [13, 23]. The shoulder peak at 475 °C matched with a peak in the formation of methane detected by mass-spectrometer (supporting material, Figure S1) suggesting gasification of carbon support in the presence of H₂. CH₄ generation started as low as 300 °C, from both mass loss calculations and QMS desorption profiles <3% of the support was gasified during TPR experiments. The low temperature, 240 °C, peak was found to have an area of 0.001 a.u. while the peak at 395 °C had an area of 0.463 a.u., the peak at 475 °C had an area of 0.150 a.u. Ideally, the Co²⁺ to Co⁰ would be 3 times the size of Co³⁺ to Co²⁺ for pure Co₃O₄ reduction, for 10Co/C it appeared that the majority of both stages of cobalt reduction occurred closer to the 395 °C reduction peak. With the addition of ZnO, 10Co5ZnO/C, the reduction peak at 240 °C shifted up to 265 °C (Figure 3A-β) and the peak at 395 °C shifted to 435 °C. The peak related to the methane formation remained at 475 °C which appeared as a slight shoulder and broadening of the 435°C peak. Again, CH₄ generation began at ~300 °C and <3% of the support was gasified
over the TPR experiment and the 265 °C reduction peak was significantly smaller than the 435 °C peak, 0.001 a.u. and 0.470 a.u. respectively. The 435 °C peak was, in part, larger because of incorporation of the CH₄ desorption peak at 475 °C, which was calculated to have an area of 0.022 a.u. The shifts in the reduction peak to higher temperature suggest that ZnO indeed showed strong interactions with cobalt oxides that suppressed the reduction of cobalt species, consistent with prior studies (i.e., ZnO addition to Co/ZrO₂ and Co/CeO₂) [23, 24].

The results of the O₂-TPO investigation are shown in Figure 3 plot B. XC-72R displayed no significant uptake of O₂ over the temperature range studied (Figure 3B-γ). Over 10Co/C, one broad oxygen consumption peaked at 372 °C was observed (Figure 3B-α). TPO above 450 °C was dominated by oxidation of the carbon support, evidenced by formation of COₓ, as detected by mass spectrometer (supporting material, Figure S2). TPO of 10Co5ZnO/C gave a similar oxygen consumption pattern, with a broad oxygen consumption profile at 372 °C and significant CO₂ generation above 450 °C. The peak areas for 10Co/C and 10Co5ZnO/C were calculated to be 0.454 a.u. and 0.357 a.u. respectively. These measurements show no clear effect of ZnO on the oxidation of Co⁰, which differs from prior studies of ZnO addition on Co/ZrO₂ [23] and Co/CeO₂ [24]. Of note, significantly (~50 %) more CO₂ was generated during TPO over 10Co5ZnO/C than over 10Co/C. This suggested that while ZnO did not display an observable interaction with Co⁰ during TPO, the addition of ZnO did affect the activation of O₂ on the catalyst.

To summarize the TPR and TPO characterization, the addition of ZnO to 10Co/C inhibited the reduction of Co oxides, which matched well with our prior studies on Co/ZrO₂ and Co/CeO₂ [23, 24]. However, the addition of ZnO enhanced oxygen activation and oxidation of carbon support, but showed no observable effect on the oxidation of cobalt. The difference of
effects from ZnO can be due to the different nature of support employed, which will be further discussed later in this paper.

It has been demonstrated that Co/Co\(^{2+}\) ratios on Co/CeO\(_2\) were controlled by the reaction atmosphere at a given reaction temperature regardless of initial oxidation state of cobalt for ESR. The higher the reaction temperature, the higher the Co/CoO ratios were [21]. Similar observations were reported for Co supported on Al\(_2\)O\(_3\) modified with 12 wt% CeO\(_2\) catalysts [22].

To further investigate the effect of ZnO on the oxidation of cobalt, in situ XANES for Co K edge was used to monitor the cobalt oxidation state under reaction conditions. To avoid the re-reduction of oxidized cobalt at high temperature [21, 22], the experiments were performed at low reaction temperature (i.e., 225 °C, Figure 4).

XANES region of XAS spectra of the fresh catalyst were similar to the spectra typical for cobalt oxides (supporting material, Figure S3) [21, 34]. Upon reduction, only metallic cobalt was observed for both 10Co/C and 10Co5ZnO/C (Figure 4A-β & 4B-β). After being exposed to vapor-phase reaction atmosphere at 225 °C, 10Co/C showed no obvious changes on the pre-edge and white line (Figure 4A-γ) suggesting no cobalt oxidation was observed by XANES. The lack of oxidation of Co\(^0\) is different from other reports of cobalt supported on the metal oxides (e.g., Co/CeO\(_2\)) [21, 22], indicating the oxidation of cobalt via steam could be related to the nature of the support.

Conversely, a significant change in the feature of pre-edge and white line intensity was detected on the 10Co5ZnO/C catalysts (Figure 4B-γ), suggesting the oxidation of cobalt [21, 22]. TPO experiments (Figure 3B) presented no evidence that ZnO has an effect on the oxidation of
metallc cobalt. The discrepancy between TPO and XANES suggests oxygen and water have
different degree of oxidation on cobalt for the 10Co5ZnO/C catalysts, which may be related to
different lavel of oxygen and water activation. It is well known that O$_2$ activation is facile on
both cobalt and ZnO surfaces [35-37]. H$_2$O activation, however, has been shown to be active
over ZnO but dependent on the particle size over cobalt [25, 26, 38]. In the current case, 10Co/C
did not show oxidation likely due to the limited H$_2$O activation. Whereas, the significant Co$^0$
oxidation on 10Co5ZnO/C is because of the more facile activation of H$_2$O over ZnO as well as
the low reducibility of cobalt at low reaction temperature (i.e., 225 °C). The difference in water
activation during vapor phase reaction suggest ZnO primarily affects the surface properties of the
support, while having negligible direct interaction with Co$^0$.

Further exposing of the catalysts to aqueous reaction media at 225 °C revealed that both
catalysts were oxidized, indicating that the aqueous phase presents too strong oxidizing
environment to maintain metallic cobalt under the reaction conditions.

2.3 Effect of ZnO on ethanol reforming activity

2.3.1 ESR at 450 °C

For the high space velocity and low conversion investigated, both 10Co/C and
10Co5ZnO/C showed rapid decrease in conversion to C$_1$ products during the first hour TOS,
likely due to the fast oxidation and coking of cobalt active sites. To avoid the complications with
long term stability and deactivation of the catalysts, the initial activity data will be focused on.

Activity data reported here is from the first 30 min TOS. The results of ESR at 450 °C are
shown in Figure 5. C-C cleavage activity, or C$_1$ product yield, was calculated by summing the
molar flow rates of C$_1$ products (CH$_4$, CO, CO$_2$) and dividing by molar feed rate of C, while H$_2$
yield was calculated by dividing the molar flow rate of H\textsubscript{2} by 6 times the molar feed rate of ethanol. Over 10Co/C, 34.8 % C\textsubscript{1} product yield and 14.8 % H\textsubscript{2} yield were observed. Selectivity to C\textsubscript{1}, C\textsubscript{2}, and C\textsubscript{3} groups were calculated by summing the molar C flow of each group and then dividing by total product molar C flow. The majority of dry gas products were C\textsubscript{1} compounds (i.e., CH\textsubscript{4} and CO\textsubscript{2}; > 98%). A small amount of C\textsubscript{2} and C\textsubscript{3} compounds (C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8} from combinations of dehydration and condensation reactions) were detected (< 2% of all dry gas products), likely due to the relatively inert nature of the support. Selectivity of C\textsubscript{1} products were calculated by dividing the molar flow rate of the compound by the molar C flow of the C\textsubscript{1} group. 10Co/C showed 5.0 % and 56.4 % selectivity to CO\textsubscript{2} and CO respectively, products from ethanol steam reforming. CH\textsubscript{4} selectivity was 38.5 %. Haga et al. demonstrated that Co supported on C is not active for the methanation reaction, the high CH\textsubscript{4} selectivity (38.6%) observed in Haga’s work over the Co/C was due to decomposition of either ethanol or acetaldehyde [16, 39]. Compared to Co/CeO\textsubscript{2}, the C\textsubscript{1} selectivity of Co/C was drastically higher [24]. At similar C\textsubscript{1} yield 10Co/CeO\textsubscript{2} showed C\textsubscript{1} selectivity of 83 %, 12 %, and 5 % for CO\textsubscript{2}, CO, and CH\textsubscript{4} respectively [24]. The higher CO\textsubscript{2} selectivity and lower methane selectivity observed over 10Co/CeO\textsubscript{2} suggest that the CeO\textsubscript{2} support is essential to the water activation and oxidation of surface carbon species. On the other hand, Sun et al. has recently shown that the performance of steam reforming could be related to the particle size of cobalt. Nano-sized cobalt (i.e., ~ 5 nm) particles supported on graphitized activated carbon exhibited enhanced water activation in acetone steam reforming (ASR) [26]. Compared to larger Co particles (> 50 nm), ASR over Co nanoparticles (~5 nm) showed more complete oxidation of products, i.e., higher CO\textsubscript{2} selectivity, and significantly enhanced stability [26]. Both experimental and theoretical work demonstrated a reduced energy barrier for H\textsubscript{2}O activation over smaller Co particles [25, 26]. The high selectivity
to CO and methane over the 10Co/C in this work was likely due to the relatively large Co particles (~9 nm) as well as the relatively inert nature of the carbon support for H₂O activation. From Sun et al.’s study on cobalt supported on graphitized carbon [26], it was shown that acetone is a more preferred intermediate to minimize methane formation in ESR. It is also known that acetone formation is dependent on the nature of support material [10, 40]. For CeO₂ supported metal catalysts, acetone is believed to be formed as an intermediate in ESR and a reaction mechanism involving acetone has been proposed [39]. Over Co/C studied here, acetone is not likely an intermediate as evidenced from liquid product analysis showing acetaldehyde (~97%) as the predominant product and no acetone formation (supporting material, Figure S4). Therefore, ethanol/acetaldehyde decomposition followed by oxidation of CH₄ and CO by dissociated water is likely the primary reaction pathway involved in ESR on Co/C studied in this work. This is also likely the reason that a much higher CH₄ selectivity (38.5 %) was observed compared to other studies (10 %) [26].

The addition of ZnO increased C₁ product yield (41.6 %) and H₂ yield (19.4 %). CO₂ selectivity increased from 5.0 % to 12.4 %, while CO and CH₄ selectivity decreased from 38.5 % and 56.4 % to 35.8 % and 51.8 %, respectively. Prior studies on Co supported on other materials (i.e., Co/ZrO₂ [23], Co/CeO₂ [24]) revealed that the addition of ZnO affects cobalt oxidation state as well as the catalytic performance in ESR. Specifically, the addition of ZnO to Co/ZrO₂ suppressed the oxidation of Co⁰ by steam, leading to increased Co⁰/Co²⁺ ratio and thus improved ethanol conversion and decreased CH₄ selectivity [14, 23]. On the other hand, the addition of ZnO to Co/CeO₂ improved the oxygen mobility of CeO₂ support which facilitated the oxidation of Co⁰, thus leading to decreased ethanol conversion [24]. However, the improved oxygen mobility increased the oxidation of surface carbon species generated from ethanol.
decomposition, resulting in increased CO$_2$ and decreased methane selectivity [24]. Over Co supported on ZnO (Co/ZnO), Llorca et al. and Casanovas et al. demonstrated that at high (~100%) conversion, Co/ZnO predominantly forms H$_2$ and CO$_2$ as dry gas products, with low selectivity to CH$_4$ and no observable CO [12, 41]. At lower conversions, however, selectivity to CO quickly increased, suggesting a limited H$_2$O activation [41, 42]. This observation is consistent with the recent observation that cobalt oxidation by H$_2$O is minimum on Co/ZnO, the H$_2$O activation on ZnO oxide is lower than those on ZrO$_2$, CeO$_2$ and CeZrO$_x$ [23]. For Co supported on carbon (i.e., XC-72R) studied in this work, despite the C$_1$ product yields being so similar after 4 hours TOS, the C$_1$ selectivity was very different for 10Co/C and 10Co5ZnO/C (supporting material, Figure S5). 10Co/C showed selectivity of 40.6 %, 31.9 %, and 27.5 % to CO$_2$, CO, and CH$_4$, respectively, while 10Co5ZnO/C displayed selectivity of 51.5 %, 26.3 %, and 22.2 % to CO$_2$, CO, and CH$_4$, respectively. While the C$_1$ selectivity differ, the similar C$_1$ product yields suggest that 10Co/C and 10Co5ZnO/C had a similar Co$^0$/Co$^{2+}$ ratio after 4 hours TOS. It has been demonstrated that the cobalt oxidation state was determined by a combination of support–metal interactions, reaction atmosphere, and reaction temperature. Karim et al. showed that the Co$^0$/Co$^{2+}$ ratio is affected by, and can be tuned using, calcining temperature of Co/MgO, demonstrating support-metal influence on the cobalt oxidation state [14]. At 450 °C, Lin et al. found that the Co$^0$/Co$^{2+}$ ratio is strongly influenced by the reactant feed composition [43]. Bayram et al. demonstrated that, under a given feed composition, the Co$^0$/Co$^{2+}$ ratio or redox properties of cobalt is governed by the reaction temperature [21]. Similarly, the Co$^0$/Co$^{2+}$ ratios in the current study resulted from a redox equilibrium during high temperature (450 °C) ESR on the 10Co/C catalyst. The addition of ZnO did not appear to change the redox equilibrium of the 10Co5Zn/C catalyst at this temperature.
The increased CO$_2$ selectivity, and decreased CO and CH$_4$ selectivity, however, suggest that activation of H$_2$O over ZnO is higher than activation of H$_2$O over carbon, and the addition of ZnO created new active sites for H$_2$O activation, leading to more complete oxidation of surface carbon species (i.e., CO and CH$_x$). This assumption is consistent with the in situ XANES studies which showed significantly enhanced oxidation on 10Co5ZnO/C compared to 10Co/C under ESR conditions at 225 °C.

2.3.2 Vapor phase and aqueous phase ethanol reforming at 250 °C

As mentioned above, the redox properties of cobalt are dependent on operating temperatures. To better understand the effect of ZnO on the cobalt oxidation state and catalytic performances, ESR was also studied at low temperature (i.e., 250 °C), where the reduction of Co$^{2+}$ is minimized (Figure 3A). The results of ESR at 250 °C are presented in Figure 6. Again, due to the fast deactivation, even at low reaction temperatures, initial activity was compared (first 30 min TOS). Over 10Co/C, C$_1$ product yield of 37.7% and H$_2$ yield of 13.9 % were observed with C$_1$ selectivity of 46.2%, 53.1%, and 0.7% to CH$_4$, CO, and CO$_2$, respectively. Acetaldehyde was the major liquid product. The ratio of CO:CH$_4$ was calculated to be 1.1, this ratio being close to 1 indicated that decomposition of ethanol or acetaldehyde was the predominant reaction while CH$_4$ and CO oxidation by steam is negligible, differing significantly from high temperature (i.e., 450 °C) ESR. With the addition of ZnO, C$_1$ product yield reduced from 37.7% to 26.2% while the H$_2$ yield only decreased slightly from 13.9 % to 13.2 % over 10Co5ZnO/C. The C$_1$ selectivity was 41.4%, 57.4%, and 1.2% for CH$_4$, CO, and CO$_2$ respectively. Liquid analysis revealed acetaldehyde is still the main liquid products (supporting material, Figure S6). The large decrease (26.2 % on 10Co5ZnO/C vs. 37.7 % on 10Co/C) in C-C cleavage suggests the more oxidation of Co$^0$ over 10Co5ZnO/C, consistent with in situ XANES
observations. The increase in CO and CO$_2$ selectivity was likely due to the fact that ZnO created sites for H$_2$O activation, as discussed earlier for high temperature ESR. However, the CO:CH$_4$ ratio was still relatively low (1.4), suggesting that over 10Co5ZnO/C catalysts the predominant reaction was still decomposition.

In line with the *in situ* XANES studies, aqueous phase ethanol reforming was also studied. As expected, due to the rapid oxidation of cobalt by liquid phase reaction atmosphere (not shown), only negligible (< 1%) conversion to gas products was observed on both 10Co/C and 10Co5ZnO/C catalysts. Acetaldehyde was the predominant liquid product followed by acetic acid and other minor products. Chu et al. investigated Co/ZnO for aqueous phase reforming of ethanol and found relatively low conversion to gas phase products, acetaldehyde formation was found to be the predominant reaction [44]. Another study on cobalt supported on carbon-nanofibers by Van Haasterecht et al. found that cobalt rapidly deactivated during aqueous reforming of ethylene glycol [45]. Both studies identified acetic acid among the liquid products, as we found in this study. In addition to the facile oxidation of Co$^0$, the leaching of cobalt and cobalt oxides into the aqueous phase could be another reason for the low C-C cleavage activity [45].

Based on the prior discussion, the effects of adding ZnO to Co/C is proposed in schematic 1. On the 10Co/C, given the relatively inert nature of the carbon support, H$_2$O activation on support is negligible. Together with the large cobalt particle size the activation of H$_2$O is very limited, minimizing the oxidation reaction under steam reforming at 225 °C; which is supported by the *in situ* XANES as well as the low CO$_2$ selectivity observed during ESR. With the introduction of ZnO active sites water activation, and thus oxidation of CH$_x$, was
significantly enhanced; leading to the increase of CO\textsubscript{x} selectivity during ESR at 450 °C and 250 °C, and facile cobalt oxidation at 250 °C where cobalt reduction is minimum.

3. CONCLUSION

The effects of ZnO on Co/C were studied in vapor and aqueous phase reforming of ethanol. The data suggests that the addition of ZnO introduced additional sites for water activation. At 450 °C, ZnO addition initially increased C\textsubscript{1} product yield, however, drive towards an equilibrium Co\textsuperscript{0}/Co\textsuperscript{2+} from balanced redox of cobalt caused long term C\textsubscript{1} yield to show negligible differences. Consistent with the trend of ZnO creating additional sites for H\textsubscript{2}O activation, selectivity of more oxidized carbon products, such as CO and CO\textsubscript{2} increased. At the low reaction temperature (i.e., 250 °C), where reduction of cobalt was minimized, the addition of ZnO facilitated the oxidation of cobalt as evidenced by \textit{in situ} XANES, leading to decreased C\textsubscript{1} product yield. Further supporting the trend of active sites created by ZnO addition, improved oxidation of surface carbon species was observed, however, ethanol/acetaldehyde decomposition was predominant at 250 °C. Exposure of both 10Co/C and 10Co5ZnO/C to aqueous phase reaction media resulted in the facile oxidation of cobalt and thus negligible C-C bond cleavage activity in aqueous phase reforming of ethanol. Finally, from this study as well as prior studies on ZnO addition to cobalt catalysts for ESR, the addition of ZnO appears to primarily affect the activation of H\textsubscript{2}O on the catalyst surface.

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REFERENCES


Table 1 The physical properties of the catalyst

<table>
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<th>Sample Name</th>
<th>BET [m$^2$/g]</th>
<th>Crystallite Size$^+$ [nm]</th>
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<td>XC-72R</td>
<td>236 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
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<td>160 ± 7</td>
<td>12.3</td>
<td>9.1 ± 4.8</td>
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<td>10Co5ZnO/C</td>
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<td>10.1 ± 7.7</td>
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$^+$ Calculated from XRD using Scherrer equation

$^\ddagger$ Estimated from TEM
Figure 1 XRD patterns for a) bare XC-72R b) fresh 10Co/C; c) fresh 10Co5ZnO/C; d) reduced/passivated 10Co/C; e) reduced/passivated 10Co5ZnO/C. Peak icons: $\alpha = \text{Co}_3\text{O}_4$; $\beta = \text{CoO}$; $\delta = \text{ZnO}$; $\chi = \text{Co fcc phase}$; $\gamma = \text{Co hcp phase}$. 


Figure 2 (B)

Figure 2 TEM images of 10Co/C (A) and 10Co5ZnO/C (B). For statistical analysis, over 300 particles were measured for each sample.
Figure 3 (B) Plot A – TPR profiles; Plot B – TPO profiles. $\alpha$ – 10Co/C, reduction or oxidation peak marked by dot line. $\beta$ – 10Co5ZnO/C, reduction or oxidation peak marked by dash line.

Dash+dot line – CH$_4$ generation (TPR only). $\gamma$ – XC-72R (TPO only).
Figure 4 (A)
Figure 4 (B) Plot A – 10Co/C; Plot B – 10Co5ZnO/C. α – Co Foil; β – Sample after reduction at 450 °C; γ – Sample after vapor phase reaction at 225 °C; δ – Sample after aqueous phase reaction at 225 °C.
Figure 5

Figure 5 ESR at 450 °C. H₂O:EtOH = 10:1 molar, P_{EtOH} = 7.4 kPa, TOS = 30 min, WHSV = 18.56 g_{EtOH}·g_{Catalyst}^{-1}·h^{-1}, 25 mg catalyst loaded.
Figure 6

Figure 6 ESR at 250 °C. H₂O:EtOH = 10:1 molar, P_{EtOH} = 2.8 kPa, TOS = 30 min, WHSV = 0.97 \text{ g}_{\text{EtOH}} \cdot \text{g}_{\text{Catalyst}}^{-1} \cdot \text{h}^{-1}, 100 \text{ mg catalyst loaded}.
Schematic 1

ESR over 10Co/C and 10Co5ZnO/C. H$_2$O cannot be activated on the C support, leaving the Co particle the primary location for H$_2$O activation in 10Co/C. With the addition of ZnO, additional sites are created where H$_2$O can be activated. Once activated the [O] migrates to surface C or Co$^0$ and oxidizes it or recombines with surface OH or H to desorb again as H$_2$O.
CHAPTER THREE:
THE EFFECT OF ZNO ADDITION ON H2O ACTIVATION
OVER CO/ZRO2 CATALYST

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ABSTRACT

The effect of ZnO addition on the dissociation of H$_2$O and subsequent effects on cobalt oxidation state and ethanol reaction pathway were investigated over Co/ZrO$_2$ catalyst during ethanol steam reforming (ESR). Catalyst physical properties were characterized by BET, XRD, and TEM. To characterize the catalysts ability to dissociate H$_2$O, Raman spectroscopy, H$_2$O-TPO, and pulsed H$_2$O oxidation coupled with H$_2$-TPR were used. It was found that the addition of ZnO to cobalt supported on ZrO$_2$ decreased the activity for H$_2$O dissociation, leading to a lower degree of cobalt oxidation. The decreased H$_2$O dissociation was also found to affect the reaction pathway, evidenced by a shift in liquid product selectivity away from acetone and towards acetaldehyde.
1. INTRODUCTION

Steam reforming is a well-established industrial process for hydrogen production, currently ~49% of world hydrogen production is from steam reforming of methane [1]. Due to the increasingly stringent limitations on CO$_2$ emissions and increasing energy demands, steam reforming of renewable feed stocks such as methanol and ethanol has received extensive attention [2-5].

A wide range of catalysts have been investigated for ethanol steam reforming (ESR). Among those studied, supported cobalt catalysts have emerged as being particularly promising. Noble metal catalysts have shown the highest activity for ethanol conversion, however, they also have shown a high selectivity to CH$_4$ at lower temperatures (e.g., below 500 °C) [6]. Ni and Co based catalysts have comparable activity for C-C cleavage, but Ni has demonstrated a higher selectivity to CH$_4$ than Co [4].

From studies of Co-based catalysts, it has been found that both cobalt oxidation state [7-13] and the reaction network [14-16] are significantly influenced by either the reaction conditions [7, 17] or catalyst support [5, 8, 9, 11, 14-16], which eventually led to different performances of the catalysts during ESR [5, 18]. Over model Co catalysts, it was found that while Co$^{2+}$ is active for ethanol dehydrogenation reaction, Co$^0$ is mainly responsible for C-C cleavage during ESR [12, 13]. These model studies have been further supported by recent work utilizing operando XAFS analysis to study the oxidation state of cobalt under realistic reaction conditions [7]. Our recent work also revealed that both the ratio of Co$^{2+}$/Co$^0$ [10, 11] and reaction network [19, 20] affected the selectivity to CH$_4$. For the former case, higher Co$^{2+}$/Co$^0$ ratio was found to favor CO methanation toward CH$_4$ [10]. For the latter case, acetone was found to be a key intermediate in ESR on Co/ZrO$_2$ [15] and acetone steam reforming resulted in the
low CH$_4$ selectivity (≤ 5%) [16]. Over Co/CNF where acetaldehyde was identified as the only intermediate, a high CH$_4$ selectivity was observed (~10%) [16].

The general trends of catalyst support material are well known in regards to surface acidity and reducibility of the support [2, 14]. Acidic supports tend to dehydrate ethanol to form ethylene while basic supports favor not only dehydrogenation of ethanol to acetaldehyde intermediate [2, 14, 21, 22], but also further condensation of acetaldehyde to acetone secondary intermediate [15, 18]. Reducible supports with high oxygen mobility (e.g., CeO$_2$) tend to give more stable performance in ESR, due to enhanced gasification of CH$_x$* species, which limits both the quantity and stability of coke deposited [23-25]. More recently, it was found that the oxidation state of cobalt should be associated with the support chemistry [8, 9, 11]. Particularly, the addition of ZnO to the ZrO$_2$ was found to inhibit the metallic cobalt oxidation via water [11].

It is apparent that water must play a key role in oxidizing the active metal and carbon species as part of the redox cycle to minimize the deposition of coke on the catalyst. Unfortunately, there are relatively few studies correlating the dissociation of water with the catalytic performances in ESR. In this work, we investigated the impact that water dissociation has on both the cobalt oxidation state and the ESR reaction network, particularly the selectivity to acetaldehyde and acetone, and subsequent C$_1$ products.

2. RESULTS AND DISCUSSION

2.1 Catalyst characterization

2.1.1 Effect of ZnO on physical properties

The results of physical properties are shown in Table 1. The ZrO$_2$ support was found to have a surface area of 50.6 m$^2$/g and the ZnO support to have a surface area of 12.6 m$^2$/g. For
both ZrO$_2$ and ZnO, the addition of 10wt% Co (10Co/ZrO$_2$ and 10Co/ZnO) decreased the surface area to 41.0 m$^2$/g and 8.9 m$^2$/g respectively. 10Co1Zn/ZrO$_2$ showed a further decrease of surface area to 35.0 m$^2$/g, possibly due to a strong interaction between the ZnO and the ZrO$_2$.

Fig. 1 shows the XRD of the supported cobalt catalysts. Over 10Co/ZrO$_2$ (Fig. 1a), and 10Co1Zn/ZrO$_2$ (Fig. 1b), strong peaks at 24.3, 28.3, 31.6, 34.4, 35.4, 41.0, 49.3, and 50.3, with minor peaks at 38.7, 45.0, 45.4, 54.2, 55.6, 57.4, 58.0, 60.2, 61.8, 62.9, 65.7, 71.3, and 75.3 corresponding to typical peaks of the tetragonal phase of ZrO$_2$ (JCPDS PDF card 00-036-0420). In addition, one strong Co$_3$O$_4$ at 36.9 can be clearly resolved. Both 10Co/ZrO$_2$ and 10Co1Zn/ZrO$_2$ showed shifts in the 45.4 and 60.2 peaks, most likely due to overlap with the Co$_3$O$_4$ peaks at 44.8 and 59.2 respectively. These observation suggest the formation of Co$_3$O$_4$ species. Over Co/ZnO, the strong peaks at 31.8, 34.5, 36.3, 47.6, 56.6, 62.9, and 68.0, as well as minor peaks at 66.4, 69.1, 72.6, and 77.0, suggest the Wurtzite structure of the ZnO support (JCPDS PDF card 00-036-1451). Additional peaks at 31.2, 38.4, 44.8, 55.6, 59.2, and 65.2, along with the formation of a shoulder at 36.6 reveal the formation of Co$_3$O$_4$ species (JCPDS PDF card 00-042-1467). Co$_3$O$_4$ peak at 36.3 was used for 10Co/ZrO$_2$ and 10Co1Zn/ZrO$_2$ crystallite calculations, while Co$_3$O$_4$ peak at 44.8 was used for 10Co/ZnO to accommodate for peak overlaps.

TEM data, shown in Fig. 2, indicated that the particle size distribution for all catalysts was log-normal, also summarized in Table 1. Over 10Co/ZrO$_2$, the average Co$_3$O$_4$ particle size was found to be 18.2 nm. The addition of Zn (10Co1Zn/ZrO$_2$) did not significantly change the average particle size, 17.2 nm. It was observed that the addition of Zn did help to minimize the frequency of occurrence of larger particles (Fig. 2B). Over 10Co/ZnO, the average Co$_3$O$_4$ particle size was found to be 26.1 nm. While it is not typical to identify the average particle size
as being larger with TEM than with XRD, there are two interpretations for the observation in this work. 1), the contrast between the Co₃O₄ and both ZrO₂ and ZnO is not very well pronounced, as they have similar diffraction patterns and atomic densities. Only the large particles are differentiated from the support material by TEM. 2), XRD provides information about the crystallite size, not directly the particle itself; the big particles observed by TEM could be secondary particle of aggregated smaller Co₃O₄ crystallites.

2.1.2 Effect of ZnO on H₂O Dissociation

To study the ability of the catalyst to dissociate H₂O, Raman spectroscopy of H₂O oxidation of Co⁰, pulsed H₂O oxidation with TPR, and H₂O-TPO were used. A summary of the results is shown in Table 2.

Operando Raman study of cobalt oxidation by H₂O

Raman spectra for the oxidation of Co over 10Co/ZrO₂ and 10Co1Zn/ZrO₂ are shown in Fig. 3 -A and -B. Fresh catalysts for both 10Co/ZrO₂ and 10Co1Zn/ZrO₂ showed features assigned to ZrO₂ support at 175/184, 325, 366, 468,515, and 612 cm⁻¹ and cobalt oxide species at 485 and 674 cm⁻¹ [27, 28]. The strong ZrO₂ doublet at 184 and 175 cm⁻¹ is most likely is masking the 195 cm⁻¹ peak of cobalt oxides. The ZrO₂ support, 10Co/ZrO₂, and 10Co1Zn/ZrO₂ all displayed Raman bands typical of monoclinic ZrO₂ in the fresh catalyst evidenced by the typical peaks at 175/184 cm⁻¹ and peaks at 325, 366, 468, 515, and 612 cm⁻¹ [19, 29]. This is contrast to the XRD pattern shown in Fig. 1, where the tetragonal ZrO₂ was observed. B-K Kim et al. found that because the monoclinic ZrO₂ has much stronger Raman activity that Raman spectroscopy can provide a better metric for measuring the ratio of monoclinic/tetragonal ZrO₂ when the monoclinic fraction is small [29]. Additionally, from C. Li and M. Li’s study of the phase transformations of ZrO₂ it appears that monoclinic ZrO₂ will form on the surface first,
while the bulk of ZrO$_2$ remains in the tetragonal phase [19]. Based on this literature, Raman spectroscopy identifying monoclinic ZrO$_2$ on the surface and XRD identifying tetragonal ZrO$_2$ in the bulk is not surprising. Following reduction, the cobalt oxide features at 485 and 674 cm$^{-1}$ were greatly diminished, however, they were not completely removed. This suggested that even following 2 h at 450 °C, some surface Co remained in the oxidation state, possibly due to strong interaction with the ZrO$_2$ support, consistent with our previous studies [15]. In addition, features ascribed to tetragonal ZrO$_2$ appeared, evidenced by the peaks at 147 and 249 cm$^{-1}$, the leading edge of the 325 cm$^{-1}$ peak, and the shift up of the 612 cm$^{-1}$ peak to 622 cm$^{-1}$ [19, 29]. It has been observed that under reducing conditions the tetragonal phase of ZrO$_2$ can be stabilized despite the monoclinic phase typically being more stable [30]. Following water exposure at 30 °C, the cobalt oxide features at 485 and 674 cm$^{-1}$ were observed to increase again, suggesting that oxidation is occurring. Looking closely at the cobalt oxide peak intensity at 674 cm$^{-1}$ and the adjacent ZrO$_2$ peak intensity at 612 cm$^{-1}$, it was found that 10Co/ZrO$_2$ had a ratio of 1.22 and 10Co1Zn/ZrO$_2$ had a ratio of 1.02. This suggests that more oxidation occurred over 10Co/ZrO$_2$ than over 10Co1Zn/ZrO$_2$. In addition, following H$_2$O exposure the features for tetragonal ZrO$_2$ again begin to diminish. The decrease of tetragonal ZrO$_2$ is most likely due to the reforming of monoclinic ZrO$_2$, which has been observed to be enhanced in the presence of water [20, 31]. As temperature increases (Supporting Fig. S2 -A and -B), the cobalt oxide features continued to grow, suggesting continued oxidation. Similarly, the features ascribed to tetragonal ZrO$_2$ continued to decrease while those features associated with monoclinic ZrO$_2$ increased.

Over 10Co/ZnO, the features of cobalt oxide were observed on the fresh sample (Fig. 4-A). In addition to the peaks at 482 and 674 cm$^{-1}$, the peak at 190 cm$^{-1}$ was also visible. It is of note that the cobalt oxide peaks were not as well defined over 10Co/ZnO as they were for either
10Co/ZrO$_2$ or 10Co1Zn/ZrO$_2$. This may be due to the strong interaction between ZnO and CoO and the possibility of a solid oxide solution of ZnO and CoO forming. Peaks assigned to ZnO were also observed at 95, 316, 430, 519, and a very broad peak at 1090 cm$^{-1}$ [32, 33]. Following reduction, the cobalt oxide features were again diminished but not completely removed. Low temperature H$_2$O exposure at 50 °C showed no change in the cobalt oxide features, suggesting that no additional oxidation occurred. With H$_2$O exposure at 150 °C growth was observed in the cobalt oxide features, suggesting that oxidation had begun.

For comparison, unsupported Co$_3$O$_4$ was also investigated, shown in Fig. 4-B. The fresh Co$_3$O$_4$ showed the typical Raman bands at 194, 482, and 686 cm$^{-1}$. There was also an additional weak Raman band at 522 cm$^{-1}$ not observed for the other samples, most likely due to how weak it was relative to the other Raman bands. Following reduction there was complete removal of the peaks at 522 and 686 cm$^{-1}$, however, the peaks at 194 and 482 cm$^{-1}$ still showed some signal. As the 686 cm$^{-1}$ is cited as being the strongest cobalt oxide Raman feature, it is unlikely that the peaks at 194 and 482 cm$^{-1}$ are from unReduced cobalt [27, 28]. Due to the slight uncertainty introduced to these two peaks, the majority of analysis of Raman peaks focused on the primary cobalt oxide peak at 686 cm$^{-1}$. For unsupported cobalt, H$_2$O exposure did not result in reformation of cobalt oxide peaks until H$_2$O exposure at 350 °C was performed. Following 350 °C H$_2$O exposure, slight growth in 686 cm$^{-1}$ peak was observed.

To summarize the data from Raman spectroscopy, all catalysts showed strong Raman peaks for cobalt oxide over the fresh sample. Following reduction, the intensity of the cobalt oxide peaks was greatly diminished but not eliminated, with the exception of the unsupported Co$_3$O$_4$. Following H$_2$O exposure at 30 °C, only 10Co/ZrO$_2$ and 10Co1Zn/ZrO$_2$ showed growth of the cobalt oxide features. Following H$_2$O exposure above 50 °C 10Co/ZnO showed growth of
the cobalt oxide features as well. Unsupported Co$_3$O$_4$ did not show evidence of oxidation until H$_2$O exposure above 250 °C. From this, unsupported Co$_3$O$_4$ can easily be ranked as the least effective for H$_2$O dissociation leading to oxidation of Co$^0$, which matches well with literature studies on H$_2$O dissociation over Co particles [16, 34]. Of the catalysts investigated, 10Co/ZnO appeared to have the lowest activity for H$_2$O dissociation leading to cobalt oxidation, again matching well with literature [35, 36]. The comparison of 10Co/ZrO$_2$ and 10Co1Zn/ZrO$_2$ was more challenging as both showed oxidation at the lowest temperature H$_2$O exposure investigated. Examining the ratio of the cobalt oxide peak intensity at 674 cm$^{-1}$ and the adjacent ZrO$_2$ peak intensity at 612 cm$^{-1}$, it was found that 10Co/ZrO$_2$ had a ratio of 1.22 and 10Co1Zn/ZrO$_2$ had a ratio of 1.02, suggesting that more oxidation occurred over 10Co/ZrO$_2$.

**Pulsed H$_2$O oxidation/H$_2$-TPR**

In order to further confirm the results from Raman spectroscopy, pulsed H$_2$O oxidation was also used to quantify the activity of the catalysts for H$_2$O dissociation and oxidation. By pulsing H$_2$O over reduced catalysts at reaction temperature (450 °C) the uptake of H$_2$O and the production of H$_2$ can be tracked. Fig. 5-A shows the peak areas for H$_2$ (m/z = 2) produced during H$_2$O pulsing. 10Co/ZrO$_2$ and 10Co1Zn/ZrO$_2$ show very similar profiles with a lower initial peak followed by an increase to the highest peak area for the second pulse and peak areas gradually decreasing with subsequent pulses. 10Co/ZnO showed a slightly different profile with a high initial peak followed by rapid decrease of H$_2$ produced. From H$_2$O uptake, 12.2% of the Co$^0$ on 10Co/ZrO$_2$ was oxidized and 11.9% of the Co$^0$ on 10Co1Zn/ZrO$_2$ was oxidized, for 10Co/ZnO only 6.6% of the Co$^0$ was calculated to be oxidized. Saturation, defined as peak areas being less than 10% different from the average final peak area, occurred after 11 pulses for 10Co/ZrO$_2$, 10 pulses for 10Co1Zn/ZrO$_2$, and only 4 pulses for 10Co/ZnO. To help confirm the extent of
oxidation via pulsed H\textsubscript{2}O oxidation, H\textsubscript{2}-TPR was run following pulsed H\textsubscript{2}O oxidation and a purge to remove excess H\textsubscript{2}O (Fig. 5-B). TPR for 10Co/ZrO\textsubscript{2} showed two primary reduction peaks centered at 288 and 402 °C. 10Co/ZrO\textsubscript{2} also showed the highest fraction of high temperature reduction species. 10Co\textsubscript{1}Zn/ZrO\textsubscript{2} also showed 2 primary reduction peaks centered at 268 and 400 °C. 10Co/ZnO showed multiple reduction peaks over a wide temperature range. 10Co/ZnO also showed the highest fraction of low temperature reduction species. From these profiles it was calculated 16.7%, 9.4%, and 9.2% of the Co\textsuperscript{0} had been oxidized in 10Co/ZrO\textsubscript{2}, 10Co\textsubscript{1}Zn/ZrO\textsubscript{2}, and 10Co/ZnO respectively. It further confirms that 10Co/ZrO\textsubscript{2} was the most active catalyst for H\textsubscript{2}O dissociation and oxidation, followed by 10Co\textsubscript{1}Zn/ZrO\textsubscript{2}, and 10Co/ZnO had the lowest activity for H\textsubscript{2}O dissociation and oxidation.

**H\textsubscript{2}O-TPO**

Additionally, H\textsubscript{2}O-TPO was also used to investigate the activity of the catalysts to dissociate H\textsubscript{2}O and oxidize Co\textsuperscript{0}. H\textsubscript{2}O-TPO profiles of the H\textsubscript{2} (m/z = 2) signal from on line QMS are shown in Fig. 6. Both 10Co/ZrO\textsubscript{2} and 10Co\textsubscript{1}Zn/ZrO\textsubscript{2} show an initial oxidation peak at 47 °C. In addition, however, a broad shoulder extending up to 100 °C was observed on 10Co/ZrO\textsubscript{2}, suggesting more oxidation at low temperatures. Although 10Co\textsubscript{1}Zn/ZrO\textsubscript{2} also showed a broad shoulder from 50-100 °C, the intensity is significantly smaller than that of Co/ZrO\textsubscript{2}. Over 10Co/ZnO the initial oxidation peak temperature was at 51 °C. There was no shoulder on the initial oxidation peak. The onset of oxidation observed here matched well with those observed during Raman spectroscopy.

In summary, 10Co/ZrO\textsubscript{2} showed the highest extent and activity for oxidation of Co\textsuperscript{0} in the presence of H\textsubscript{2}O while 10Co/ZnO showed the lowest. 10Co\textsubscript{1}Zn/ZrO\textsubscript{2} displayed an intermediate degree of H\textsubscript{2}O dissociation and oxidation, as would be expected from coating some
of the more active ZrO$_2$ surface with less active ZnO. These results also matched well with the following ESR selectivity to acetaldehyde and acetone, as dissociation of H$_2$O is critical to the conversion of acetaldehyde to acetone.

2.2 Effect of ZnO on Ethanol Steam Reforming

The ESR activity of the catalysts are shown in Fig. 7. The 10Co/ZrO$_2$ catalyst showed a 12.2% C$_1$ product yield and 13.5% H$_2$ yield at a total ethanol conversion of 41.6%. The gas products were predominantly C$_1$ products with CO$_2$ being the most abundant at 19.3% selectivity, followed by CO and CH$_4$ at 5.3% and 1.5% selectivity respectively. A small amount of ethylene was observed with selectivity of 2.7%, ethane was also detected, however, the selectivity was <0.5% and was not considered significant. The majority of products produced were collected in the liquid phase. Acetaldehyde showed a selectivity of 27.4% while acetone had a selectivity of 39.4%. Ethyl acetate and acetic acid were also observed in the liquid products with 0.9% and 3.3% selectivity respectively. Acetone, acetaldehyde, ethyl acetate, and acetic acid have all been reported previously intermediates of the ESR reaction pathway [16, 21, 37, 38]. Additionally, the requirement of water for conversion of ethanol to acetone via acetaldehyde has also been reported [39-41]. The high selectivity of acetone, especially being higher than the selectivity to acetaldehyde suggests that the conversion of acetaldehyde to acetone is very facile over the 10Co/ZrO$_2$.

The addition of a small amount of ZnO, 10Co1Zn/ZrO$_2$, increased the C$_1$ product yield to 12.7%, H$_2$ yield to 15.3%, and overall ethanol conversion to 51.1%. The selectivity to gas products, however, decreased. CO$_2$, CO, and CH$_4$ selectivity all decreased to 17.5%, 3.9%, and 1.2% respectively. Ethylene selectivity also decreased to 1.4%, ethane selectivity remained <0.5%. While the gas product distributions remained relatively similar, the liquid product
selectivity changed significantly. The selectivity to acetaldehyde increased to 36.9% while the selectivity to acetone decreased to 33.2%, ethyl acetate selectivity remained at 0.9% and acetic acid selectivity increased slightly to 4.5%. The large shift in acetaldehyde selectivity can be attributed to a combination of effects. First is that the dehydrogenation reaction converting ethanol to acetaldehyde is more active over basic catalysts than over acidic catalysts, ZnO has higher basicity than ZrO$_2$ [42]. Second, that the conversion of acetaldehyde to acetone requires H$_2$O dissociation [16, 40], which is suppressed by the addition ZnO on the ZrO$_2$ support as evidenced by the aforementioned Raman, H$_2$O uptake, and H$_2$O-TPO data. A decrease in H$_2$O dissociation is further supported by the increase in CO selectivity. The water-gas shift (WGS) reaction is cited as operating in parallel with, or as part of, the ESR reaction mechanism, the WGS reaction is also cited as being more dependent on H$_2$O and H$_2$O dissociation than it is on CO adsorption [14, 21, 35, 36, 43].

Over 10Co/ZnO the residence time was doubled to keep conversion similar to 10Co/ZrO$_2$ and 10Co1Zn/ZrO$_2$, the C$_1$ product yield was found to be 12.9% with a H$_2$ yield of 15.5% and an overall ethanol conversion of 52.0%. The CO$_2$ selectivity was close to that over 10Co1Zn/ZrO$_2$ at 17.7%, while the CO and CH$_4$ selectivity increased to 6.8% and 2.1% respectively. Ethylene selectivity was 2.3% and ethane selectivity remained <0.5%. The selectivity to acetaldehyde continued to increase to 54.7% and acetone selectivity dropped to only 5.1%, ethyl acetate selectivity increased slightly to 1.2% and acetic acid selectivity increased significantly to 10.0%. The low activity on Co/ZnO can be, in part, explained by the difference in surface area shown in section 3.1. Notably, the further shift in acetaldehyde and particularly acetone selectivity indicate the importance of H$_2$O dissociation. 10Co/ZnO has more than sufficient basic sites for conversion of ethanol to acetaldehyde, however, it is not able to convert the acetaldehyde to
acetone effectively. This is also evidenced by the CO selectivity being the highest among the catalysts.

From the ESR activity testing, it does appear that the ability of the catalyst to dissociate and activate H\textsubscript{2}O could be ranked as 10Co/ZrO\textsubscript{2} > 10Co1Zn/ZrO\textsubscript{2} > 10Co/ZnO as evidenced by both the CO\textsubscript{2}/CO ratio and the acetone/acetaldehyde ratios. H\textsubscript{2}O dissociation and Co oxidation in presence of H\textsubscript{2}O were more directly tested to confirm this hypothesis and are outlined in Section 3.1.2.

3. CONCLUSION

The effects of ZnO and thus H\textsubscript{2}O dissociation were investigated on 10Co/ZrO\textsubscript{2} for the steam reforming of ethanol. The data suggests that ZnO decreased the ability of 10Co/ZrO\textsubscript{2} to dissociate water. This was directly reflected in Raman spectroscopy of catalysts during H\textsubscript{2}O exposure, pulsed H\textsubscript{2}O oxidation coupled with H\textsubscript{2}-TPR, and H\textsubscript{2}O-TPO where cobalt oxidation was consistently more facile over 10Co/ZrO\textsubscript{2} than over 10Co1Zn/ZrO\textsubscript{2}. This also matched well when comparing to 10Co/ZnO, which showed the least facile and lowest degree of oxidation. The dissociation of H\textsubscript{2}O was also reflected in ESR product distribution, shifting the most favored product from acetone over 10Co/ZrO\textsubscript{2} to acetaldehyde over 10Co/ZnO. Based on this and prior work it appears that the dissociation of H\textsubscript{2}O on the catalyst surface can be tuned by adding a promoting material, in this case ZnO, to adjust the product distribution and the oxidation stability of cobalt. With a higher degree of H\textsubscript{2}O dissociation, the catalyst will favor acetone formation from acetaldehyde, which can lead to more complete steam reforming; however, the oxidation of cobalt is also more facile, leading to a decrease in the C-C cleavage. With lower degree of H\textsubscript{2}O dissociation, the catalyst will favor acetaldehyde formation and acetaldehyde steam reforming,
which can limit the extent of steam reforming; the oxidation of cobalt is also less facile, helping to increase C-C cleavage.

ACKNOWLEDGEMENTS

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REFERENCES


Table 1 Physical properties of catalyst

<table>
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<th>Particle Size b [nm]</th>
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<tr>
<td>ZnO</td>
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<td>10Co/ZnO</td>
<td>8.9 ± 0.3</td>
<td>19.2</td>
<td>26.1 ± 1.3</td>
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</table>

a Calculated from XRD using Scherrer equation

b Estimated from TEM using log-normal distribution
Figure 1 XRD patterns for (a) 10Co/ZrO$_2$; (b) 10Co1Zn/ZrO$_2$; (c) 10Co/ZnO. Peak icons: $\alpha = \text{Co}_3\text{O}_4$; $\gamma = \text{ZrO}_2$; $\zeta = \text{ZnO}$.
Figure 2 A

A

Relative Frequency

0.0

0.1

0.2

0.3

0.0

10

20

30

40

50

60

Particle Size [nm]
Figure 2 B

![Bar chart showing particle size distribution. The x-axis represents particle size in nm, ranging from 0 to 60. The y-axis represents relative frequency, ranging from 0.0 to 0.4. The chart shows a peak at around 10-20 nm, with smaller peaks at 20-30 nm and 30-40 nm.]
Figure 2 C

Figure 2 Particle size distributions from TEM images for A) 10Co/ZrO₂; B) 10Co1Zn/ZrO₂; C) 10Co/ZnO. For each analysis, at least 100 particles were measured.
<table>
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$^a$ Calculated from H$_2$O uptake from m/z = 18

$^b$ Calculated from calibrated TCD signal
Figure 3 A

![Graph showing Raman spectra with labeled modes α, β, and χ.](image)
Figure 3 Plot A – 10Co/ZrO₂; Plot B – 10Co1Zn/ZrO₂. Raman spectra for: α – fresh catalyst; β – reduced catalyst; χ – H₂O exposure at 30 °C. Cobalt oxide peaks highlighted by dashed line.
Figure 4 A
Figure 4 B

Figure 4 Plot A – 10Co/ZnO; Plot B – Co$_3$O$_4$. Raman spectra for: $\alpha$ – fresh catalyst; $\beta$ – reduced catalyst; $\delta$ – H$_2$O exposure at 50 °C; $\epsilon$ – H$_2$O exposure at 150 °C; $\phi$ – H$_2$O exposure at 250 °C; $\kappa$ – H$_2$O exposure at 350 °C. Cobalt oxide peaks highlighted by dashed line.
Figure 5 B

Figure 5 Plot A – $H_2$ (m/z = 2) peak areas during $H_2O$ pulsed oxidation; Plot B – TPR profiles following $H_2O$ pulsed oxidation. $\alpha$ – 10Co/ZrO$_2$, reduction peaks marked by dash line; $\beta$ – 10Co1ZnO/ZrO$_2$, reduction peaks marked by dash-dot line; $\chi$ – 10Co/ZnO, reduction peaks marked by dot line.
Figure 6 QMS m/z = 2 signal for H$_2$O-TPO A – 10Co/ZrO$_2$; B – 10Co1Zn/ZrO$_2$; C – 10Co/ZnO
Figure 7 ESR at 450 °C, H₂O:EtOH = 10:1 molar, P_{EtOH} = 7.4 kPa, WHSV was varied from 9.3 g_{EtOH}·g_{Catalyst}^{-1}·h^{-1} to 18.5 g_{EtOH}·g_{Catalyst}^{-1}·h^{-1} to control the total ethanol between 40%-50%. Other products is the cumulative selectivity of ethylene, ethane, ethyl acetate, and acetic acid.
CHAPTER FOUR:
ETHANOL STEAM REFORMING ON CO/CEO$_2$:
THE EFFECT OF ZNO PROMOTER

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ABSTRACT

A series of ZnO promoted Co/CeO\textsubscript{2} catalysts were synthesized and characterized using XRD, TEM, H\textsubscript{2}-TPR, CO chemisorption, O\textsubscript{2}-TPO, IR-Py, and CO\textsubscript{2}-TPD. The effects of ZnO on the catalytic performances of Co/CeO\textsubscript{2} were studied in ethanol steam reforming. It was found that the addition of ZnO facilitates the oxidation of metallic Co\textsuperscript{0} via enhanced oxygen mobility of the CeO\textsubscript{2} support which decreases the activity of Co/CeO\textsubscript{2} in C–C bond cleavage of ethanol. 3 wt % ZnO promoted Co/CeO\textsubscript{2} exhibits minimum CO and CH\textsubscript{4} selectivity and maximum CO\textsubscript{2} selectivity. This results from the combined effects of the following factors with increasing ZnO loading: 1) enhanced oxygen mobility of CeO\textsubscript{2} facilitates the oxidation of CH\textsubscript{x} and CO to form CO\textsubscript{2}; 2) increased ZnO coverage on CeO\textsubscript{2} surface reduces the interaction between CH\textsubscript{x}/CO and CeO\textsubscript{2}; and 3) weakened CO adsorption on Co\textsuperscript{0} reduces CO oxidation rate to form CO\textsubscript{2}. In addition, the addition of ZnO also modifies the surface acidity and basicity of CeO\textsubscript{2}, which consequently affects the C\textsubscript{2} – C\textsubscript{4} product distributions.

Key words: ethanol steam reforming, hydrogen, cobalt, CeO\textsubscript{2}, ZnO promoter
1. INTRODUCTION

Hydrogen is widely used in petrochemical industries and has also gained popularity as a clean energy carrier. At present, hydrogen is primarily produced from dwindling fossil feedstock [1]. Together with increasingly stringent environmental regulations, an alternative and renewable feedstock is being increasingly demanded. Over the last few decades alcohol steam reforming has been recognized as a potential process for hydrogen production [2-7]. As one of the main products derived from biomass, ethanol has received much attention, due to its low toxicity and easy transportation [3, 6].

Ethanol steam reforming has been widely studied over the last decade [2, 4-5]. The catalysts that have been investigated range from noble metals to the group VIII metals and several other metals [8]. Although the noble metals have consistently shown the best C–C cleavage activity, they have given high methane selectivity at low temperatures (e.g., 450 °C) [9]. The high cost also limited its practical application. While a wide range of non-noble metals have been investigated, Ni and Co have shown the highest activity for C–C bond cleavage [4-5]. Compared with Co, Ni exhibited higher C–C cleavage activity at temperatures below 400 °C, however, Ni also showed higher methane selectivity [10-11]. At temperatures above 400 °C, Co, unlike Ni, has shown higher H₂ and CO₂ selectivity with similar C–C cleavage activity [12-14].

From the studies on the Co based catalysts, nature of the support, Co oxidation states, and reaction atmospheres have played important roles in determining the reaction pathway and deactivation of the catalysts. Co supported on acidic supports and non-reducible supports, such as Al₂O₃ and SiO₂, typically show a high conversion of ethanol. This conversion, however, is not necessarily to H₂ and CO₂, instead C₂H₄ and CH₄ formation are favored by dehydration and ethanol decomposition or methanation, respectively [15-19]. Co supported on basic or reducible
supports (e.g., ZnO, CeO$_2$ and ZrO$_2$) have shown promising activity and stability in ESR, especially higher selectivity to H$_2$ and CO$_2$ [13, 19-21]. For example, Llorca et al. has performed a detailed study on ESR over Co supported on ZnO, which showed high stability with only minimal deactivation. Even after 75 hours TOS, analysis shows the Co is still well dispersed and mostly (92%) reduced with CoO being the only other phase of Co detected [18]. Song et al. investigated ESR, focusing on the comparison of Co supported on ZrO$_2$, CeO$_2$ and CeO$_2$-ZrO$_2$. They found that Co supported on CeO$_2$ provides high conversion of ethanol and high selectivity to H$_2$ and CO$_2$. The high oxygen mobility of CeO$_2$ was attributed to mitigate coke formation and improve catalyst stability [22-23]. Lin et al. investigated the addition of CeO$_2$ to Co for ESR. It was found that the addition of CeO$_2$ suppressed Co sintering and meanwhile improved C-C cleavage activity [24].

The oxidation state of Co and its effect on the reaction activity and selectivity in ESR has been the subject of several recent studies. Martonon, Hyman et al. conducted a series of investigations under ultra-high vacuum using model Co catalysts. It was found that, compared with metallic Co alone, CoO is more active for converting ethanol to acetaldehyde. Metallic Co was found to be the active site for acetaldehyde decomposition to methyl and carbonyl groups. This implies that under ESR reaction conditions both Co$^0$ and Co$^{2+}$ would be required [25-28]. Karim et al. investigated the effects of the Co$^0$/Co$^{2+}$ ratio in ESR and found that as the amount of Co$^{2+}$ increases, the catalyst activity decreases and the selectivity to CH$_4$ increases, which has been attributed to Co$^0$ being required for steam reforming and the Co$^{2+}$ being more active for the methanation reaction [29]. Consistent with Karim’s observation, Lebarbier et al. found that ZnO promoted Co/ZrO$_2$ could prevent oxidation of Co$^0$ under ESR conditions, as the result, higher catalytic activity and lower methane selectivity was achieved [30].
Despite the investigations of ZnO’s effect on the Co oxidation state, studies regarding its potential modification of both the Co oxidation state and the support chemistry are still limited. In this work, the effects of ZnO loading on Co/CeO$_2$ were investigated. The main focus is on the modifications of both the Co oxidation state and the surface acid-base chemistry of the CeO$_2$ support with the addition of ZnO, and thus their effects on the catalysts’ activity and selectivity. It was found that the addition of ZnO to CeO$_2$ stabilizes Co$^{2+}$ against reduction in TPR. In addition, TPO results revealed that oxidation of Co$^0$ was favored under oxidative atmosphere, possibly due to an enhancement of the oxygen mobility on ZnO promoted CeO$_2$. Consistent with the TPO results, C–C cleavage activity in ESR decreased with the increasing ZnO loading on ZnO promoted Co/CeO$_2$ which is likely due to a lower fraction of metallic cobalt present. It was also found that the CO$_2$ selectivity increased while CO and methane selectivity decreased with ZnO addition to CeO$_2$, and CO$_2$ selectivity reached a maximum at 3 wt% ZnO loading. From this study it is apparent that ZnO addition affects the oxygen mobility, Co oxidation state, and support surface properties which are critical to the activity and selectivity of the catalyst.

2. RESULTS AND DISCUSSION

2.1 Effect of ZnO on the physical-chemical properties

The results of the physical and chemical properties are shown in Table 1. From nitrogen sorption, the BET surfaces show negligible change with ZnO loading. However, the CO uptake and the corresponding Co dispersion decrease with the increase of ZnO loading. This could be due to either the increased cobalt particles size or suppression of CO adsorption on Co with the addition of ZnO. XRD patterns (Figure 1) of the reduced and passivated samples show typical CeO$_2$ diffraction peaks characteristic of the fluorite structure, peaks at 28.5, 33.1, 47.5, 56.3, and 59.1° [31]. Separate fine scans (Figure 2) reveal a very weak peak corresponding to the
diffraction of metallic Co fcc phase (111) at 44.3° [24]. Also observed from XRD was the
development of a ZnO phase with increased ZnO loading. A peak at 36.2° begins to develop on
10Co3ZnO/CeO2 and becomes more prominent for 10Co5ZnO/CeO2 and 10Co10ZnO/CeO2.
However, even on 10Co10ZnO/CeO2, the ZnO peak is not well resolved indicating small
crystallite sizes. Based on the Scherrer equation, the Co particle size for all samples are similar at
~18-25 nm, far larger than those calculated from CO chemisorption. A possible source for this
discrepancy is that small particles, especially those smaller than 3 nm, are beyond detection limit
of XRD, but they can still contribute to the CO chemisorptions.

TEM was also used to check the catalysts morphology and cobalt particle sizes, shown in
Figure 3. Due to the higher atomic number of Ce in the support compared to Co, it is difficult to
differentiate cobalt from support. However, large spherically shaped cobalt particles are
observed on the CeO2 crystals, which is consistent with XRD observations. This suggests that the
CO chemisorption is skewed by the interaction between Co and CO, and indicates a weakening
of this interaction with the addition of ZnO. From TEM it is also observed that the addition of
ZnO to the catalyst system causes slight changes of CeO2 morphology, which indicate a strong
interaction of ZnO and CeO2 support, which matches well with the results from XRD. ZnO
forming a segregated phase on CeO2 at higher loading is also well supported in literature [32-33].

2.2 Effect of ZnO on the reduction/oxidation properties of Co

TPR results are shown in Figure 4. No hydrogen consumption is observed on the CeO2
support within the temperature range studied (Figure 4f). A typical 2-peak reduction profile is
observed on 10Co0ZnO/CeO2 (Figure 4a). The first reduction peak at 270 °C is ascribed to the
reduction of Co3+ to Co2+, and the second reduction peak at 325 °C corresponds to the reduction
of Co2+ to Co0 [34-35]. After loading of 1 wt% ZnO (Figure 4b), the first reduction peak shows
no appreciable change, while the second reduction peak at 325 °C decreases in area with a new shoulder peak appearing at 390 °C. It indicates that the addition of ZnO suppresses the reduction of Co$^{2+}$. This assumption can be confirmed by further increasing ZnO loading from 1 to 10wt% (Figure 4c-4e). The first reduction peak remains at 270 °C, unchanged. The second reduction peak, in contrast, progressively shifts to higher temperatures (390 °C), suggesting that more Co$^{2+}$ is being stabilized against reduction by ZnO on the CeO$_2$. This trend is consistent with the observation on the 8Co0.8ZnO/ZrO$_2$ [30]. For the CoZnOZrO$_2$ system, the reduction peak for Co$^{2+}$ was observed to shift above 450 °C. The reduction peaks in this study remain below 400 °C, suggesting that the cobalt should be fully reduced on the fresh xCoyZnO/CeO$_2$ catalysts.

TPO studies were conducted to investigate the effect of ZnO on the oxidation of Co as shown in Figure 5. Over the CeO$_2$ support, no oxygen consumption was observed (data not shown). On 10Co0ZnO/CeO$_2$ no oxygen desorption is observed, instead it shows two oxygen consumption peaks. The small oxygen peak at 56 °C appears to be due to the oxidation of CeO$_2$ support, suggesting the Co promoted the reduction of CeO$_2$ support during the reduction prior to TPO. The main peak corresponding to the oxidation of cobalt is centered at 218 °C on 10Co0ZnO/CeO$_2$. The addition of ZnO shifts the cobalt oxidation temperature to 188 °C regardless of loading amount. This result is in contrast to what observed on the ZnO modified Co/ZrO$_2$ catalysts [30], where ZnO was shown to inhibit both the reduction and oxidation of Co on the ZrO$_2$ support. This discrepancy can be attributed to the difference in oxygen mobility between ZrO$_2$ and CeO$_2$, which has been reported on previously [22]. The addition of ZnO appears to improve the oxygen accessibility/mobility of the xCoyZnO/CeO$_2$ catalysts, facilitating the oxidation of Co. Laguna et al. observed enhanced oxidation of CO on the Au/ZnOCeO$_2$ catalysts at relatively low loadings of ZnO (e.g. <10 mol% ZnO) [36]. This was attributed to
increased oxygen mobility, observed as an increase in oxygen vacancies from Raman spectroscopy, and an increase of the total reduction of the ZnO/CeO$_2$, observed from TPR.

2.3 Effect of ZnO on the acid-base properties of the catalysts

The surface acidity has shown significant effect on ESR over cobalt based catalysts, including the reaction pathway, adsorption of ethanol and catalysts stability etc. [37-39]. From the above results, it has been shown that the properties of Co (e.g. redox and CO chemisorption) have changed significantly after adding ZnO on Co/CeO$_2$. In this section the modifications of the surface acid-base properties from the addition of ZnO are explored.

Figure 6 shows the DRIFTS analysis of adsorbed pyridine on the catalysts. Both Lewis (L) and Brønsted (B) acid sites were observed on the catalysts studied. No B acid sites were observed on the bare CeO$_2$ support (data not shown). The formation of B sites on the 10Co0ZnO/CeO$_2$ is not clear. The addition of ZnO is observed to decrease the B acid sites, while the L acid sites remain relatively unaffected.

CO$_2$ provides a standard probe for the surface basicity of solid catalysts and was utilized in this study to further investigate the effects of ZnO on the surface basicity as shown in Figure 7. A broad CO$_2$ desorption peak centered at ~103 °C was observed on the 10Co0ZnO/CeO$_2$ catalyst. While the peak desorption temperature does not change with ZnO addition, the area of the desorption peak does change. At lower ZnO loadings (e.g. 10Co1ZnO/CeO$_2$ and 10Co3ZnO/CeO$_2$) the desorption peak area decreases, while at higher ZnO loadings (e.g. 10Co5ZnO/CeO$_2$ and 10Co10ZnO/CeO$_2$) the desorption peak area increases, the reason of which is still unclear and deserves further investigations. However, this observation indicates that the total number of basic sites changes with the amount of ZnO loaded, while the strength does not.
In summary, the ZnO dopant affects both Co and support properties in the \( x\text{Co}_y\text{ZnO}/\text{CeO}_2 \) system. ZnO suppresses the reduction of Co\(^{2+}\) to Co\(^0\), while facilitating the oxidation of Co\(^0\) under oxidative atmospheres (e.g., under reaction conditions). These changes are likely due to enhanced oxygen mobility on the \( x\text{Co}_y\text{ZnO}/\text{CeO}_2 \) catalysts. Addition of ZnO was observed to passivate the surface Brønsted acidity and change the total number of the basic sites without affecting the overall strength of the basic sites.

### 2.4 Effect of ZnO on the ESR

To investigate the effect of ZnO on the catalytic performance of the CoZnO/CeO\(_2\) catalysts, steady state activity tests were performed.

It has been shown that metallic cobalt is the main active phase for C–C cleavage in ESR [25-27, 30]. Figure 8 shows the effect of ZnO loading on the C–C cleavage activity in ESR. It is clear that, under the same reaction conditions, the C–C cleavage activity decreases with the ZnO loading. From the aforementioned TPO results, ZnO was observed to facilitate the oxidation of Co\(^0\). It is therefore expected that under reaction conditions more Co\(^0\) will be converted to Co\(^{2+}\), leading to a lower C–C cleavage rate.

The effect of ZnO on the distribution of C\(_1\) products is plotted in Figure 9. C–C cleavage conversions are between 12 to 18%. On 10Co0ZnO/CeO\(_2\), CO\(_2\) selectivity is 83% in the C\(_1\) products with CO and methane selectivity being 12 % and 5%, respectively. As the ZnO loading increases, CO\(_2\) selectivity increases while CO and methane selectivity decrease. A maximum of 92% CO\(_2\) is achieved on the 10Co3ZnO/CeO\(_2\) catalysts, and CO and methane selectivity decrease to 6% and 2%, respectively. Further increasing the ZnO loading, however, results in decreased CO\(_2\) and increased CO; methane selectivity increases but not by the same amount. At
10Co10ZnO/CeO$_2$ the CO$_2$ selectivity decreases to 87%, the CO and CH$_4$ selectivity increase to 10% and 3%, respectively.

Karim *et al.* found that ethanol steam reforming over Co followed water-gas-shift and/or methanation reaction, dependent on the ratio of Co$^{2+}$/Co$^0$. Because the CO selectivity was consistently above equilibrium and was relatively independent of ethanol conversion, it was inferred that CO was a reaction intermediate that was then converted to CO$_2$ or methane based on whether a Co$^0$ site or a Co$^{2+}$ was available respectively [29]. It has also been shown, however, that the catalyst support plays a significant role in the types of surface reactions [19, 22, 40]. In this study, methane selectivity is far below its equilibrium (37%) on all catalysts investigated. As methane primarily forms either via ethanol decomposition (Equation 4) or methanation (Equation 5), the methanation activity was also investigated to understand its contribution to methane selectivity in this study.

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 \quad (4)
\]

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (5)
\]

It was found that all catalysts exhibited minimal methanation activity, i.e., methane selectivity was ~2.5% under reaction conditions mimicking the steam reforming investigations (data not shown). From this, it appears that the change in methane selectivity with ZnO addition is primarily affected by the relative rates of oxidation and hydrogenation of CH$_x$ species that is formed from C–C cleavage of ethanol [21, 32], with the oxidation rate dependent on the oxygen mobility. Therefore, it is expected that addition of a small amount of ZnO will decrease methane selective due to enhanced oxygen mobility of CeO$_2$ as discussed earlier. As the ZnO loading further increases, it will progressively cover the CeO$_2$, shifting the surface property to be more
similar to ZnO than to CeO$_2$, leading to a reduced interaction between CH$_x$ and CeO$_2$ and consequently a reduced oxidation rate of CH$_x$. Therefore, a minimum methane selectivity was observed at 3wt% ZnO loading. In addition, from the CO chemisorption, ZnO was found to weaken the CO adsorption on Co$^0$. The maximum CO$_2$ selectivity is likely due to the following combination of effects. With no ZnO loading, the Co/CeO$_2$ system behaves as has been previously observed [18, 21, 24]. At lower loadings of ZnO (e.g. 10Co1ZnO/CeO$_2$ and 10Co3ZnO/CeO$_2$), the increased oxygen mobility leads to increased oxidation rate of CO and CH$_x$ (Scheme 1), evidenced by the increase in CO$_2$ selectivity. At higher loadings of ZnO (e.g. 10Co5ZnO/CeO$_2$ and 10Co10ZnO/CeO$_2$), while the oxygen mobility is still increased, the increased ZnO coverage on CeO$_2$ reduces the interaction of CO and CH$_x$ with CeO$_2$. This combined with weakened CO adsorption on Co$^0$ by ZnO results in reduced oxidation rate of CO and CH$_x$, and consequently reduced CO$_2$ selectivity.

Due to the change of surface acid-base properties, we also compared the selectivity to the C$_2$ – C$_4$ light alkanes (Figure 10) that are well known from acid-base catalyzed dehydration or condensation reactions [5, 21, 34].

Not shown in Figure 10, the C$_1$ selectivity remained relatively constant at ~88%. The C$_2$ alkane is primary composed of C$_2$H$_4$ (> 90%) produced via dehydration of ethanol and C$_2$H$_6$ formed via hydrogenation of C$_2$H$_4$. The addition of ZnO clearly decreases the selectivity to C$_2$ products which matches well with the results previously reported by Llorca et al. [18]. Meanwhile, C$_3$ (e.g., propylene) and C$_4$ (e.g., isobutene) selectivity increase slightly. The decreased C$_2$ formation can be attributed to the suppression of dehydration of ethanol related to the surface Brønsted acidic sites, evidenced by the IR-Py investigation. The C$_3$ products can be attributed to the aldol condensation of acetaldehyde to acetone, which then hydrogenates to
isopropyl alcohol and rapidly dehydrates to form propylene followed by hydrogenation to propane [40-42]. As discussed previously, the addition of ZnO facilitates the oxidation of Co$^0$ to Co$^{2+}$. As demonstrated by Martonon, Hyman et al., with an increased concentration of Co$^{2+}$ it is expected that there would be an increased concentration of surface aldehyde species for the aldol condensation [25, 28], leading to increased C$_3$ products. Isobutene formation occurs from further condensation of acetone [42-44].

3. CONCLUSION

Co/CeO$_2$ with different amounts of ZnO were prepared and studied in ESR. The addition of ZnO was observed to facilitate the oxidation of metallic Co$^0$ via enhanced oxygen mobility of the CeO$_2$ support which decreases the activity of Co/CeO$_2$ in C–C bond cleavage of ethanol. It was found that 3 wt %ZnO promoted Co/CeO$_2$ exhibits minimum CO and CH$_4$ selectivity and maximum CO$_2$ selectivity. This is due to a compromise between the oxidation of CH$_x$ and CO by enhanced oxygen mobility of CeO$_2$ and reduced interactions of CH$_x$ and CO with Co and CeO$_2$ with the addition of ZnO. The addition of ZnO also modifies the surface acidity and basicity of CeO$_2$, which consequently affects the C$_2$ – C$_4$ product distributions.

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REFERENCES


**Table 1** The physical-chemical properties of the catalysts.

<table>
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<th>Sample name</th>
<th>BET ([m^2/g])</th>
<th>CO Uptake ([\mu mol/g])</th>
<th>Particle Size(^*) ([\text{nm}])</th>
<th>Particle Size(^&amp;) ([\text{nm}])</th>
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<td>-</td>
<td>-</td>
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<td>71.1</td>
<td>11.21</td>
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\(^*\) Particle size calculated from CO chemisorptions

\(^&\) Particle size calculated from Scherrer equation based on the XRD of Co.
**Figure 1** XRD spectra of catalyst. CeO$_2$ shows strong peaks for all catalysts at 28.6, 33.1, 47.5, 56.4, and 59.1°. Co, reduced prior to scan, shows a weak and broad peak centered near 44.3°. ZnO shows a weak peak at 36.2° 2θ.
Figure 2 High resolution XRD spectra of catalyst. CeO$_2$ shows strong peaks for all catalysts at 47.5°. Co, reduced prior to scan, shows a weak and broad peak centered near 44.3°. ZnO shows a weak peak at 36.2° 2θ
Figure 3 TEM images of 10Co0ZnO/CeO₂ (top) and 10Co3ZnO/CeO₂ (bottom).
**Figure 4** TPR profiles for a) 10Co0ZnO/CeO₂, b) 10Co1ZnO/CeO₂, c) 10Co3ZnO/CeO₂, d) 10Co5ZnO/CeO₂ e) 10Co10ZnO/CeO₂ f) CeO₂.
Figure 5 TPO profiles on a) 10Co0ZnO/CeO₂, b) 10Co3ZnO/CeO₂, c) 10Co10ZnO/CeO₂.
Figure 6 DRIFTs analysis of adsorbed pyridine at 150°C on a) 10Co/CeO$_2$, b) 10Co3ZnO/CeO$_2$, c) 10Co10ZnO/CeO$_2$. Peaks at 1597 cm$^{-1}$ and 1441 cm$^{-1}$ correspond to Lewis acid sites, the peak at 1539 cm$^{-1}$ is associated with Brønsted acid sites and the peak at 1481 cm$^{-1}$ is a combination of Lewis and Brønsted acidity.
Figure 7 CO$_2$-TPD on a) 10Co/CeO$_2$, b) 10Co3ZnO/CeO$_2$, c) 10Co10ZnO/CeO$_2$. 
Figure 8

The C–C cleavage conversion for different ZnO loadings. 100 mg catalyst loaded, 10:1 H\textsubscript{2}O:EtOH ratio, P\textsubscript{EtOH} = 7.3%, WHSV = 9.27 g\textsubscript{EtOH}\cdot g\textsubscript{cat}\textsuperscript{-1}\cdot hr\textsuperscript{-1}. 
Figure 9

Figure 9 C¹ selectivity for different loadings of ZnO. 100 mg, 10:1 H₂O:EtOH ratio, P_{EtOH} = 7.3%, WHSV = 9.27 g_{EtOH}·g_{cat}⁻¹·hr⁻¹. Ethanol conversion to C¹ products between 12-18%.
Scheme 1

Scheme 1 Schematic oxidation of CH\textsubscript{x}/CO species by water on 10Co3ZnO/CeO\textsubscript{2}
Figure 10

The effect of ZnO on the selectivity to light alkanes.
CHAPTER FIVE:
CONCLUDING REMARKS

We have examined cobalt on a variety of supports to cover a wide range of activity for water dissociation. Activated carbon was used to provide information on the cobalt performance in the ESR system when the support has virtually no activity for water dissociation. Both ZrO$_2$ and CeO$_2$ were selected to provide information on cobalt performance in ESR when the support has high activity for water dissociation. In all cases the effect of adding ZnO was also investigated as ZnO has more activity for water dissociation than carbon but lower activity than ZrO$_2$ or CeO$_2$.

In Chapter Two it was demonstrated that the addition of ZnO created additional sites for water dissociation. This was primarily evidenced by \textit{in situ} XANES measurements, which showed that 10Co/C had no measurable bulk oxidation during ESR at 225 °C while 10Co5ZnO/C showed significant bulk oxidation. This was further supported by the increase in CO and CO$_2$ selectivity during ESR at both 250 °C and 450 °C.

In Chapter Three, we again showed that addition of ZnO to Co/ZrO$_2$ decreased activity for water dissociation. This was primarily evidenced by Raman spectroscopy of catalysts during H$_2$O exposure, pulsed H$_2$O oxidation coupled with H$_2$-TPR, and H$_2$O-TPO where cobalt oxidation was consistently more facile over 10Co/ZrO$_2$ than over 10Co1Zn/ZrO$_2$. This was further supported by reaction data showing a slight increase in C-C cleavage with the addition of ZnO and a slight decrease in CO$_2$ selectivity. Most dramatic was the change in liquid product selectivity change from acetone with acetaldehyde with the introduction of ZnO. Over
10Co/ZrO$_2$ acetone was the primary product at 39.4% selectivity while acetaldehyde selectivity was only 27.4%. With the addition of ZnO the selectivity to acetone dropped to 33.2% while acetaldehyde selectivity increased to 36.9%. This trend continued to 10Co/ZnO, where acetaldehyde selectivity increased to 54.7% and acetone selectivity decreased to 5.1%.

In Chapter Four we showed how a range of ZnO loadings impacts catalyst performance. For all samples the addition of ZnO facilitated the oxidation of cobalt. This is because the ZnO is able to interact with the CeO$_2$ and stabilize oxygen vacancies, thus increasing oxygen mobility. This was reflected both in O$_2$-TPO and by the decrease in C-C cleavage during ESR with the addition of ZnO. 3wt% ZnO was found to be an optimal loading as it had the highest CO$_2$ selectivity and lowest CO and CH$_4$ selectivity. It is unclear, this may be due to a balance between the increase in oxygen mobility and decrease in H$_2$O dissociation activity, however, further experiments would be needed.

From these studies we can now propose the ESR system shown in scheme 1. Over supports with low H$_2$O dissociation activity, ethanol will adsorb and convert to acetaldehyde. Acetaldehyde then under goes steam reforming. As discussed in Chapter Three, the acetaldehyde steam reforming mechanism tends to lead to higher CH$_4$ selectivity. However, the low H$_2$O dissociation activity also limits the extent that cobalt is oxidized, leaving more metallic cobalt for C-C cleavage. Over supports with high H$_2$O dissociation activity, ethanol adsorbs and converts to acetaldehyde. Acetaldehyde is then able to convert to acetone and acetone then undergoes steam reforming. Again, as discussed in Chapter Three the acetone steam reforming mechanism tends to limit CH$_4$ selectivity. However, in this case the high H$_2$O dissociation activity will lead to a greater extent of cobalt oxidation, thus limiting C-C cleavage activity.
Overall, it can be seen that H$_2$O dissociation activity is ultimately a balancing act. A sufficiently high activity is needed for carbon removal from the surface and to convert acetaldehyde to acetone. However, the activity cannot be so high as to cause excessive cobalt oxidation, severely limiting C-C cleavage and ESR activity in general.

Over the course of this work, we have shown how a dopant like ZnO can be added to a catalyst system to either increase or decrease the catalyst activity for H$_2$O dissociation, depending on the nature of the support. While there is still more work required to design an optimal ESR catalyst, this is a useful tool for more intelligent catalysts designs.
Scheme 1 Over supports with low water activation that ethanol will convert to acetaldehyde, which will then undergo its own steam reforming. While some cobalt may be oxidized in these systems, it is relatively small amounts. In systems that have high activity for water activation, acetaldehyde is able to convert to acetone. The steam reforming of acetone tends to result in lower selectivity to methane and higher selectivity to CO₂. However, in these systems more cobalt will be oxidized.
CHAPTER SIX:
FUTURE WORK – NSF PROPOSAL

INTRODUCTION

Hydrogen is a widely used chemical commodity the market of which was estimated at ~254 billion m³ and $103.5 billion [1, 2]. Uses of hydrogen range from chemical synthesis of ammonia and methanol to metal and petroleum processing [3]. More recently, hydrogen has also gained attention as a clean energy carrier with use in proton exchange membrane (PEM) fuel cells. At present, the majority of H₂ is produced via methane steam reforming [3]. Over the last several decades, a great deal of work has been done on bio-derived feed stocks for H₂ production [4, 5]. While the majority of work in steam reforming of bio-derived compounds has focused on simple molecules, like ethanol and methanol, some work has also been done on higher order alcohols and polyols [6]. Polyols like ethylene glycol and glycerol can be easily derived from biomass and are relatively limited in their current utilization [4]. This makes them excellent candidates for H₂ feed stock.

While some work has been done, the work is still in early stages. Overall catalyst activity has been investigated, but very few studies have looked into the reaction mechanism. To our knowledge, no studies have investigated the role of H₂O dissociation in the steam reforming of polyols.

Objective 1: Co particle size effects

The first step to studying the activity of a catalyst to dissociate H₂O is to study H₂O dissociation over Co itself. We will study and measure the effect of Co particle size on H₂O
dissociation activity and those effects on both the oxidation stability of the Co and steam reforming activity.

**Objective 2: Low support activity for H$_2$O dissociation**

Next we will study reaction mechanisms in the low range of H$_2$O dissociation activity and those effects on the oxidation stability of Co and both steam reforming activity and steam reforming mechanism. Here we will focus on support material that has no activity for H$_2$O dissociation.

**Objective 3: High support activity for H$_2$O dissociation**

Finally we will study reaction mechanism in the high range of H$_2$O dissociation activity and those effects on the oxidation stability of Co and both steam reforming activity and steam reforming mechanism. Here we will focus on support material that has high activity for H$_2$O dissociation.

**SIGNIFICANCE**

**Intellectual Merit**

The purpose of this project is to provide an in depth analysis of the role of H$_2$O dissociation in the steam reforming of ethylene glycol, glycerol, and acetic acid. Intellectual challenges include identifying key intermediates in the steam reforming pathways to begin building a picture of the reaction mechanism,

**Broader Impact**

By shifting hydrogen production away from natural gas and towards bio-derived products, greenhouse gas emissions can be reduced. A key limiting factor to a more hydrogen based economy is the transportation and storage of hydrogen, leading many to identify point-of-
source hydrogen generation to be the best solution. As cost of feed stocks and processing decrease, a distributed hydrogen production network becomes more viable with this technology already established.

We will coordinate with the department to design a course to cover renewable energies and the roles that catalysts can play. This course will be open to both undergraduate and graduate students with more emphasis on the undergraduates to expose them to ideas and nomenclature unique to area of catalysis.

BACKGROUND

Currently ~49% of the world’s hydrogen is produced via natural gas steam reforming [3, 7]. Steam reforming itself is a very versatile process and over the last several decades a great deal of work has been done investigating use of bio-derived compounds as feed stock for steam reforming [5, 8, 9]. Of the compounds investigated, bio-ethanol has received a great deal of attention [5, 6]. From the work already done, noble metal based catalysts have shown some of the highest activity for C-C cleavage, however, they have also shown relatively high CH$_4$ selectivity below 500 °C [10]. Studies have found that both Ni and Co are good catalysts for ethanol steam reforming (ESR) and they have shown comparable activity for C-C cleavage, however, Co has demonstrated a lower selectivity to CH$_4$ than Ni [5, 6].

From studies of Co-based catalysts, it has been found that both cobalt oxidation state and the reaction network are significantly influenced by either the reaction conditions or catalyst support, which eventually led to different performances of the catalysts during ESR [5, 6, 11-14]. Over model Co catalysts, it was found that while Co$^{2+}$ is active for ethanol dehydrogenation reaction, Co$^0$ is mainly responsible for C-C cleavage during ESR [15, 16]. These model studies
have been further supported by recent work utilizing operando XAFS analysis to study the oxidation state of cobalt under realistic reaction conditions [12]. Recent work also revealed that both the ratio of Co$^{2+}$/Co$^{0}$ and reaction network affected the selectivity to CH$_4$ [13, 14, 17, 18]. From studies on cobalt oxidation state higher Co$^{2+}$/Co$^{0}$ ratio was found to favor CO methanation toward CH$_4$ [13]. In the case of reaction mechanism, acetone was found to be a key intermediate in ESR on Co/ZrO$_2$ and acetone steam reforming resulted in the low CH$_4$ selectivity (≤ 5%) [17, 18], details are shown in Figure 1-A. Over cobalt supported on carbon nano-filaments (Co/CNF) where acetaldehyde was identified as the only intermediate, a high CH$_4$ selectivity was observed (~10%) [18], details are shown in Figure 1-B. A key point of interest with these two studies is the ability of the support material to dissociate H$_2$O. The ZrO$_2$ support has high activity for H$_2$O dissociation while the CNF has negligible activity for H$_2$O dissociation. Other studies of indicated the importance of H$_2$O dissociation for conversion of ethanol to acetone [19, 20].

The majority of this work has been focused on simple alcohols, like methanol and ethanol, however, some work has been done on higher order alcohols and polyols [21, 22]. Cai et al. studied butanol steam reforming over supported Co (i.e., Co/ZnO, Co/CeO$_2$, Co/TiO$_2$) [23]. Co/ZnO was shown to have the highest H$_2$ yield and stability. Co/CeO$_2$ initially showed similar H$_2$ yield but higher CO$_2$ selectivity. However, by 36 hours time on stream (TOS) Co/CeO$_2$ showed a higher degree of deactivation than Co/ZnO. Co/TiO$_2$ displayed comparable initial activity but quickly deactivated due to coke formation [23]. These results mirror Llorca’s findings for the case of ethanol steam reforming (ESR) over supported Co catalyst discussed earlier [23, 24]. Llorca et al. observed the highest ESR activity over Co/ZnO and Co/CeO$_2$ and that Co/CeO$_2$ showed both higher initial CO$_2$ selectivity and higher deactivation as TOS increased; additionally, Co/TiO$_2$ displayed the lowest activity and stability due to significant
coke formation [24]. Despite the large amount of work done in steam reforming, there are very few overlaps like this, validating the hypothesis that trends observed in ESR can be extrapolated to other steam reforming systems.

While there are many means of converting bio-mass to fuel and commodity compounds, pyrolysis remains one of the most economical [3, 4, 25]. Pyrolysis liquid is generally split into two phases, an aqueous phase and an oil phase; the oil phase contains larger molecules suitable for upgrading to fuel range compounds while the aqueous phase contains primarily small oxygenates suitable for steam reforming [26]. Based on these studies, ethylene glycol, glycerol, and acetic acid have been selected as model compounds of the aqueous phase of pyrolysis liquid.

While some studies have been done on the steam reforming of ethylene glycol, glycerol, and acetic acid, they are not as extensive as the studies on ESR. Hu et al. studied steam reforming of ethylene glycol on 30 wt% Ni/Al2O3 catalysts [22]. At 400 °C, both ethylene glycol conversion and H2 selectivity increase with steam-to-carbon ratio; 89% H2 was achieved at a steam-to-carbon ratio of 9 while CO and methane selectivity decreased significantly (3% and 6% respectively). Serious coking and catalyst deactivation were observed at the stoichiometric steam-to-carbon ratio (i.e., S/C = 2) [22]. A recent study compared steam reforming of ethylene glycol on Ni/Al2O3, Ni/MgO, Ni/CeO2 and Ni/ZrO2 catalysts [27]. At similar ethylene glycol conversion, selectivity to CH4 and CO were found to vary significantly with supports, while the CO2 selectivity remained relatively constant. This was attributed to the significant effect the support has on activity for CO methanation and water gas shift reactions. Methane selectivity was highest over Ni/Al2O3 at 400 °C (28.7%), and decreased with increasing reaction temperature via steam methane reforming, however, reverse water gas shift became favored as temperature increased. Ni/MgO showed the highest H2 yield and lowest CH4 selectivity (64.2%
and 14.1% respectively) at 400 °C, however, it also showed the highest CO selectivity (17.8%) [27]. Iriondo et al. investigated glycerol steam reforming on the Pt, Ni and Pt-Ni supported on La2O3 modified Al2O3 catalysts [28]. It was found that Ni/Al2O3 modified with an optimal amount of La2O3 (6 wt%) exhibited the highest H2 and CO2 selectivity, attributed to high water gas shift activity and low methanation activity. Promoted Pt/Al2O3 catalyst was shown to produce primarily oxygenated products (e.g., aldehyde); the Pt/Al2O3 catalyst also showed rapid deactivation, possibly related to the high rate of aldehyde formation, similar to a deactivation mechanism proposed for cobalt elsewhere [29].

It has been suggested that H2O dissociation activity can impact the ESR reaction network [11, 17, 18]. Our aim in this work is to demonstrate that H2O dissociation activity will have a similar impact on the steam reforming of other small oxygenates.

RESULTS FROM PRIOR WORK

To study the effects of ZnO addition to cobalt based catalysts in ESR several studies were conducted. For one system we selected an activated carbon support (XC72R) to minimize support-metal interactions [11]. For the case of 10wt% cobalt supported on carbon (10Co/C) we found that ZnO addition generally increased H2O dissociation activity. This was most strikingly demonstrated with in situ XANES measurements (Figure 2), where 10Co/C shows no observable deviation from the reduced state during ESR at 225 °C. In contrast, 10Co5ZnO/C (10wt%Co and 5wt% ZnO) showed significant deviation from the reduced state, indicated that bulk oxidation of cobalt was occurring. In addition, investigation of ESR activity showed a decrease in C-C cleavage activity and an increase in CO and CO2 selectivity with the addition of ZnO to Co/C, further indicating more oxidation of both cobalt and surface carbon species during ESR. For both
10Co/C and 10Co5ZnO/C the primary liquid product detected was acetaldehyde and neither catalysts was found to produce acetone [11].

To investigate a system with high H$_2$O dissociation activity, we studied cobalt supported on ZrO$_2$ (Co/ZrO$_2$). For the case of Co/ZrO$_2$, the addition of ZnO increased the C-C cleavage activity and decreased the CO$_2$ selectivity slightly. Even more pronounced were the changes in liquid product selectivity, the addition of ZnO caused the selectivity to acetone to decrease from 39.4% to 33.2% while acetaldehyde selectivity increased from 27.4% to 36.9%. This trend continued to 10Co/ZnO, where the acetone selectivity decreased even further to 5.1% and acetaldehyde selectivity increased to 54.7%. Figure 3 shows a summary of the work for Co/ZrO$_2$.

Investigations of H$_2$O dissociation activity via Raman spectroscopy, H$_2$O-TPO, and pulsed H$_2$O oxidation coupled with H$_2$-TPR identified the ranking of H$_2$O dissociation activity as 10Co/ZrO$_2$ > 10Co1Zn/ZrO$_2$ > 10Co/ZnO. From these studies, it appears that a general ranking of H$_2$O dissociation activity can be made of: 10Co/ZrO$_2$ > 10Co1Zn/ZrO$_2$ > 10Co/ZnO > 10Co5ZnO/C > 10Co/C.

**PROJECT PLAN**

Based on our prior work in ESR, we propose that similar trends can be found extending to the steam reforming of ethylene glycol, glycerol, and acetic acid. Because each of the objectives of this project (identify cobalt particle size effects, study of low H$_2$O dissociation activity, and study of high H$_2$O dissociation activity) will be using similar characterization and testing protocols, the protocols are listed in detail first followed by further details for each of the project objectives. A proposed time line for the project objectives is given in Table 1.
Catalyst Synthesis

For this project several catalysts will be synthesized. To cover a range of H2O dissociation activities support material of carbon-nanotubes, ZnO, and ZrO2 will be used. Carbon-nanotubes are selected because they have negligible activity for H2O dissociation and will have a minimal amount of potential contaminants, such as S. ZrO2 is selected for high H2O dissociation activity and good hydrothermal stability. ZnO is selected for an intermediate H2O dissociation activity and to be used as a promoter type material with both carbon-nanotubes and ZrO2. Co and ZnO will be added to the supports via incipient wetness impregnation [32]. Loadings of Co and ZnO will range from 0 to 25wt%; for some of the higher loadings sequential impregnations may be needed due to solubility constrains on the metal precursors. Carbon-nanotubes will be used as-is from vendor. ZrO2 support will be synthesized by calcining Zr(OH)4 at 400 °C (3 °C/min) for 3 hr and then at 500 °C (5 °C/min) for 5 hr. ZnO support will be synthesized by decomposing Zn(CH3COOH)2·2H2O at 500 °C (10 °C/min) for 3 hr. Co(NO3)2·6H2O and Zn(NO3)·6H2O will be used for metal precursors.

Physical/Chemical Characterization

The aim of these experiments is to get general information about the catalyst system.

Experiment 1: Surface Area Analysis

N2 physisorption will be used to obtain information on the Braun-Emmett-Teller (BET) surface area as well as the Barrett-Joyner-Halenda (BJH) pore volume and pore size distribution. This standard practice in heterogeneous catalysis as the reactions are taking place at gas- or liquid-solid interface. These experiments will be carried out utilizing a Micromeritics TriStar 3020 surface area analyzer.
**Experiment 2: Particle Size Analysis**

X-ray diffraction (XRD) and transmission electron microscopy (TEM) will be used in conjunction to characterize the Co and ZnO particle sizes. This is critical as the amount of Co available for reaction will be key for normalizing kinetic activity data and accounting for Co particle size effects. Both XRD and TEM will be utilized as complimentary techniques. XRD provides good bulk information about the entire sample, however, it also tends to be skewed towards larger crystallites, as those provide stronger signal. TEM provides data on the particle size distribution profile, however, is limited in sample sizes as the imaged area is small. Between XRD and TEM, we can be confident in the particle sizes identified.

**Experiment 3: Redox Properties**

H₂ temperature programmed reduction (H₂-TPR) and O₂ temperature programmed oxidation (O₂-TPO) will both provide information about the catalyst general redox properties. The H₂ and O₂ uptake quantities can be measured, allowing for calculation of extent of reduction and oxidation. The ESR reaction itself is a redox process and, as discussed in the background, the cobalt oxidation state plays a large role in the ESR reaction system. These experiments will be carried out on a Micromeritics AutoChem 2920.

**H₂O Dissociation Activity**

The aim of these experiments is to identify how facile H₂O dissociation is over the catalysts.

**Experiment 1: Raman Spectroscopy**

Raman spectroscopy can be used to probe the surface oxidation state. Cobalt oxides have characteristic Raman peaks at 195, 485, and 674 cm⁻¹ while metallic cobalt has no Raman active
features [30]. This allows for probing of the surface oxidation state following H$_2$O exposure. Samples will be exposed to H$_2$O at increasing temperatures, both the onset temperature and the size/area of the peaks can be used to qualitatively rank activity for H$_2$O dissociation and oxidation of metallic cobalt. These experiments will be carried out on a Horiba LabRAM HR Raman/FTIR microscope spectrometer, equipped with a 532 nm diode laser source (Ventus LP 532), a Synapse CCD (Charge Coupled Device), and an in situ cell (Linkam CCR1000).

**Experiment 2: H$_2$O Temperature Programmed Oxidation (H$_2$O-TPO)**

H$_2$O-TPO is similar to O$_2$-TPO in that both yield information on the oxidative stability of the catalyst. However, H$_2$O and O$_2$ are not equivalent oxidizers and it is expected that H$_2$O will show oxidation onset at lower temperatures than O$_2$-TPO. In addition, some separation of cobalt oxidation and support oxidation will be possible by tracking the H$_2$ produced during H$_2$O-TPO as H$_2$ is primarily generated during oxidation of metals while oxidation of partially reduced oxides tends to not produce H$_2$. Similarly to O$_2$-TPO, both H$_2$O uptake and H$_2$ generation can be measured to calculate extent of oxidation of metallic cobalt. These experiments will be carried out on a Micromeritics AutoChem 2920.

**Experiment 3: Pulsed H$_2$O Oxidation coupled with H$_2$-TPR**

By pulsing H$_2$O over the reduced sample we can observe the oxidation of cobalt. Similarly to H$_2$O-TPO, by tracking H$_2$ produced an estimate of extent of oxidation can be made. This is further studied by utilizing H$_2$-TPR to quantify the extent of material that can be re-reduced by H$_2$ following pulsed oxidation. These experiments will be carried out on a Micromeritics AutoChem 2920.
Kinetic Testing

The aim of these tests is to identify changes in the reaction activity and correlate those changes back to differences identified during characterization.

**Experiment 1: Zero Residence Time Extrapolation**

Catalyst activity for steam reforming of ethylene glycol, glycerol, and acetic acid will be conducted on a home built reactor stand. The reactor stand is a fixed-bed, single-pass quartz tube reactor (I.D., 6.5 mm). A downstream cold trap (-5 °C) is used to capture the condensable components (e.g., unreacted H₂O, ethylene glycol, glycerol, and/or acetic acid) in the effluent gas stream. The dry gases (e.g., N₂, H₂, COₓ, CH₄) are analyzed with an on-line Agilent CP490 micro gas chromatograph equipped with 4 parallel columns (5Å molecular sieve, PPQ, Al₂O₃ and SiO₂) and thermal conductivity detectors (TCD) for quantifications. N₂ is used as an internal standard. Liquid products collected by the cold trap are analyzed by an Agilent 7890A gas chromatograph with a 30 meter DB-FFAP column and flame ion detector (FID), acetonitrile is used as an internal standard.

After screening for mass and heat transfer limitations, catalyst will be loaded into the quartz tube and reduced (typical pretreatment temperature 450 °C) under 10%H₂/N₂. Once all of the Co is reduced and the system is purged a reactant mixture of H₂O and polyol (ethylene glycol, glycerol, or acetic acid) at steam to carbon ratio of 3 is fed to the evaporator and then flown over the catalyst. After the online microGC shows stable measurements the space velocity will be changed and then allowed to stabilize again. By running a range of space velocities we can gain insight into the primary steps of the reaction mechanism. A key point that we are looking for is what role H₂O dissociation plays in each reaction mechanism, which intermediates
does H₂O dissociation favor or inhibit, and how H₂O dissociation and the cobalt oxidation state affect the reaction mechanism.

**Experiment 2: Selectivity Comparison**

Once a general understanding is established of the catalysts activity, reaction selectivity can be compared at similar conversions. The same test apparatus described in Experiment 1 will be used here.

The aim of these tests, in contrast to the zero residence time extrapolation, is to compare reaction selectivity across the different catalysts. It is important to match overall conversion so that the kinetic data that is obtained in comparable, i.e., reaction environment is as similar as possible.

**Objective 1: Cobalt Particle Size Effect**

The first step to studying the activity of a catalyst to dissociate H₂O is to study H₂O dissociation over Co itself. It is generally known that large Co particles have relatively low activity for H₂O dissociation [18, 31]. Over small (<4 nm) Co particles, however, H₂O dissociation is very active [18, 31]. Thus it is important to understand what activity the Co particles have for dissociating H₂O in the systems that we are studying. In order to generate a range of Co particle sizes the Co loading will be varied from 1 to 25wt%. This will be done for all three supports and provide a reference point for when ZnO is added in Objectives 2 and 3.

Anticipated results: because the activity for H₂O dissociation is known to be dependent on Co particle size, being more active over smaller particles, and because smaller Co particles are easier to oxidize it is likely that an optimal particle size will be found.
Objective 2: Low H$_2$O Dissociation Activity

To study the effects of H$_2$O dissociation at low activity levels, the carbon nanotubes will be used for support material and Co loading will be fixed at 10wt%. ZnO loading will be varied from 0 to 25wt%.

Anticipated results: sample with no ZnO will show highest C-C cleavage but lowest CO$_2$ selectivity. As ZnO loading increases C-C cleavage will decrease and CO$_2$ selectivity will increase.

Objective 3: High H$_2$O Dissociation Activity

To study the effects of H$_2$O dissociation at high activity levels, ZrO$_2$ will be used for support material and Co loading will be fixed at 10wt%. ZnO loading will be varied from 0 to 25wt%.

Anticipated results: sample with no ZnO will show lowest C-C cleavage but highest CO$_2$ selectivity. As ZnO loading increases C-C cleavage will increase and CO$_2$ selectivity will decrease.

PRELIMINARY RESULTS

N/A

MANAGEMENT PLAN

N/A

EVALUATION ASSESSMENT

To provide an initial assessment of the project 5 catalysts will be synthesized: 10Co/CNT, 10Co5Zn/CNT, 10Co/ZnO, 10Co5Zn/ZrO$_2$, and 10Co/ZrO$_2$. These samples provide a wide range of H$_2$O dissociation activity and will allow for an overview of reaction activity.
Before Q2 of year 1, these samples will be synthesized, characterized for H$_2$O dissociation activity, and evaluated in steam reforming. Assuming the findings match with expectations, then the remainder of the project can continue. If the findings show large discrepancies across the different supports, the project can still continue, however, it will then be more compartmentalized; Measuring that findings would still be useful, but could not be applied as generally.

**DISSEMINATION**

The primary means of dissemination of the findings of this work will be via publication in peer reviewed journals. In addition, conference presentations such as the American Institute for Chemical Engineers (AIChE) and the American Chemical Society (ACS) are planned on a semi-annual basis. Washington State University also offers several venues for presentation of research at a more local level, such as the Wiley Research Symposium and regular seminar presentations where our work will be presented and critiqued.

**SUMMARY**

As demand for H$_2$ increases coupled with a need to reduce CO$_2$ emissions an alternative to natural gas steam reforming is needed. Bio-derived compounds, such as ethylene glycol, glycerol, and acetic acid could prove to be such a feedstock, however, a deeper understanding of the nature of the reaction mechanism and role of H$_2$O dissociation is needed to better design catalysts. In this project we will investigate steam reforming of ethylene glycol, glycerol, and acetic acid over cobalt based catalysts with a range of H$_2$O dissociation activity. By studying the roles of H$_2$O dissociation and the reaction mechanisms of these steam reforming reactions, catalysts can be better designed.
REFERENCES


127


Figure 1 A
Figure 1 A) ESR over Co/ZrO$_2$ conditions: temp = 450 °C; S/C = 5 [17]; B) ESR over Co/CNF conditions: temp = 450 °C; S/C = 5 [18]
Figure 2 A

![Graph showing data with labels: Co Foil, Reduced, ESR at 225 °C.](image-url)
Figure 2 A) *in situ* XANES of 10Co/C B) *in situ* XANES of 10Co5ZnO/C conditions: temp = 225 °C; S/C = 5; PEtOH = 7.3%; Catalyst loading: 5 mg; C dilution x2 [11]
Figure 3 Product selectivity over Co supported on ZrO₂. Conditions: temp = 450 °C; S/C = 5; 10Co/ZrO₂ and 10Co1Zn/ZrO₂: W/F = 0.055 gₐlcohol·g-cat⁻¹·h⁻¹; 10Co/ZnO: W/F = 0.11 gₐlcohol·g-cat⁻¹·h⁻¹
**Table 1: Project time table for experiments**

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<th>Year 3</th>
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<td>Objective 3: High H₂O Dissociation Activity</td>
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APPEDIX A:
SUPPORTING INFORMATION

STABILITY TEST DATA – CHAPTER TWO AND THREE

Not directly reported in chapters two and three is the data from stability tests of the catalysts. For Co/C both samples with and without ZnO showed steep initial deactivation for C-C cleavage, shown in Figure 1. 10Co5ZnO/C showed a greater initial deactivation than 10Co/C, following the initial deactivation, both catalysts showed continued, but far more gradual deactivation. We believe that the initial deactivation is due to the surface cobalt oxidizing as the catalysts reach operating redox equilibrium and the slower deactivation is most likely from gradual coke deposition on the catalyst surface; however, with current data it is not possible to deconvolute the two parallel deactivation mechanisms. Figure 2-A shows the C₁ selectivity to CH₄ with TOS. The selectivity to CH₄ decreases slowly and then stabilizes, suggesting that the majority of CH₄ is produced via decomposition of ethanol; as reaction time goes on and more surface cobalt is oxidized there is also more oxidation of the surface carbon species, leading to the decrease in CH₄ selectivity. The C₁ selectivity to CO and CO₂ are shown in Figure 2-B. Initial CO selectivity is very high over both 10Co/C and 10Co5ZnO/C and rapidly decreased while CO₂ selectivity started low and rapidly increased. After a period of time, CO and CO₂ selectivity stabilized and changed more gradually. The large
10Co/ZrO$_2$
C1 Selectivity

C1 Selectivity [%]

TOS [min]
10Co1Zn/ZrO₂
APPENDIX B: EXPERIMENTAL METHODS

1. CHAPTER TWO EXPERIMENTAL METHODS

1.1 Catalyst Synthesis

All catalysts were prepared via incipient wetness impregnation. Carbon black (Vulcan XC-72R, Fuel Cell Store 590106) was used as catalyst support. Metal precursors used were Co(NO$_3$)$_2$·6H$_2$O (Aldrich 239267, 98+% purity) and Zn(NO$_3$)$_2$·6H$_2$O (Aldrich 228737, 98+% purity). Before impregnation, the XC-72R was pre-dried at 80 °C for ~24 hours to remove the majority of adsorbed water. Metal precursors weighed out to values close to those calculated for the desired loadings and then dissolved in deionized (DI) H$_2$O (> 18 MΩ resistance at room temperature, created on site). The total volume of the metal precursor solution was set to reach the incipient wetness of the XC-72R surface. Catalyst precursors were dried at ambient temperature for ~24 hours and then at 80 °C for 12 hours. The obtained powder was then ramped to 120 °C at 5 °C/min and held at 120 °C for 1 hour under N$_2$ (50 SCCM) to further remove H$_2$O and then further ramped to 350 °C (5 °C/min ramp rate) and held for 4 hours to complete the calcination. The catalysts synthesized were 10 wt% Co on XC-72R (10Co/C) and 10 wt% Co + 5 wt% ZnO on XC-72R (10Co5ZnO/C).

1.2 Catalyst Characterization

Nitrogen physisorption experiments were performed on a MicroMeritics 3020 TriStar II physisorption analyzer at -196 °C. The fresh catalysts were degased under vacuum at 120 °C for 2 hours prior to measurement. Catalyst surface area was calculated using the Brunauer–Emmett–Teller (BET) model.
XRD patterns were collected using a Philips X-Pert X-ray powder diffractometer with a Cu-Kα (incident wavelength = 0.15406 nm) radiation source at 50 kV and 40 mA. Before XRD measurement, the catalyst was reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10%H₂/N₂ (50 SCCM) and then passivated at 25 °C for 1 hour under 0.1%O₂/N₂ (50 SCCM). Diffraction patterns were collected from 30 to 80° (2θ) using continuous accumulation with 0.04° step size and dwelling 35 seconds per step. Crystallite sizes were calculated from XRD patterns using the Scherer equation.

TEM images were collected on a Philips CM-200 equipped with a LaB6 filament and energy-dispersive X-ray spectrometer (EDX). An acceleration voltage of 200 kV was used during imaging. Catalysts were reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10%H₂/N₂ (50 SCCM) and then passivated at 25 °C for 1 hour under 0.1%O₂/N₂ (50 SCCM) and then dispersed in ethanol using an ultra-sonic bath. The suspension was then loaded onto a copper grid coated with ultrathin lacy carbon for TEM imaging.

For particle size analysis, spherical particles were assumed and ImageJ software was used to calculate the diameter of the particles [30]. For statistical analysis over 300 particles were measured for each sample. From analysis using Origin software, the population distributions were neither normal nor log-normal, however, the normal distribution provided a better fit. Assuming a Gaussian distribution the first moment, average; second moment, variance; third moment, skewness; and fourth moment, Kurtosis or peakedness, were calculated. Variance yielded the standard deviation of the population from the average value. Skewness provided quantitative information on how skewed the distribution was above the average value. Peakedness provided quantitative information on how sharp the distribution peak was and how heavily the tails of the distribution were weighted.
Hydrogen TPR (H$_2$-TPR) and oxygen TPO (O$_2$-TPO) experiments were performed on a MicroMeritics AutoChem 2920. 50 mg of catalyst was loaded into a U-shaped quartz tube, sandwiched between two pieces of quartz wool. Outlet gases were monitored by both thermal-conductivity detector (TCD) and a Pfeiffer ThermoStar quadrupole mass-spectrometer (QMS). For H$_2$-TPR, the temperature was ramped from 35 °C to 600 °C at 10 °C/min under 10%H$_2$/Ar (50 SCCM). A cold trap at -10 °C was used to remove H$_2$O from the effluent gas. For O$_2$-TPO, the catalyst was first reduced at 450 °C (5 °C/min ramp rate) for 2 h under 10%H$_2$/Ar (50 SCCM). The catalyst was then cooled to 35 °C under He (50 SCCM). Next, the gas flow was switched to 10%O$_2$/He (50 SCCM) and the temperature was ramped to 500 °C at 10 °C/min.

*In situ* XANES studies on Co K edge were performed at beam X-18A at the National Synchrotron Light Source at Brookhaven National Laboratory. 5 mg of catalyst was diluted with carbon (1:2 catalyst:carbon ratio) and packed into a 1/8” glassy carbon reactor tube. The reactor was then loaded into an in-house built stainless steel cell, heated with resistive cartridge heaters; the setup details have been previously reported [31]. Because of system limitations, aqueous reactions could not be carried out at 250 °C and were instead carried out at 225 °C. The catalyst was reduced under H$_2$ (50 SCCM) at 450 °C for 1 hour (10 °C/min ramp rate) then cooled to 225 °C. ESR was carried out at 225 °C for ~30 minutes, with a H$_2$ gas flow of 20 SCCM, an aqueous ethanol solution (H$_2$O:EtOH molar ratio of 10:1) was flown rate of 0.5 mL/hour. The catalyst was then cooled to ambient temperature, and the reactor was filled and pressurized with the aqueous ethanol solution to 3450 kPa. With the aqueous ethanol solution flowing through the reactor at 0.5 mL/hour, the temperature was raised back to 225 °C and aqueous phase reforming of ethanol was carried out for ~60 minutes. XANES spectra were collected throughout the experiment. XANES data was collected in transmission mode with a Co foil spectrum collected.
simultaneously with each scan. XANES data processing and analysis were performed using Athena program of the IFEFFIT data analysis package [32, 33]

1.3 Catalyst Activity Evaluation

ESR activity tests were performed in a fixed-bed, single pass quartz tube reactor (I.D. 6.5 mm). Catalyst was pressed and sieved to 60 – 100 mesh and diluted 9x in SiC (70 mesh), then loaded and held in place using quartz wool. The catalyst was reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10%H₂/Ar. An aqueous solution of H₂O and ethanol, 10:1 molar ratio, was fed to the evaporator (175 °C) using a Cole Parmer syringe pump. The vaporized H₂O/EtOH solution was carried to the reactor by flowing N₂. An upstream pressure gauge measured pressure drop across the reactor, the pressure drop was less than 7 kPa. A downstream cold trap (-5 °C) was used to capture the condensable components (e.g., unreacted H₂O/EtOH, acetaldehyde) in the effluent gas stream.

The dry gases (e.g., N₂, H₂, COₓ, CH₄) were analyzed with an on-line Agilent CP490 micro gas chromatograph equipped with 4 parallel columns (5Å molecular sieve, PPQ, Al₂O₃ and SiO₂) and thermal conductivity detectors (TCD) for quantifications. N₂ was used as an internal standard.

Liquid products collected by the cold trap were analyzed by an Agilent 7890A gas chromatograph with a 30 meter DB-FFAP column and flame ion detector (FID), acetonitrile was added to the collected liquid sample during analysis as an internal standard.

For ESR at 450 °C, 25 mg of catalyst was loaded, a liquid feed rate of 2.4 mL/hour and gas flow of N₂ at 10 SCCM was used, resulting in a WHSV = 18.5 gEtOH gCatalyst⁻¹ h⁻¹ and an ethanol partial pressure in the reactant gas of 7.4 kPa.
For the testing at 250 °C, 100 mg of catalyst was used along with N\textsubscript{2} flow of 20 SCCM and a liquid flow rate of 0.5 mL/hour, resulting in a WHSV = 0.96 g\textsubscript{EtOH} g\textsubscript{Catalyst}\textsuperscript{-1} h\textsuperscript{-1} and the ethanol partial pressure in reactant gas to 2.8 kPa.

APRE was performed in a 300 mL Parr pressure reactor. 500 mg of catalyst was reduced at 450 °C (ramp rate 5 °C/min) for 2 hours under 10%H\textsubscript{2}/N\textsubscript{2} (50 SCCM) followed by passivation at 25 °C for 1 hour under 0.1%O\textsubscript{2}/N\textsubscript{2} (50 SCCM), and then transferred into a glass liner. 50 mL aqueous ethanol solution (H\textsubscript{2}O:EtOH molar ratio of 10:1) was then introduced and the glass liner containing catalyst and aqueous ethanol solution was loaded on to the Parr reactor. At ambient temperature, the reactor was pressurized to 830 kPa using N\textsubscript{2}. The reactor was then heated to 250 °C, which brought the total system pressure to ~5515 kPa.

2. CHAPTER THREE EXPERIMENTAL METHODS

2.1 Catalyst Synthesis

All catalysts were prepared via incipient wetness impregnation. The ZrO\textsubscript{2} support was synthesized by calcining Zr(OH)\textsubscript{4} (MEL Cat XZO1247/01, 97+% purity) at 400 °C (3 °C/min) for 3 hours, then ramping to 500 °C at 5 °C/min and holding for another 5 hours. ZnO support was made by decomposing Zn(CH\textsubscript{3}COOH)\textsubscript{2}·2H\textsubscript{2}O (Alfa Aesar 11559, 98+% purity) at 500 °C (10 °C/min) for 3 hours. Prior to the decomposition, the Zn(CH\textsubscript{3}COOH)\textsubscript{2}·2H\textsubscript{2}O precursor was dried at 125 °C (10 °C/min) for 2 hours. Metal precursors used were Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (Aldrich 239267, 98+% purity) and Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (Aldrich 228737, 98+% purity). Before impregnation, the ZrO\textsubscript{2} or ZnO was pre-dried at 80 °C for ~24 hours to remove the majority of adsorbed water. A calculated amount of metal precursor was dissolved in a given amount of deionized (DI) H\textsubscript{2}O. The total volume of the metal precursor solution was set to reach the incipient wetness of the support surface. After the impregnation, the obtained wet powders were
dried at ambient temperature for ~24 hours and then at 80 °C for 12 hours and then at 120 °C for 12 h, after that the temperature was then ramped to 550 °C at 10 °C/min for 5 hours to complete the calcination. For ZnO doped catalysts cobalt and zinc precursors were dissolved into a single solution and the same process was followed.

2.2 Catalyst Characterization

Nitrogen physisorption experiments were performed on a MicroMeritics 3020 TriStar II physisorption analyzer at -196 °C. The fresh catalysts were degassed under vacuum at 300 °C for 1 hour prior to measurement. Catalyst surface area was calculated using the Brunauer–Emmett–Teller (BET) model.

XRD patterns were collected using a Rigaku Mini-Flex X-ray powder diffractometer with a Cu-Kα (incident wavelength = 0.15406 nm) radiation source at 40 kV and 15 mA. Diffraction patterns were collected from 20 to 80° (2θ) using continuous accumulation with 0.01° step size at a rate of 1.5°2θ/min. Crystallite sizes were calculated from XRD patterns using the Scherer equation.

TEM images were collected on a Philips CM-200 equipped with a LaB6 filament. An acceleration voltage of 200 kV was used during imaging. Catalysts were dispersed in ethanol using an ultra-sonic bath, the suspension was then loaded onto a copper grid coated with ultrathin lacy carbon for TEM imaging.

For particle size analysis, spherical particles were assumed and ImageJ software was used to calculate the diameter of the particles [26]. For statistical analysis over 100 particles were measured for each sample. From analysis using Origin software, the population distributions were determined to be log-normal, based on this mean and variance were calculated accordingly.
Hydrogen TPR (H₂-TPR), oxygen TPO (O₂-TPO), as well as pulsed water oxidation and water TPO (H₂O-TPO) experiments were performed on a MicroMeritics AutoChem 2920. 50 mg of catalyst was loaded into a U-shaped quartz tube, sandwiched between two pieces of quartz wool. Outlet gases were monitored by both thermal-conductivity detector (TCD) and a Pfeiffer ThermoStar quadrupole mass-spectrometer (QMS). For H₂-TPR, the temperature was ramped from 35 °C to 600 °C at 10 °C/min under 10%H₂/Ar (50 SCCM). A cold trap at -10 °C was used to remove H₂O from the effluent gas. For O₂-TPO, the catalyst was first reduced at 450 °C (5 °C/min ramp rate) for 2 h under 10%H₂/Ar (50 SCCM). The catalyst was then cooled to 35 °C under He (50 SCCM). Next, the gas flow was switched to 10%O₂/He (50 SCCM) and the temperature was ramped to 500 °C at 10 °C/min. For pulsed water oxidation, the catalyst was first reduced at 450 °C (5 °C/min ramp rate) for 2 h under 10%H₂/Ar (50 SCCM), and then purged under He (50 SCCM) for 30 min. ~10%H₂O/He was generated by bubbling He (50 SCCM) through DI H₂O in a flask heated to 55 °C followed by a reflux at 45 °C. H₂O was then pulsed over the catalyst at 450 °C, pulses were repeated until TCD indicated the catalyst surface was saturated. QMS was used to monitor the effluent gases, particularly hydrogen. Following water pulses the catalyst was again purged under He (50 SCCM) at 450 °C for 30 min, then cooled to 35 °C. To confirm degree of oxidation, H₂-TPR was run and H₂ uptake was quantified. Percentage oxidized by both H₂O pulses and H₂-TPR were calculated by taking the ratio of Co loaded and either H₂O taken up or H₂ consumed respectively. For H₂O-TPO, the catalyst was first reduced at 450 °C (5 °C/min ramp rate) for 2 h under 10%H₂/Ar (50 SCCM). The catalyst was then cooled to 35 °C under He (50 SCCM). Next, the gas flow was switched to ~10%H₂O/He (50 SCCM) and the temperature was ramped to 500 °C at 10 °C/min.
2.3 Catalyst Activity Evaluation

ESR activity tests were performed in a fixed-bed, single-pass quartz tube reactor (I.D., 6.5 mm). ESR reactions were carried out at 450 °C under atmospheric pressure. 50-100 mg of the catalyst (60-100 mesh) diluted 9x in SiC (70 mesh) was loaded and held in place using quartz wool. Prior to the reaction, the catalyst was reduced in situ at 450 °C (5 °C/min ramp rate) for 2 hours under 10%H₂/Ar (100 SCCM), followed by a N₂ purging (20 SCCM) for 60 min. An aqueous solution of H₂O and ethanol, 10:1 molar ratio, was fed to the evaporator (175 °C) using a Cole Parmer syringe pump. The vaporized H₂O/EtOH mixture was then carried to the reactor by flowing N₂. The ethanol partial pressure (PₑH₂) in the reactant gas was 7.4 kPa and WHSV was varied from 9.3 gₑ₁·g⁻¹·h⁻¹ to 18.5 gₑ₁·g⁻¹·h⁻¹ to control the ethanol conversion. A downstream cold trap (-5 °C) was used to capture the condensable components (e.g., unreacted H₂O/EtOH, acetaldehyde) in the effluent gas stream.

The dry gases (e.g., N₂, H₂, COₓ, CH₄) were analyzed with an on-line Agilent CP490 micro gas chromatograph equipped with 4 parallel columns (5 Å molecular sieve, PPQ, Al₂O₃ and SiO₂) and thermal conductivity detectors (TCD) for quantifications. N₂ was used as an internal standard. Liquid products collected by the cold trap were analyzed by an Agilent 7890A gas chromatograph with a 30 meter DB-FFAP column and flame ion detector (FID), acetonitrile was used as an internal standard. H₂-yield was calculated using equation 1.

\[
\text{H}_2 \text{ yield} = \left[ \frac{\text{H}_2 \text{ molar flow}}{(6 \cdot \text{EtOH molar feed rate})} \right] \cdot 100
\]

(1)

C₁ product yield was calculated using equation 2

\[
\text{C}_1 \text{ yield} = \left[ \frac{(\text{CO}_2 + \text{CO} + \text{CH}_4 \text{ molar flows})}{(2 \cdot \text{EtOH molar feed rate})} \right] \cdot 100
\]

(2)

Ethanol conversion was calculated using equation 3
EtOH conversion = ([EtOH in product liquid]/[EtOH in feed liquid])·100 \hspace{1cm} (3)

Product selectivity was calculated using equation 4, integration is over the run time of the experiment to get total C of the product over the entire experiment.

\[ \text{Selectivity} = \left( \int \frac{\text{(molar C flow of product)}}{\sum \text{(all C in products over experiment)}} \right) \cdot 100 \hspace{1cm} (4) \]

2.4 \textit{In situ} Raman characterization of cobalt oxidation by H$_2$O

\textit{In situ} Raman spectra characterizing cobalt oxidation by H$_2$O were collected on a Horiba LabRAM HR Raman/FTIR microscope spectrometer, equipped with a 532 nm diode laser source (Ventus LP 532), a Synapse CCD (Charge Coupled Device), and an \textit{in situ} cell (Linkam CCR1000). Samples were first reduced at 450 °C (5 °C/min ramp rate) for 2 hours under 10%H$_2$/He (50 SCCM) then cooled to ambient temperature. H$_2$O oxidation experiment was performed by bubbling He (10 SCCM) through H$_2$O at ambient temperature while the sample was heated to the target temperature and held for 30 min. Following the H$_2$O pretreatment, the sample was purged in flowing He (50 SCCM) for xx min and then cooled down to ambient temperature where Raman spectra were collected.

3. \textbf{CHAPTER FOUR EXPERIMENTAL METHODS}

3.1 Catalyst Synthesis

All catalysts were prepared by incipient wetness impregnation. The CeO$_2$ support (700290, >99.95% purity) used for all catalysts, Co(NO$_3$)$_2$·6H$_2$O (239267, 98+% purity) and Zn(NO$_3$)$_2$·6H$_2$O (228737, 98+% purity) precursors were from Sigma-Aldrich, and used as received. Before the catalysts loading, the support was first pretreated in air at 700 °C for 5 hours (10 °C/min). A given amount of metal salt precursors were dissolved in a calculated amount of DI H$_2$O (>18MΩ resistance) and then added drop-wise to the dried ceria until just...
wetting the entire surface. The concentrations of the precursors were adjusted to keep a constant cobalt loading (i.e., 10 wt%) and vary the ZnO loadings. The catalysts were then dried at ambient temperature for ~24 hours, after which the catalysts were heated to 120 °C (held 2 hrs) to remove water and then to 550 °C (10 °C/min) and held for 5 hours. The catalysts are denoted as \( xCo\text{ZnO}/CeO_2 \), where \( x \) and \( y \) refer to the weight percentage of Co and ZnO, respectively.

3.2 Nitrogen adsorption-desorption

Nitrogen sorption experiments were conducted on a Micromeritics TriStar II 3020 physisorption analyzer at -196 °C using UHP N\(_2\). The surface areas of the catalysts were calculated based on the Brunauer-Emmett-Teller (BET) model. Before the measurement, 0.2 g of catalyst was degassed at 300 °C for 1 hr under vacuum.

3.3 CO Chemisorption

CO titration was used to identify the metal dispersion of the catalyst. All the experiments were performed on a Micromeritics AutoChem 2920. 0.1 g of catalyst was loaded into a U-shaped quartz tube. Before CO titration, the catalyst was first reduced at 450 °C (ramping rate, 5 °C/min) for 2 hours under flowing 10% H\(_2\)/Ar (50 SCCM), followed by a He purge (50 SCCM) for 1 hour at the same temperature to remove hydrogen. While under flowing He, the catalyst was then cooled down to 150 °C. At 150 °C 10% CO/He was pulsed from a 0.5 mL loop until the catalyst was saturated. CO peaks were monitored by Thermal Conductivity Detector (TCD).

3.4 X-ray Diffraction (XRD)

XRD was conducted on a Siemens D-500 X-ray powder Diffractometer. Prior to XRD analysis, samples were reduced at 450 °C for 2 hours under 10%H\(_2\)/N\(_2\) (50 SCCM) and then cooled down to 25 °C, where they were further passivated under 50 SCCM 1% O\(_2\)/N\(_2\) for 1 hour.
XRD spectra were collected at ambient temperature and pressure, from 20 to 80° (2θ) at step size of 0.02° with a dwell time of 2.0 seconds. Refined XRD spectra were collected from 35 to 55° (2θ) at a step size of 0.01° with a dwell time of 8.0 seconds.

3.5 Temperature Programmed Reduction/Oxidation/Desorption (TPR/TPO/TPD)

All the following TPR/TPO/TPD experiments were performed on a Micromeritics AutoChem II 2920.

For TPR, 50 mg of catalyst was loaded into a U-shaped quartz tube. The temperature was then ramped from ambient to 600 °C at 10 °C/min under flowing 10%H₂/Ar (50 SCCM). The gas concentration is monitored by TCD. A cold trap at -10 °C was used to remove the H₂O in the effluent gas.

For the TPO experiments, the catalyst was first reduced at 450 °C for 2 hours under flowing 10% H₂/Ar (50 SCCM), then cooled to 35 °C under He (50 SCCM). The sample was then heated from 35 °C to 600 °C at 10 °C/min under flowing 10% O₂/He (50 SCCM). A cold trap at -10 °C was used to remove any H₂O generated/desorbed and the gas flow was monitored with TCD.

For the CO₂-TPD experiments, 100 mg of catalyst was loaded into a U-shaped quartz tube. Before CO₂ titration, catalyst was reduced at 450 °C for 2 hours under flowing 10%H₂/Ar (50 SCCM) and then cooled down to 50 °C for CO₂ pulse saturation. Pulses were delivered from a 0.5 mL loop and repeated until peaks were uniform, peaks were tracked via TCD. After saturation the sample was purged for 60 minutes under flowing He (50 SCCM) to remove physisorbed CO₂, and then heated to 500 °C at 5 °C/min under flowing He (50 SCCM). CO₂ desorption was monitored with TCD.
3.6 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis of adsorbed pyridine (IR-Py)

IR-Py experiments were used to identify the nature and strength of the catalysts’ surface acidity. All the spectra were collected on a Bruker TENSOR 27 FTIR system equipped with an in situ DRIFTS cell (Harrick, Praying Mantis cell). Prior to analysis, the catalyst was ground into a fine powder and loaded into the holder in the DRIFTS cell. The catalyst was then reduced under flowing 10%H₂/Ar (50 SCCM) at 450 °C for 1 hour. The sample was then cooled under flowing He (50 SCCM) to 50 °C where the background was taken. A mixture of pyridine/He (5 SCCM He flown through a bubbler filled with pyridine) was then flown over the catalysts for 30 min for adsorption, followed by a He purge (50 SCCM) for another 30 min. All spectra were collected at 50 °C under He (50 SCCM). For spectra corresponding to higher temperatures, samples were heated to the temperature and held there for 30 min and then cooled to 50 °C for collection.

3.7 Transmission Electron Microscope (TEM)

TEM images were taken on a FEI Tecnai T20 equipped with a LaB6 filament. Samples were dispersed in ethanol in ultrasonic bath, and then loaded onto the copper grid coated with ultrathin lacy carbon film.

3.8 Activity Test

For catalyst activity data, reactions were performed in a fixed-bed, single pass quartz tube reactor (I.D. 6.5 mm). 0.1 g of catalyst diluted in 0.9 g of SiC (both 150 – 250 μm) was loaded and held in place with quartz wool. Prior to reaction, the catalyst was reduced at 450 °C for 2 hours under flowing 10% H₂/Ar (100 SCCM), followed by a nitrogen purge at the same temperature for another 30 min. (20 SCCM). A H₂O:EtOH solution (steam to carbon molar ratio
of 5) was then pumped into the vaporizer at 4.8 mL/hr and vaporized at 175 °C. The vaporized H₂O/Ethanol gases were then brought into the reactor by flowing N₂ (20 SCCM). Pressure drop across the reactor was measured using a pressure gauge upstream of the reactor and assuming the outlet was at ambient pressure, pressure drop was observed to never be more than 2 psig. A thermocouple positioned at the top of the reactor bed was used to monitor reaction temperature. At the exit of the reactor, a cold trap was used to separate condensable products from the dry gases, which passed through another trap with dryrite to remove remaining H₂O. The dry gas products were analyzed using an Agilent CP490 microGC with 4 parallel columns. A 5Å molecular sieve was used to separate and analyze H₂, N₂, CH₄ and CO. A PPQ column was used to separate and analyze CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈. An Al₂O₃ column was used to separate and analyze C₃H₆, C₃H₈ and C₄H₈, any additional hydrocarbons would appear on this column as well.

Partial pressure of EtOH (P_{EtOH}) was kept 7.3%. All the reported product selectivity and conversion to dry gas products were collected after the reaction reached steady state. The methanation reaction investigation followed the same pretreatment of catalyst. A mixture of CO/H₂ (1/2, vol/vol) was used with N₂ being a diluent inert. The CO concentration was controlled at 23.2%. Equation 1 was used to calculate the dry gas conversion. “n” is the number of carbon atoms in the product molecule.

\[
\text{Dry gas conversion(%) = } \frac{\sum n \cdot \text{molar flow rate C product}}{2 \cdot \text{molar feed rate EtOH}} \times 100 \quad (5)
\]

Equation 2 was used to calculate C₁ selectivity.

\[
\text{C₁ Selectivity(%) = } \frac{\sum \text{Molar flow rate C₁ product}}{\sum \text{Molar flow rate C₁ product}} \times 100 \quad (6)
\]
Equation 3 was used to calculate $C_i$ selectivity, where “$i$” represents the carbon number in each molecule and “$n$” is to indicate all carbon containing species.

$$C_i \text{ Selectivity}(\%) = \frac{\sum_{i} i \cdot \text{molar flow rate} \cdot C_i \text{ product}}{\sum_{n} n \cdot \text{molar flow rate} \cdot C \text{ product}} \times 100 \quad (7)$$
APPENDIX C: EXPERIMENTAL PROTOCOLS

CATALYST SYNTHESIS – INCIPIENT WETNESS

Support preparation

1. Select support material
2. Select metal precursors
   a. Typically use hydrated nitrate ligands; e.g., cobalt (II) nitrate hexahydrate
      \[ \text{Co(II)} \cdot (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \]
3. Calculate amount of precursor needed for desired loading and desired amount of catalyst to produce
   a. **NOTE:** it is recommended to make as large of a batch as possible (typically a few grams) because incipient wetness does not have good repeatability batch to batch
   b. Be aware of solubility limits of the precursors in chosen impregnation medium
4. Weigh out desired amount into crucible
   a. Weigh 1 g of support material into a separate crucible for wetting test
5. Cover crucibles with foil to prevent contaminants from falling into crucible
   a. Puncture several holes in foil to allow for air flow
6. Place crucibles in drying oven set to 120 °C to dry
7. Dry at least 12 hours to remove majority of adsorbed water from support

Wetting test

1. Remove the crucible with 1 g of support material from drying oven and let cool
2. Fill beaker with impregnation medium, e.g., water
3. Measure initial weight of medium and support
   a. It is okay to include the weight of beaker and crucible for these measurements, just be sure to be consistent with how measurements are taken
4. Use either pipet or eye dropper to add medium to support drop by drop
   a. Mix vigorously while adding medium
5. Continue until the support is wetted
   a. When the support is wetted it will just start to clump together when mixing
   b. Support will also show slight sheen when wetted
   c. If support completely clumps together, appears like mud or clay, or medium is visible the support is overly wet
6. Measure final weight of medium and support
7. Calculate amount of medium needed to wet support
   a. This will be used for the other samples
8. **NOTE:** it is not recommended to try to re-dry this support material for catalyst synthesis
   a. This support material can be saved and run through the same process the other catalyst samples are to provide a support reference for activity tests

Incipient wetness impregnation of catalysts

1. Weigh out desired amount of metal precursor(s)
2. Measure out target amount of impregnation medium
   a. **NOTE:** if using water and a hydrate precursor, you need to account for the water content of the precursor
3. Dissolve metal precursor(s) in impregnation medium
a. **NOTE:** if required amount of metal precursor is above the saturation limit of the impregnation medium, use multiple impregnations

4. Remove support material from drying oven and let cool

5. Add solution of precursor and medium to support material

6. Mix thoroughly
   a. Watch to make sure that sample is properly wetted

7. Cover with foil to prevent contaminants from falling into sample
   a. Puncture holes in foil to allow for air flow

8. Let dry at ambient temperature ~12 hours
   a. Place samples in location where they are not likely to be disturbed

9. Move samples to drying oven and dry at 120 °C for ~12 hours

10. Remove foil cover from samples

11. Calcine samples in box furnace
    a. **NOTE:** check if synthesis method has specific ramp rate requirements; typical ramp rate 10 °C/min
    b. **NOTE:** if using carbon support or other support material that is damaged by high temperature oxidation, use tube furnace and inert environment for calcination
    c. Calcination temperature should be selected to be above anticipated reaction temperature for catalysts, e.g., if reaction is planned at 450 °C, then 500 °C is an acceptable calcination temperature
    d. If low calcination temperature is planned use TGA to check that temperature is sufficient to completely decompose and remove ligand group

12. After cooling, weigh and collect calcined sample
Sample sieving

1. Determine desired sieving range
   a. Typical range is 60 – 100 mesh (150 – 250 μm)
   b. May need to test for internal mass transfer limitations

2. Select and stack appropriate sieves
   a. Be sure that smaller mesh size is below larger mesh size
   b. Place base piece on bottom
   c. Top piece is helpful for keeping powder in but is not necessary

3. Add desired amount of catalyst to top sieve

4. Shake and vibrate sieve stack

5. Use spatula to force/grind powder through top sieve

6. Repeat steps 4 and 5 until all powder is sieved

7. Collect
AUTOCHEM 2920/ CHEMISORPTION ANALYZER OPERATIONS

Sample preparation

1. Find a clean sample tube.
   a. If tube is in oven, set out to cool

2. Load pinch of quartz wool into tube
   a. Should just fill conical section of tube

3. Weigh sample tube with quartz wool

4. Weigh out sample
   a. Typically 50 – 100 mg
      b. At least 5 mg of compound of interest

5. Load sample into sample tube

6. Weigh loaded sample tube
   a. Use the difference between the loaded sample tube and the sample tube with only quartz wool as sample weight

7. Load a second pinch of quartz wool
   a. Can be smaller than first pinch, but must cover sample

8. On the 2920, check that all appropriate gasses are connected.
   a. If the are not, isolate one gas line, typically on gas line 2
   b. After isolating the gas line, disconnect it and connect the desired gas line
   c. In the 2920 software select “Unit 1” and then “Gas Selections”
      i. Set all channels that were changed to the new gas
   d. Open the gas cylinder so the 2920 can pull from it
Using manual control run a quick (5 min at 50 ml/min) purge on the analysis line of the new gas

i. If manual control is not enabled select “Unit 1” and then click “Enable Manual Control”

Loading Sample

1. Check the software. Make sure that:
   a. there is not a method already running
   b. the analysis gas is flowing
   c. the analysis gas is not flowing through sample tube

2. Open the furnace and unload the loaded sample tube
   a. Wear thermal resistant gloves
   b. Keep one hand on bottom of sample tube so if the metal tubes drop they hit your fingers and not the sample tube
   c. Unthread both metal tubes and lower gently to bottom of sample tube
   d. Carefully remove sample tube
      i. O-rings should still be attached to top of sample tube
      ii. If not, after setting sample tube aside retrieve o-rings from 2920.
   e. Carefully set sample tube and o-rings aside

3. Place metal tubes on sample tube and fresh o-rings on

4. Load sample tube into 2920
   a. Carefully slide sample tube into sample port of 2920
      i. Be sure sample tube goes all the way in and is flush with top of port
b. Use one hand to keep the sample tube held firmly in place, thread metal tubes into 2920.
   i. Can check if properly loaded by pulling lightly on sample tube, should remain in place
   ii. If sample tube moves, reload sample tube

c. Check that thermocouple is just above (~3 mm) sample
   i. If necessary, open top of 2920 and loosen thermocouple nut and adjust position of thermocouple.

5. Once sample tube is properly loaded, close and latch furnace

Setting up software; start here if making new method, if not making new method skip to step 4

1. Under file select “Open” then “Analysis Conditions”

2. Select the method that most closely matches the procedure you would like to use
   a. The following can only be added before an “Experiment” section (i.e. must have “Experiment” selected)
      i. Experiment
         1. Additional experiment sections help separate out data from method. It is recommended that a separate experiment section be used for each process to be measured
      ii. Gas calibration
         1. Should only be needed if gas calibrations for gasses to be used in process are not already calibrated. Also, should only need to be run once every few months.
   iii. Loop calibration
1. Should only be needed if changing pulsed chemisorption loop.

iv. Vapor calibration

1. Similar to gas calibration, should only be need if calibration not already done. Should only be need once every few months.

b. The following can be added inside an “Experiment” section

i. Change gas flows

1. Allows for change of gasses, flow rates and valve positions

ii. Change temperature zones

1. Allows for changing of any of the temperature zones
   a. Valve box temperatures
   b. Flask temperature
   c. Reflux temperature
   d. TCD temperature

iii. Change valves

1. Allows for change of valve positions
   a. Same can be done with “change gas flows”

iv. DDE command

1. Should not be needed

v. Dose

1. Sends command to pulse the loop valve
   2. Typically contained in a “Repeat” step

vi. Recording

1. Starts the TCD signal recording
2. Automatically creates “Stop Recording” immediately after “Recording” step
   
a. Place recording where you want to start recording, then add what you want to record between start and stop recording.

vii. Repeat
   
1. Set conditions to repeat whatever follows the “Repeat” step
2. Typically followed by “Dose” step.

viii. Set outputs
   
1. Set digital and relay outputs from 2920
2. To signal ThermoStar mass spectrometer to start recording set DO1 to be checked, to stop mass spectrometer set DO1 to be unchecked.

ix. Temperature ramp
   
1. Allows for temperature ramping of the sample
   
a. Be sure to select “Sample Ramp” to reference the thermocouple in the sample tube
   b. Furnace ramp references the thermocouple on the furnace
   c. Do not select “enable kwik cool” if heating above 300°C
   d. Do select “enable kwik cool” when returning to ambient.

x. Wait
   
1. Set a wait
   
a. Fixed amount of time
   b. For baseline to be stable
c. For operator
   i. This will wait until the operator acknowledges a message by clicking “okay”

d. For change from baseline or X minutes
   i. Typically used with pulsed chemisorption

e. Return to baseline

f. Digital input
   i. Not typically used

g. Synchronization message
   i. Not typically used

3. Some quick rules of thumb
   a. Preparation gas is most useful for pretreatment of sample that not important.
      i. The preparation gas line bypasses the TCD, so it cannot be recorded
      ii. If a sample is very dirty, this can help protect the TCD.
   b. For pulsed chemisorption, analysis gas should match the inert gas of the pulsed gas
      i. E.g. flow He for pulsing O\textsubscript{2}/He, flow Ar for pulsing H\textsubscript{2}/Ar
   c. The reflux should be set 20°C lower than the flask temperature.

4. Under “file” select “open” then “sample information”
   a. To create a new sample file, simply click “OK” on the window that pops up
      i. To open older sample data set the filter to “All” the select desired sample file
b. In the new sample window on the first tab “Sample Information”, name your sample, designate the operator (who is involved with running the sample), enter the sample weight and add any pertinent comments.

c. In the new sample window on the second tab “Analysis Conditions”, select the method you wish to run
   i. Check over this method and be sure that it does everything you want it to.

d. In the new sample window on the third tab “Report Options”, select what you want to appear in the method report
   i. Typical report would be
      1. Summary
      2. TCD vs. Time
      3. Temperature vs. Time
      4. TCD vs. Temperature or Pulsed Chemisorption

e. Once everything is set up click “Save” then “Close”

5. Select “Unit 1” and then “Start Analysis”
   a. Select the sample file that was just made
   b. Review all of the details and make sure that everything is correct
   c. Review the method one more time to be sure that everything is correct
      i. If something is not correct it can be changed now
      ii. If something is not correct and the run is started the only option is to abort the run
   d. Click “Next” and select the appropriate calibration curve if it exists
i. Note, it is as easy to run without a calibration curve, export the data and apply the calibration curve in post processing as it is to run with a calibration curve.

e. Click “Next” and select where you want the report to print to
   i. Typically “Screen” is selected
      1. If “Screen” is selected the report is still stored internally and can be accessed later

f. Click “Next”, this screen will ask you to double check that everything is correct.

   If so click “Start”, if not make what corrections are possible at this point.
   i. Gas lines can be changed (see Sample Preparation Step 8)
   ii. If there is a problem with the sample, click “close” and then open the sample file and modify it as needed.

6. Once the run is started, unless there is an operator prompt the AutoChem 2920 will automatically run through the entire method.
   a. This does not mean you can leave it entirely alone. Be sure to check on the software from time to time and be sure that everything is running properly.
   b. If running overnight, double check that there is sufficient gas BEFORE starting the run.

7. When the run is finished the AutoChem 2920 should go to the standby conditions of 10mL/min He flowing on the analysis line, no other gases flowing. The sample tube is bypassed and the cold trap is bypassed with the TCD turned off (disabled).
   a. If this is not the case, use manual control to set it to these conditions.
8. To help keep the AutoChem 2920 clean, it is best to leave a sample tube always loaded. Wait to unload sample tube until there is another sample ready to run.

After running the sample

1. The report from the run should appear automatically on the screen. If the report is not on the screen click “Reports” then “Start Report”, then select the sample you would like a report of.

2. Review the data and make sure everything makes sense
   a. If it appears that there is a great deal of data missing check the Peak Editor.
      i. Click “Reports” then click “Peak Editor” then select the data file
      ii. This will display all the recorded data for the run
      iii. If there is more data displayed here than in the report simply delete all peaks, then all of the data will appear in the report.
   b. If the missing data does not appear in the peak editor, double check that the method run was set up to do everything you wanted it to.
   c. If the method was correct and the missing data does not appear in the peak editor further trouble shooting may be needed. Unfortunately in this case the data was most like either not recorded or overwritten and is lost.
      i. A possible cause for this is having two “Record” steps in the same experiment section.
      ii. If there are two or more “Record” steps in the same experiment section, rewrite method so that there is only one “Record” step in each experiment section.
3. To export data, the easiest way is to click “Save As” in the report. Select the data sets that you would like to save and then save them as either an Excel file or in ACII format.
TRISTAR 3020/PHYSISORPTION ANALYZER OPERATIONS

Sample preparation

1. Find clean sample tube(s)
   a. If in oven, remove from oven and let cool.

2. Weigh empty sample tube
   a. Note: there is an interaction between the sample tube and the glass panels on the scale. Position the sample tube to maximize distance between sample tubes and panels to minimize this interaction.

3. Weigh out sample.
   a. Typically between 100 and 500 mg
   b. Target surface area between 20 and 100 m²
   c. Can measure as low as only 0.5 m² loading, but more accurate with higher surface area loaded.

4. Load sample into sample tube.

5. Attach sample tube, with sample, to sample preparation station.
   a. To ensure good seal, entirely unthread retaining nut and place retaining nut, ferrule and o-ring on the sample tube. Insert sample tube as far as it will go into the vacuum attachment. Then slide retaining nut up so it pushes the ferrule and o-ring into place. Tighten retaining nut to seal.
   b. Slowly turn appropriate control knob towards vacuum, while watching pressure gauge.
      i. When pressure gauge initially jumps up stop and wait for the gauge to drop below 1 Torr.
ii. Continue to slowly turn control knob towards vacuum, keep pressure
gauge between 500 mTorr and 2 Torr.

iii. When pressure stops rising turn control knob all the way to vacuum.

c. With the sample under vacuum start increasing the temperature to 300°C
   i. To help protect samples slowly increase temperature by 25°C increments
      up to 300°C.

d. Once at 300°C wait for pressure to drop below 100 mTorr
   i. When the pressure drops below 100 mTorr, wait 1 additional hour

e. Remove sample from heat and set in the cooling section of the preparation station.
   i. Wait for sample tube to cool while still under vacuum.

f. When sample tube has cooled, slowly turn control knob from vacuum to gas
   i. Wait about 20 to 30 seconds for the sample tube to pressurize
   ii. Can check pressurization extent by gently pushing on retaining nut

g. Unthread retaining nut and remove sample tube

6. Weigh sample tube with sample
   a. Again, be sure to minimize the interaction between the sample tube and the scale

7. For sample weight use weight from step 6 and subtract weight from step 2.

8. If sample will not be loaded onto TriStar II 3020 for some time, seal top with rubber
   stopper.

Loading Samples

1. Check software for 3020 and make sure that
   a. Nothing is currently running
   b. The manifold is under vacuum
c. None of the sample tubes are under vacuum

2. Unload previous sample(s)
   a. Unthread retaining nut
   b. Carefully slide sample tube out of dewar cap
   c. Remove capillary sheath from sample tube and set aside
   d. Set sample tube aside

3. Load new sample tube
   a. Slide capillary sheath as far down sample tube as it will go
   b. Carefully slide the sample tube up through the dewar cap
   c. Place retaining nut, ferrule and o-ring over top of sample tube
   d. Slide sample tube up into 3020 until it stops
   e. Thread retaining nut onto 3020 so it pushes the ferrule and o-ring into place until tight
      i. Sample tube should not move when pulled on lightly
   f. Repeat for all sample tubes
   g. Note which samples are loaded onto which ports.

4. Fill liquid nitrogen dewar
   a. Carefully set liquid nitrogen dewar on ground
   b. Place fill indicator in dewar
   c. Carefully pour liquid nitrogen into dewar until filled to the hole of the fill indicator
      i. Note: the liquid nitrogen will boil quite a bit, pour slowly and wait for it to settle to read indicator


d. Remove indicator

e. Carefully set filled dewar back on 3020

Setting up software (should not need to set up new method)

1. Under “File” select “Open” then “Sample Information”
   a. To create a new file simply click “OK” on the window that pops up.
   b. In the new sample window on the first tab “Sample Information”, name your sample, designate the operator(s), enter the sample weight (either subtract the weight yourself or enter the weights from steps 2 and 6 of “Sample preparation” in the appropriate fields) and enter any additional comments in the comments window.
   c. In the new sample window on the second tab “Sample Tube” the dimensions and properties of the sample tube are set.
      i. These are default and should not need to be changed.
   d. In the new sample window on the third tab “Degas Conditions” the degassing conditions are set.
      i. These are default and should not need to be changed.
   e. In the new sample window on the fourth tab “Analysis Conditions” select the analysis method to be run (typically either “5 Point BET” or “BJH Adsorption/Desorption”)
      i. **NOTE:** If your sample is a very fine, light powder (aka fluffy) and you notice significant movement in it during the cleaning process use a slower evacuation rate. Click on “Preparation” and check the “Fast Evacuation” box and set the evacuation rate to be 0.5 mmHg/s.
ii. If additional data points are needed the collection of data points can be modified using both the “Pressure” and “Options” buttons under “Isotherm Collection”

1. “Pressure” allows for selection of which data points to use for calculations
2. “Options” allows for changing the frequency or difference in P/P₀ that data points are collected.

f. In the new sample window on the fifth tab “Adsorptive Properties” the adsorbate can be defined.

i. The adsorbate is typically N₂, however, there are preset parameters for CO₂ and Kr as well.

ii. This 3020 is not equipped to handle Kr, but CO₂ and an ice bath allow for a higher reference pressure.

g. In the new sample window on the sixth tab “Report Options”, the options for what data is reported can be selected.

i. These are typically:

1. Summary
2. Isotherm
3. BET Surface Area
4. BJH Adsorption

h. Once everything is set, click “Save” then “Close”

2. Repeat Step 1 for all samples.

3. After defining all samples, click on “Unit 1” and select “Sample Analysis”
a. For each port assign the appropriate sample file

b. If a port is not being used, leave it blank

4. After assigning all appropriate samples click “Start”
   a. At this point the TriStar II 3020 will mostly take care of itself.
   b. This does not mean you can entirely ignore it, you should check on it from time to time while it is running.
   c. The “Leak Test” step is a very good one to keep an eye.
      i. If a sample is out gassing too much it may appear as a leak and the 3020 will not run analysis on that sample tube.

5. When the run has finished the TriStar II 3020 should return to the state of the manifold being open to vacuum, with all the gas lines closed and all sample tube isolated.
   a. If this is not the case, use manual control to do so.
      i. Under “Unit 1”, “Enable Manual Control” should be checked.

6. To help keep the TriStar II 3020 clean, leave all sample ports loaded with sample tubes.

After running the sample

4. The report from the run should appear automatically on the screen. If the report is not on the screen click “Reports” then “Start Report”, then select the sample you would like a report of.

5. Review the data and make sure everything makes sense.

6. To export data, the easiest way to is to click “Save As” in the report. Select the data sets that you would like to save and then save them as either an Excel file or in ACII format.
REACTOR STAND OPERATIONS

Sample preparation

1. Find clean reactor tube
2. Load pinch of quartz wool to desired height/position
   a. **NOTE:** this position will likely change with position of sample thermocouple, so measure accordingly ahead of time
3. Weigh out desired amount of sieved sample
   a. Refer to Sample Synthesis for sieving directions
   b. Typically sieving size is 60 – 100 mesh
   c. Amount of sample will depend on target residence time for experiment
      i. Typical ranges are 50 – 200 mg
4. Weigh out desired amount of silicon carbide (SiC)
   a. Choose amount for proper dilution ratio, typical values range from 3x to 9x dilution, i.e., 150 mg SiC for 3x dilution of 50 mg catalyst
   b. **NOTE:** refer to later section on identification of thermal and mass transfer limitations for more details on selection of dilution ratio and mixing requirements
   c. Match SiC particle size as closely to catalyst as possible, typically 70 mesh
   d. Green SiC is slightly more pure than black SiC, but both work
5. Thoroughly mix catalyst and SiC together to ensure good distribution of catalyst particles
6. Load mixed catalyst and SiC into reactor tube
   a. May need to tap reactor sides to knock particles off of sides
7. Load pinch of quartz wool on other side of catalyst mixture to hold mixture in place
   a. Can use this piece of quartz wool to push remaining stuck particles down
Loading Sample

1. Remove prior reactor tube if still loaded on reactor stand
   a. Carefully unthread top and bottom compression fittings
   b. Slide top compression fitting off
   c. Slide reactor tube out of bottom compression fitting
   d. Place prior reactor tube off to side for cleaning

2. Remove retaining nut, compression ring, and o-ring from compression fittings

3. Place retaining nut, compression ring, and o-ring on both sides on reactor tube
   a. Recall order should be o-ring, compression ring, retaining nut going from the end
      of the tube towards the center

4. Slide reactor tube into bottom fitting and lightly seal compression fitting

5. Slide reactor tube into top fitting and seal compression fitting
   a. **NOTE:** support bottom fitting while doing this

6. If necessary place support under reactor tube exhaust

7. Completely tighten top and bottom compression fittings

Leak test

1. Use mass flow controller (MFC) to flow $N_2$ through the reactor tube
   a. Typical value 50 SCCM
   b. **NOTE:** MFC control box can only control two controllers at a time, make sure
      that the correct one is selected by tracing the controller cable from the control box
      to the MFC

2. Let flow stabilize and purge reactor, 1 – 2 minutes
3. Close down stream valve after cold trap and before Drierite trap
4. Pressurize reactor to ~10 psig
5. Close upstream valve
6. Stop flow on MFC
7. Wait ~10 minutes
   a. Goal is to have <1 psi pressure drop over 10 minutes, if pressure is dropping rapidly then a leak is likely and leak test can be terminated early
8. If after 10 minutes the pressure has dropped by 1 psi or less, then the reactor system is ready for experiments
9. If after 10 minutes the pressure has dropped by more than 1 psi, then there is likely a leak in the setup
   a. Release pressure by slowly opening downstream valve
   b. Most likely point is reactor tube
      i. Attempt to tighten compression seals
      ii. If seals as tight as possible, remove reactor tube and attempt to reseal
      iii. If leak persists after resealing reactor tube, and you are confident in the seal on the reactor tube, then the leak is elsewhere; proceed to leak test reactor system

If necessary, replace Drierite in Drierite trap

1. Remove Drierite trap by loosening compression fittings
   a. Slide top off of Drierite trap
   b. Remove trap from bottom fitting
2. Remove top piece of quartz wool
a. Use small piece of wire to hook and remove quartz wool

3. Pour out old Drierite
   a. Can either throw out or recollect for regeneration

4. If necessary, remove bottom piece of quartz wool and rinse Drierite tap with ethanol
   a. Only necessary to do if hydrocarbon contamination of quartz wool and tube suspected
   b. After rinsing, dry with air and let sit in drying oven for 2 hours
   c. Pack new quartz wool into bottom of tube

5. Pour new Drierite into tube
   a. Most easily done by pouring Drierite onto weigh-paper and the pouring from the weigh-paper into the tube
   b. Fill tube to ~0.75 cm from top

6. Pack new quartz wool into top

7. Replace Drierite trap on exhaust line
   a. Remove retaining nut, compression ring, and O-ring from compression fitting
   b. Place retaining nut, compression ring, and O-ring on top and bottom of Drierite tube
   c. Connect bottom of Drierite tube to exhaust line
   d. Connect top of Drierite tube to exhaust line
   e. Tighten compression fittings

Reactor stand operations

1. Purge system with N$_2$
   a. Set MFC to flow 90 SCCM of N$_2$
b. Flow for ~10 minutes to flush system

c. Can use this time to also check MFC controller accuracy and check outlet flow with mass flow reader

2. Switch on cold trap chiller

   a. **NOTE:** cold trap chiller temperature controller does not work, chiller should be filled with 50/50 mixture of ethylene glycol and water to ensure that freezing does not occur in the chiller

   b. Ensure that only “cool” light is illuminated on chiller

      i. If “heat” light is illuminated, change switch position on back of chiller

   c. Typical value reached on cold trap is -6 °C

   d. Typical value reached in cold trap chiller is -11 °C

3. If pretreatment is needed

   a. For reduction set MFC to add 10 SCCM H\(_2\)

      i. Total gas flow should be 100 SCCM and 10% H\(_2\)/N\(_2\)

      ii. Check concentration of H\(_2\) using microGC

   b. For oxidation set MFC to add desired amount of O\(_2\)

      i. Check that total gas flow is close to target using mass flow reader

      ii. Check concentration of O\(_2\) using microGC

   c. Alternative oxidation, change MFC to flow air

   d. If only inert is needed, leave only N\(_2\) flowing

   e. **NOTE:** MFC control box can only control two controllers at a time, make sure that the correct ones are selected by tracing the controller cables from the control box to the MFCs
4. Set tube furnace to run desired temperature profile
   a. Turn on tube furnace control
   b. Set desired program by holding up and down arrows until enter into menu
   c. Press down to get to menu level selection
   d. Press star and down to change to program level “P”
   e. Press up to enter program level
   f. Use star and up/down to select desired program
      i. To make a program press star and up until get to “ADD”
      ii. Press up to enter into new program
      iii. Press up to Step, this will be the first step of the program
      iv. Press up again, and use star and up/down to select desired step (for more details see CAL 9500P manual page 12 – 15)
         1. Ramp = SPr; will ramp from current temperature to new temperature at fixed rate; units degree/hour
            a. Need to set both ramp rate (SPrr) and set point temperature (t.SP)
         2. Soak = SoAK; will hold at temperature for set amount of time; units minutes
         3. Step = StEP; will change set point to new value immediately; units none
            a. **NOTE:** this is not recommended because only the set point can change instantly, the furnace will take time to change
temperature, ramp is a much more controlled means of changing temperature.

4. Hold = hoLd; will hold at point until hold switched off

5. Loop = LooP; will repeat steps in order up to loop

v. Once program is set, press down arrow to run and change value from off to on by pressing up

g. Once everything is set press and hold star to save changes and start program

5. Set evaporator temperature controller to desired set point

a. Typically around 180 °C

6. Set exhaust temperature controller to desired set point

a. Should be at least 110 °C to prevent condensation in exhaust line

7. Refill syringe if necessary

a. Make sure “L” valve is set so that the reactor system is isolated from the syringe line

b. Detach syringe line from “L” valve

c. Remove syringe from syringe pump

i. Press brass button on side of pusher block and slide to end plate

ii. Lift syringe clamp off syringe, rotate so that syringe clamp will not hold syringe

iii. Remove syringe from pump stand

d. Empty any remaining liquid into waste container

e. Flush with fresh liquid solution

i. Fill syringe with 5 – 10% volume liquid
ii. Pull syringe plunger to maximum fill point

iii. Slowly push syringe plunger back up making sure that no air bubbles are left in the syringe

iv. Repeat 2 or 3 times

v. Fill syringe with desired amount of fresh reactant solution

f. Replace syringe in syringe pump

i. Place syringe back onto syringe pump stand

ii. Lift syringe clamp and rotate so that it will hold syringe, lower syringe clamp to hold syringe in place

iii. Press brass button on side of pusher plate and move up to be in contact with syringe plunger

g. Reconnect syringe line to “L” valve

h. Set desired flow rate and volume on syringe pump

1. Turn on syringe pump

2. Press “Set” and select “Volume”

3. Set desired volume to be injected total

   a. **NOTE:** once this volume is reached the syringe pump will stop

4. Once volume is set, the syringe pump should immediately prompt for pump rate, set desired pump rate

8. Once pretreatment is completed, change gas flow back to N\textsubscript{2} to purge pretreatment gasses from system

   a. If pretreatment was under inert, this step can be skipped
b. Use microGC to check that pretreatment gasses have been sufficiently purged
   i. <1% concentration

9. Start syringe pump flowing to purge line
   a. This will allow the syringe pump flow to stabilize and also flush any remaining
      liquid from “L” valve

10. Once syringe pump flow is stable and system has been purged, change “L” valve so
    syringe pump is flowing to evaporator

11. Set microGC to collect data for duration of experiment
   a. Make sure the correct method is selected
   b. Go to menu “Method Options” and “Advanced”
      i. Make sure that each channel is set to export to the same folder
   c. Press “collect single sample” or play button
   d. Select delayed start and then select to collect at a certain time
   e. Repeat until all data points are set

Shut down

1. Change “L” valve to flow syringe line to purge line

2. Purge N$_2$ until value are at 1% or lower

3. While purging collect liquid product
   a. Close valve between cold trap and Drierite trap
   b. Wait for pressure to reach ~10 psig
   c. Slowly open collection valve at bottom of cold trap
   d. Collect liquid product
      i. Weigh collected products
e. Close collection valve and let pressure reach ~10 psig again
f. Collect remaining products
   i. Weigh additional collected products

4. Set tube furnace set point to zero
   a. Wait to see that temperature is decreasing
   b. Turn off tube furnace

5. Set evaporator set point to zero
   a. Wait to see that temperature is decreasing
   b. Turn off evaporator temperature controller

6. Set exhaust line set point to zero
   a. Wait to see that temperature is decreasing
   b. Turn off exhaust temperature controller

7. Set microGC to bakeout over night