ACTIVITY AND SELECTIVITY IN OXIDATION CATALYSIS

DISSERTATION

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* * * * *

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ABSTRACT

In oxidation catalysis, a fine balance must be struck between catalyst activity and selectivity. The existence of complex networks of reactions involving oxygen can prove difficult to deal with and obtaining high activity in the desired reaction without undesired consecutive or parallel reactions is a major challenge. This research investigates the challenges associated with achieving high activity and selectivity in the oxidative dehydrogenation of ethane and the preferential oxidation of carbon monoxide in hydrogen rich streams.

Worldwide production of olefins exceeds that of any other chemicals and constitutes a sizable fraction of total petrochemical production. Traditional methods of olefin production require high temperatures, high energy input and are also limited by coke deposition and thermodynamic considerations. Oxidative dehydrogenation (ODH) is an alternate method of olefin production and does not suffer from the drawbacks of traditional methods. The major drawback of ODH is selectivity control. The olefin produced can easily react with oxygen to form the undesired combustion products CO$_2$ and H$_2$O.

In this work, the use of N$_2$O as oxidant, rather than O$_2$, in ethane ODH was investigated. A 10%Mo/Si:Ti catalyst was tested for ethane oxidative dehydrogenation
(ODH) activity using either O₂ or N₂O as the oxidant. Ethane ODH activity was tested at contact times varying from 0.46 to 1.0 mg s cm⁻³. N₂O gives superior ethylene selectivities at a given ethane conversion outperforming oxygen at all contact times tested. Ethylene selectivities decrease with contact time at a far slower rate when using N₂O as the oxidant. XPS experiments demonstrate that molybdenum in the catalyst is fully oxidized to Mo(VI) during ethane ODH using O₂ while the reduction state decreases to an average of +5.8 when using N₂O as the oxidant. Temperature programmed oxidation experiments of pre-reduced 10%Mo/Si:Ti were carried out at different temperature ramp rates. The activation energy of reoxidation when using N₂O is 98 kJ/mol while that of O₂ is 41 kJ/mol leading to a reoxidation rate of at least 1700 times faster when O₂ is the oxidant. This difference in rates accounts for the less oxidized state of molybdenum during ethane ODH with N₂O and explains the behavior observed during reaction experiments. The concept of site isolation provides a satisfactory framework for understanding the steady state reaction results. Some carbon deposition was observed when using N₂O as oxidant during ethane ODH as determined from post ODH TPO and XPS experiments but it did not affect ODH activity.

Proton exchange membrane (PEM) fuel cells promise to be clean and efficient alternatives to combustion of fuels for power generation. Unfortunately, the catalysts used in PEM anodes are easily poisoned by trace amounts of carbon monoxide. Reduction of the carbon monoxide concentration to a level of approximately 10 ppm is
currently necessary to prevent this poisoning. Preferential oxidation of carbon monoxide (PROX) offers an economic and simple method of CO removal but in high concentrations of hydrogen maintaining a high catalyst activity and selectivity simultaneously can be problematic due to unselective H₂O oxidation and CO methanation.

This work demonstrates the preparation of a 10%CoOₓ/CeO₂ catalyst that is highly effective for the preferential oxidation of carbon monoxide in a hydrogen rich feed. The CoOₓ/CeO₂ catalyst had a high surface area of 78m²/g and was able to maintain a near 100% CO conversion while maintaining a selectivity of 58% during PROX experiments in high concentrations of hydrogen. The catalyst is able to obtain high CO conversions under a wide range of weight hourly space velocities. Introducing H₂ into the feed has a negative effect on the CO consumption rate and decreases O₂ selectivity to CO₂. This shows that the reaction rates for CO oxidation and H₂ combustion are not independent and suggests that hydrogen may competitively adsorb on sites responsible for CO oxidation. Separate H₂ and CO oxidation experiments give activation energies of 74 and 52 kJ/mol, respectively. Additionally, the preexponential factor for H₂ is 25 times higher than that for CO under the reaction conditions employed. It is possible that there are more sites available for H₂ oxidation but this reaction requires high temperatures to occur at appreciable rates. Temperature programmed PROX reaction experiments show three temperature regions where different reactions are important. Below 175°C, CO oxidation
is dominant but above this temperature, CO oxidation and H₂ combustion compete with one another. The temperature necessary to obtain high activity in the PROX reaction occur near this transition at 175°C. At even higher temperatures, irrelevant to the PROX reaction, methanation begins to occur. Raman spectroscopy and X-ray diffraction experiments have demonstrated that the cobalt takes the form of Co₃O₄ and no CoO was detected under any experimental conditions. It is likely that the octahedral Co³⁺ sites are the active sites for oxidation of carbon monoxide
ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS

ABSTRACT ............................................................................................................................... ii

ACKNOWLEDGEMENTS ........................................................................................................ vi

VITA ...................................................................................................................................... vii

LIST OF TABLES .................................................................................................................... xii

LIST OF FIGURES ................................................................................................................. xiii

PART 1 OXIDATIVE DEHYDROGENATION OF LOWER ALKANES .................. 1

CHAPTER 1 INTRODUCTION TO OXIDATIVE DEHYDROGENATION .......... 2

CHAPTER 2 OXIDATIVE DEHYDROGENATION LITERATURE REVIEW .... 9

2.1 Benefits of Oxidative Dehydrogenation ............................................................... 9

2.2 High Temperature Catalysts ............................................................................... 10

2.3 Low Temperature Catalysts ............................................................................... 12

2.4 Structure of Supported Catalysts ...................................................................... 13

2.5 Mixed Oxide Catalysts ...................................................................................... 16

2.6 Mars-van-Krevelen Mechanism ....................................................................... 20

2.7 ODH Using N₂O as Oxidant ............................................................................ 26

CHAPTER 3 EXPERIMENTAL METHODS ................................................................. 29

3.1 Catalyst Preparation .......................................................................................... 29

3.2 BET Surface Area Analysis ............................................................................ 30
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 Catalyst Activity Testing</td>
<td>31</td>
</tr>
<tr>
<td>3.4 Temperature Programmed Oxidative Dehydrogenation</td>
<td>34</td>
</tr>
<tr>
<td>3.5 Determination of Post Reaction Chemical State of Molybdenum using XPS</td>
<td>35</td>
</tr>
<tr>
<td>3.6 Laser Raman Spectroscopy</td>
<td>36</td>
</tr>
<tr>
<td>3.7 Temperature Programmed Reduction/Oxidation</td>
<td>38</td>
</tr>
<tr>
<td>3.8 Post-Reaction Temperature Programmed Oxidation</td>
<td>41</td>
</tr>
<tr>
<td>3.9 Transmission Electron Microscopy</td>
<td>42</td>
</tr>
<tr>
<td>CHAPTER 4 RESULTS AND DISCUSSION</td>
<td>43</td>
</tr>
<tr>
<td>4.1 Influence of N₂O on Steady State C₂H₆ Oxidative Dehydrogenation</td>
<td>43</td>
</tr>
<tr>
<td>4.2 Influence of N₂O on Temperature Programmed C₂H₆ ODH</td>
<td>53</td>
</tr>
<tr>
<td>4.3 Post-Reaction Oxidation State</td>
<td>56</td>
</tr>
<tr>
<td>4.4 Reduction and Oxidation of 10%Mo/Si:Ti</td>
<td>63</td>
</tr>
<tr>
<td>4.5 10%Mo/Si:Ti Activation Energies of Reoxidation Using O₂ and N₂O</td>
<td>70</td>
</tr>
<tr>
<td>4.6 Surface Carbon Formation</td>
<td>79</td>
</tr>
<tr>
<td>CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS</td>
<td>88</td>
</tr>
<tr>
<td>PART 2 PREFERENTIAL OXIDATION OF CARBON MONOXIDE</td>
<td>94</td>
</tr>
<tr>
<td>CHAPTER 6 INTRODUCTION TO PREFERENTIAL CARBON MONOXIDE OXIDATION</td>
<td>95</td>
</tr>
<tr>
<td>CHAPTER 7 LITERATURE REVIEW OF PREFERENTIAL CO OXIDATION</td>
<td>98</td>
</tr>
<tr>
<td>7.1 Early Work</td>
<td>98</td>
</tr>
</tbody>
</table>
7.2 Gold and Platinum Catalysts................................................................. 100
7.3 Non-Precious Metal Catalysts.............................................................. 100
7.4 Cobalt-Based Catalysts ......................................................................... 102

CHAPTER 8 EXPERIMENTAL METHODS ...................................................... 104
8.1 Catalyst synthesis.................................................................................... 104
8.2 Surface Area Analysis............................................................................ 105
8.3 Cobalt Metal Dispersion ........................................................................ 107
8.4 Transmission Electron Microscopy ......................................................... 107
8.5 Laser Raman Spectroscopy .................................................................... 108
8.6 X-ray Diffraction .................................................................................... 108
8.7 Diffuse Reflectance Infrared Spectroscopy .............................................. 109
8.8 Steady State Preferential CO Oxidation Experiments.............................. 111
8.9 Temperature Programmed Reduction Studies ........................................ 112
8.10 CO Oxidation and H₂ Oxidation Experiments ........................................ 113
8.11 Temperature Programmed Preferential CO Oxidation .............................. 114
8.12 Time on Stream Reaction Experiments ................................................. 115

CHAPTER 9 RESULTS AND DISCUSSION..................................................... 117
9.1 Characterization of Catalyst Textural Properties..................................... 117
9.2 Catalyst Activity at Various Weight Hourly Space Velocities ................. 122
9.3 Crystallographic Properties of 10% CoOₓ/CeO₂ ...................................... 126
9.4 Activity of 10% CoOₓ/CeO₂ Under High H₂ Concentrations ....................... 127
9.5 Reducibility and Stability Studies on 10% CoOₓ/CeO₂ ............................... 133
9.6 CO and H₂ Oxidation on 10% CoOₓ/CeO₂ ............................................... 139
9.7 Determination of Surface Species on 10% CoOₓ/CeO₂ .............................. 147
CHAPTER 10 CONCLUSIONS AND RECOMMENDATIONS ......................... 153
APPENDIX A  LIST OF ACRONYMS ......................................................... 157
APPENDIX B RESPONSE FACTORS ....................................................... 159
LIST OF REFERENCES .............................................................................. 160
LIST OF TABLES

Table 1-1 – Methods of olefin production ................................................................. 6

Table 4-1 - Determination of activation energies using Kissinger method for 2% O2/He temperature programmed oxidation at various heating rates. ........................................ 73

Table 4-2 - Determination of activation energies using Kissinger method for 4% N2O/He temperature programmed oxidation at various heating rates. ............................. 76
LIST OF FIGURES

Figure 1-1 – Yield of C₂H₆ → C₂H₄ + H₂ reaction at thermodynamic equilibrium .......... 5

Figure 2-1 – Possible structures of monomeric supported molybdenum ......................... 19

Figure 2-2- Oxidative dehydrogenation reaction scheme ............................................. 22

Figure 2-3 – Mars van Krevelen redox mechanism....................................................... 24

Figure 2-4 - Electron Transfer Processes During Catalyst Re-oxidation .......................... 25

Figure 3-1 – ODH steady-state reaction system configuration ....................................... 33

Figure 4-1 – Nitrogen adsorption and desorption isotherms on 10%Mo/Si:Ti. .............. 44

Figure 4-2 – Pore size distribution of 10%Mo/Si:Ti as determined from nitrogen adsorption isotherm ........................................................................................................ 45

Figure 4-3 – Ethane conversion at various contact times during steady-state ethane ODH. Reaction conditions: 600°C (●) C₂/H₂O/He = 5/5/90, (■) C₂/O₂/He = 5/2.5/92.5. 48

Figure 4-4 – Selectivity at various ethane conversions during steady-state ethane ODH at 600°C. (□) C₂H₄ selectivity C₂/H₂O/He=5/5/90, (○) C₂H₄ selectivity C₂/O₂/He = 5/2.5/92.5, (●) CO selectivity C₂/O₂/He = 5/2.5/92.5, (▲) CO selectivity C₂/H₂O/He = 5/5/90, (■) CO₂ selectivity C₂/O₂/He = 5/2.5/92.5, (●) CO₂ selectivity C₂/H₂O/He = 5/5/90. .............................................................................. 49

Figure 4-5 – Ethane conversion at various atomic oxygen/ethane ratios during steady-state ODH. Reaction conditions: 600℃, W/F = 0.625 mg s/cm³ , (●) 5% ethane, 2.5, 5, 7.5 and 10% nitrous oxide, balance helium and (■) 5% ethane, 1.25, 2.5, 3.75 and 5% oxygen, balance helium. ................................................................. 51

Figure 4-6 – Selectivities at various ethane conversions during ethane ODH using N₂O as oxidant, (▲) ethylene selectivity (■) CO₂ selectivity (●) CO selectivity ............. 52

Figure 4-7 – Temperature programmed reaction– C₂H₆ to N₂O ratio of 2:1 [40] ............ 54
Figure 4-8 – Temperature programmed reaction – C$_2$H$_6$ to O$_2$ ratio of 2:1 [40] ............... 55

Figure 4-9 – X-ray photoelectron spectroscopy of Mo3d region collected on pristine 10% Mo/Si:Ti catalyst.......................................................................................................................... 57

Figure 4-10 – X-ray photoelectron spectroscopy of Mo3d region collected after steady-state ethane ODH using C$_2$/O$_2$/He = 10/5/85............................................................................................ 58

Figure 4-11 – X-ray photoelectron spectroscopy of Mo3d region collected after steady-state ethane ODH using C$_2$/N$_2$O/He = 10/10/80....................................................................................... 60

Figure 4-12 – Temperature programmed reduction using 5% H$_2$/He........................................ 64

Figure 4-13 – Temperature programmed oxidation of pre-reduced 10% Mo/Si:Ti with 2%O$_2$/He and 4%N$_2$O/He. ............................................................................................................. 66

Figure 4-14 - spectra of fresh, 5%H$_2$/N$_2$ reduced, 4% N$_2$O/He reoxidized and 2% O$_2$/He reoxidized 10% Mo/Si:Ti. Bulk MoO$_3$ included as reference. ........................................ 68

Figure 4-15 – Possible molybdenum structures for fully oxidized (6+) and reduced molybdenum (4+). ............................................................................................................................. 69

Figure 4-16 - Temperature programmed oxidation of pre-reduced 10% Mo/Si:Ti (in 5% H$_2$/He) using various temperature ramp rates and 2%O$_2$/He.................................................. 71

Figure 4-17- Determination of activation energies using Kissinger method for 2% O$_2$/He temperature programmed oxidation at various heating rates............................................ 72

Figure 4-18 - Temperature programmed oxidation of pre-reduced 10% Mo/Si:Ti (in 5% H$_2$/He) using various temperature ramp rates and 4%N$_2$O/He......................................................... 74

Figure 4-19- Determination of activation energies using Kissinger method for 4% N$_2$O/He temperature programmed oxidation at various heating rates................................. 75

Figure 4-20 – Possible peroxomolybdate species........................................................................ 80

Figure 4-21 – CO$_2$ profiles during temperature programmed oxidation of post-reaction 10% Mo/Si:Ti catalyst. (a) C$_2$/O$_2$/He = 10/5/85, (b) C$_2$/N$_2$O/He = 10/10/80 ............... 82

Figure 4-22 – Post-N$_2$O ODH reaction Raman spectroscopy...................................................... 83

Figure 4-23 – Post-N$_2$O ODH transmission electron microscopy............................................. 84
Figure 4-24 – X-ray photoelectron spectroscopy of C1s region collected after steady-state ethane ODH - comparison of fresh, post-O2 ODH and post-N2O ODH spectra. ..... 86

Figure 4-25 – X-ray photoelectron spectroscopy of C1s region collected after steady-state ethane ODH - deconvolution of post-N2O ODH spectra........................................ 87

Figure 5-1 – Simplified representation of effect of catalyst oxidation state..................... 93

Figure 7-1 – PROX reaction scheme ................................................................................ 99

Figure 9-1 – Nitrogen adsorption and desorption isotherms on 10%Co/CeO2.......... 119

Figure 9-2 – Pore size distribution of 10%Co/CeO2 as determined from nitrogen adsorption isotherm................................................................. 120

Figure 9-3 – TEM micrograph of CeO2 support nanoparticles........................................ 121

Figure 9-4 – CO conversion at WHSV of (▲) 7500, (●) 15000 and (■) 30000 cc g(cat)^{-1} h^{-1} over 10%CoO_x/CeO_2. Feed composition: 1% CO, 1% O_2, 10% H_2, balance He. ................................................................. 124

Figure 9-5 – O_2 selectivity to CO_2 at WHSV of (▲) 7500, (●) 15000 and (■) 30000 cc g(cat)^{-1} h^{-1} on 10%CoO_x/CeO_2. Feed composition: 1% CO, 1% O_2, 10% H_2, balance He................................................................. 125

Figure 9-6 – Raman spectra of CeO_2, Co_3O_4 and CoO_x/CeO_2. ........................................ 128

Figure 9-7 – X-ray diffraction patterns of CeO_2, Co_3O_4 and CoO_x/CeO_2. ..................... 129

Figure 9-8 – Influence of CO/O_2 ratio on CO conversion: (●)1% CO, 1% O_2, 60% H_2 balance He over 10% CoO_x/CeO_2 (■) 1% CO, 0.5% O_2, 60% H_2, balance He over 10% CoO_x/CeO_2 (▲) 1% CO, 1% O_2, 60% H_2, balance He over CeO_2 nanoparticle support................................................................. 131

Figure 9-9 – Influence of CO/O_2 ratio on O_2: (●)1% CO, 1% O_2, 60% H_2 balance He over 10% CoO_x/CeO_2 (■) 1% CO, 0.5% O_2, 60% H_2, balance He over 10% CoO_x/CeO_2................................................................. 132

Figure 9-10 – Hydrogen and carbon monoxide temperature programmed reduction profiles over 10% CoO_x/CeO_2................................................................. 135
Figure 9-11 – Time on stream conversion over 10%Co/CeO₂. Reaction conditions: 175°C and 1% CO, 1% O₂, balance helium. ................................................................. 137

Figure 9-12 – Time on stream O₂ to CO₂ selectivity over 10%Co/CeO₂. Reaction conditions: 175°C and 1% CO, 1% O₂, balance helium. ................................................ 138

Figure 9-13 – (●) CO conversion and (■) O₂ selectivity to CO₂ during steady-state PROX at 150°C over 10%Co/CeO₂ at various hydrogen concentrations. ......... 140

Figure 9-14 - CO conversion over 10%CoOₓ/CeO₂ during steady-state carbon monoxide oxidation experiments. Reaction conditions: 3.3% CO, 3.3% O₂, balance helium. .............................................................................................................................................. 142

Figure 9-15 – CO oxidation activation energy as calculated from steady-state carbon monoxide oxidation experiments. Reaction conditions: 3.3% CO, 3.3% O₂, balance helium. .............................................................................................................................................. 143

Figure 9-16 – H₂ conversion over 10%CoOₓ/CeO₂ during steady-state hydrogen oxidation experiments. Reaction conditions: 3.3% H₂, 3.3% O₂, balance argon. 145

Figure 9-17 – H₂ oxidation activation energy as calculated from steady-state hydrogen oxidation experiments. Reaction conditions: 3.3% H₂, 3.3% O₂, balance argon. 146

Figure 9-18 – Temperature programmed PROX reaction over CoOₓ/CeO₂. Reaction conditions: 30 ml/min 1% CO, 1% O₂, 60% H₂, balance He. ......................... 148

Figure 9-19 – DRIFTS spectra of hydroxyl region during CO temperature programmed desorption on CoOₓ/CeO₂. .............................................................................................................................................. 151

Figure 9-20 – DRIFTS spectra of carbonate region during CO temperature programmed desorption on CoOₓ/CeO₂. .............................................................................................................................................. 152
PART 1

OXIDATIVE DEHYDROGENATION OF LOWER ALKANES
CHAPTER 1
INTRODUCTION TO OXIDATIVE DEHYDROGENATION

The chemical industry relies heavily on unsaturated hydrocarbons as feedstock for many industrially significant processes. Olefins are unsaturated chemical compounds that contain at least one carbon-carbon double bond. Ethylene is the simplest olefin and its formula is $\text{H}_2\text{C}=\text{CH}_2$.

Worldwide production of olefins exceeds that of any other chemicals [1] and propylene production alone was 56 million-tons in 2003 [2] constituting a significant fraction of total petrochemical production. The traditional method of olefin production is steam cracking of naptha or alkanes though other methods such as fixed bed or fluidized catalytic cracking (FCC) and direct dehydrogenation are also in use.

Steam cracking is by far the most prominent technique accounting for 70% of total olefin production [1]. It is a gas phase homogeneous reaction carried out at temperature in excess of 800°C paraffinic naphtha is decomposed in the presence of water and the absence of air. The reaction is highly endothermic and requires substantial energy to activate the reactant molecules. In steam cracking, the paraffinic naphtha decomposes in the presence of water to form a variety of products including olefins, paraffins and hydrogen.
The endothermic nature of the reaction coupled with the high temperature leads to substantial fuel consumption and costs. Energy costs typically account for 70% of total production costs in the steam cracking process [1]. Additionally, coke deposition is a major problem. Coking occurs on the reactor lowering heat transfer, increasing pressure drop through the reactor and increasing corrosion [3]. While the presence of steam does offer some ability to oxidize coke deposits, it is unable to prevent gradual coke accumulation. Consequently, commercial reactors must be periodically de-coked resulting in increased downtime. Decoking is typically performed every 14 to 100 days in a naptha steam cracker [1].

Fluidized or fixed bed catalytic cracking (FCC), the second most frequently used processes for olefin production, account for 28% of total olefin production [1] and typically use zeolite based catalysts (see Table 1-1). In FCC, alkane or paraffinic naphtha feedstocks are primarily used to produce gasoline but they also produce ethylene and propylene as co-products in yields of 1-2% and 5%, respectively [1]. Some refineries, especially when situated near a petrochemical facility, choose to install olefin recovery units to separate and purify the olefins to chemical grade. FCC can be operated at temperatures at 550°C (200°C lower than steam cracking) which leads to substantial energy savings [2]. The reaction is endothermic and, despite the lower temperatures, still requires substantial energy input. Some catalyst coking also occurs, leading to deactivation, but FCC units can be usually be run for a few years without shutdown.

The relatively low cost, relative abundance and environmentally benign nature of light alkanes provides incentive to use them in the production of higher value intermediates. Alkane dehydrogenation, also a heterogeneous catalytic process, usually uses either a Cr₂O₃/Al₂O₃
catalyst or a Pt/Sn/Al₂O₃ catalyst. In this reaction, the alkane decomposes into an olefin and an H₂ molecule.

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (\Delta H^0_{\text{rxn}}=137 \text{ kJ/mol}) \]

Dehydrogenation suffers from some of the same difficulties encountered in steam cracking and FCC, namely: the high endothermicity of the reaction and catalyst deactivation due to coke formation. An additional difficulty encountered with dehydrogenation is the thermodynamic limitation of the reaction (see Figure 1-1). Direct dehydrogenation is thermodynamically limited at low temperatures making it impossible to achieve acceptable yields at low temperatures. The combination of high temperatures and endothermic reaction makes the process very energy intensive. Additionally, at the high temperatures required to achieve adequate conversion, selectivity can be difficult to control.

The limitations of the current olefin production methods are clear (see Table 1-1). All three of these processes are endothermic and require high temperatures to obtain acceptable yields. Direct dehydrogenation is thermodynamically limited making it impossible to achieve acceptable yields at low temperatures. Additionally, coking is a problem for all three processes. In steam cracking, reactor coking forces routine de-coking shutdowns. In FCC and direct dehydrogenation, coking causes catalyst deactivation with time on stream.

A number of alternative technologies have been investigated including: coupling direct alkane dehydrogenation with alkane combustion or hydrogen combustion to supply the required heat, membrane assisted direct dehydrogenation to separate hydrogen from the products to bypass the thermodynamic limitations and the oxidative dehydrogenation (ODH) reaction [4-7]. Among these options, oxidative dehydrogenation appears to be the simplest option and the production of ethylene by (ODH) does not suffer the same shortcomings as thermal cracking, FCC and direct
Figure 1-1 – Yield of $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ reaction at thermodynamic equilibrium
<table>
<thead>
<tr>
<th>Method</th>
<th>Commercial</th>
<th>Feed</th>
<th>Catalysts</th>
<th>Advantages</th>
<th>Limitations</th>
<th>Yield (%)</th>
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<tr>
<td>de-hydrogenation</td>
<td>YES</td>
<td>propane</td>
<td>Cr₂O₃/Al₂O₃, Pt/Sn/Al₂O₃</td>
<td>high selectivity</td>
<td>endothermic, coking</td>
<td>84% propylene</td>
</tr>
<tr>
<td>steam cracking</td>
<td>YES</td>
<td>ethane, naphtha</td>
<td>none</td>
<td>produces other high value products</td>
<td>high temperatures, endothermic, fouling, coking</td>
<td>30% ethylene, 13-16% propylene</td>
</tr>
<tr>
<td>catalytic cracking</td>
<td>YES</td>
<td>ethane, naphtha</td>
<td>zeolites</td>
<td>lower temperatures, better heat transfer</td>
<td>endothermic, coking, deactivation</td>
<td>1-2% ethylene, 5% propylene</td>
</tr>
<tr>
<td>oxidative dehydrogenation</td>
<td>NO</td>
<td>ethane or propane</td>
<td>V and Mo oxides</td>
<td>no thermo limitations, exothermic</td>
<td>tends to form COₓ</td>
<td>75% ethylene, 28% propylene</td>
</tr>
</tbody>
</table>

Table 1-1 – Methods of olefin production

^a-values assuming naphtha feed which is the most common feedstock

^b-values represent yield for ethane and propane ODH, respectively.

All values taken from [1].
dehydrogenation. In oxidative dehydrogenation, ethane and oxygen are reacted over a catalyst to form ethylene and water.

\[ C_2H_6 + \frac{1}{2} O_2 \rightarrow C_2H_4 + H_2O \quad (\Delta H_{\text{rxn}}^{\circ} = -105 \text{ kJ/mol}) \]

Oxidative dehydrogenation, unlike steam cracking and direct dehydrogenation, is a thermodynamically favorable, exothermic reaction forming thermodynamically stable water. Additionally, ODH can operate at lower temperatures (300 to 550°C) than any of the aforementioned processes when using an appropriate catalyst. The exothermic nature of the reaction together with the lower temperature requirement leads to substantial energy savings when using oxidative dehydrogenation as compared to direct dehydrogenation. In fact, the energy consumption is expected to be substantially less than any of the current olefin production methods due to their endothermic natures. Furthermore, the deposition of coke is largely eliminated due to the presence of oxygen, which can oxidize coke to form carbon dioxide preventing the routine de-coking procedures necessary in current commercial reactors.

There are, however, a number of current challenges preventing oxidative dehydrogenation from being widely implemented. The difficulties inherent in oxidative dehydrogenation reactions revolve around selectivity control. Typically, alkane activation (which requires abstraction of the first hydrogen atom) is considered the rate-limiting step. Unfortunately, at the temperatures required for alkane activation, the olefinic product is easily oxidized. In these undesired pathways, lattice, adsorbed or gas phase oxygen can be inserted into ethane or ethylene to ultimately form combustion products.

\[ C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O \quad (H_{\text{rxn}}^{\circ} = -1430 \text{ kJ/mol}) \]
\[
\text{C}_2\text{H}_6 + \frac{3}{2} \text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2\text{O} \quad (\Delta H^\circ_{\text{rxn}} = -860 \text{ kJ/mol})
\]

Due to these limitations, the only current commercial process that utilizes lower alkanes as a feedstock in an oxidation reaction is the selective oxidation of butane to maleic anhydride and acetic acid. Currently, there are no commercial processes producing ethylene from ethane using oxidative dehydrogenation and ethylene yields up to 70% may be necessary to compete with the current steam cracking technology [8].
2.1 Benefits of Oxidative Dehydrogenation

Current olefin production methods suffer from the limitations of high temperatures and the endothermic nature of the reactions. These lead to substantial energy costs associated with olefin production. Additionally, coking occurs requiring the periodic shutdown and decoking of the reactor systems. The low cost, abundance and environmentally benign nature of light alkanes has provided incentive for their use in the production of higher value intermediates. Direct dehydrogenation is thermodynamically limited making it impossible to achieve acceptable yields at low temperatures.

Oxidative dehydrogenation, unlike direct dehydrogenation, is a thermodynamically favorable reaction. Additionally, ODH can operate at lower temperatures (300 to 550°C) when using an appropriate catalyst. The exothermic nature of the reaction together with the lower temperature requirement leads to substantial energy savings when using oxidative. Furthermore, coke deposition is largely eliminated due to the presence of oxygen, which is able to oxidize coke to form carbon dioxide preventing the routine de-coking procedures necessary in current commercial reactors.
There are still a number of current research challenges preventing oxidative dehydrogenation from becoming commercial. These challenges involve the difficulty of controlling selectivity. Due to these limitations, the only current commercial process that utilizes lower alkanes as a feedstock in an oxidation reaction is the selective oxidation of butane to maleic anhydride and acetic acid. It has been suggested that, due to the well-established, highly efficient and fully depreciated existing plants, oxidative dehydrogenation will need to achieve even higher selectivities than the current technologies [9]. Currently, there are no commercial processes producing ethylene from ethane using oxidative dehydrogenation and yields up to 70% may be necessary to compete with the current technology [8].

ODH catalysts are generally divided into two general classes: high temperature (above 600 °C) and low temperature (below 600 °C) catalysts [10, 11]. The high temperature catalysts typically contain ions and oxides of group IA or IIA metals (alkali or alkali earth metals) such as Ni, Li and Mg. Low temperature catalysts generally contain easily reducible transition metal oxides such as V, Mo and Nb.

2.2 High Temperature Catalysts

Catalysts containing ions and oxides of group IA and IIA metals such as Li and Mg are active and selective in the oxidative dehydrogenation of ethane. High selectivities can be achieved when chlorine compounds are added to the feed components or if the catalysts are modified with halide compounds. Kung [12] suggests that these catalysts may work in two ways: through a surface reaction or a homogeneous gas phase reaction. An ethane species adsorbs to a surface oxygen atom before having a C-H bond cleaved to
form a surface ethyl. This ethyl species can then further react with an oxygen molecule to form ethane. Alternatively, the adsorbed ethyl species can desorb from the surface into the gas phase. In this case, the catalyst mainly work as a radical initiator creating charged ethyl radicals through heterolytic C-H bond cleavage. The radicals then desorb from the surface and participate in homogeneous gas phase radical chemistry. It has been reported that these gas phase radicals can be more selective than the heterogeneous reactions leading to an increase in ethylene selectivity as temperature is increased [13]. Large void fractions and high temperatures are employed to maximize the homogeneous gas phase reaction and it has been reported that packing a reactor with quartz wool can suppress this homogeneous reaction [14]. Over this class of catalysts, yield improves with increasing temperature due to ethyl radical desorption into the gas phase to undergo homogeneous gas phase reactions with oxygen, ultimately forming ethylene.

Kung [12] points out that the catalysts achieving high activity and selectivity in high temperature ODH typically do not contain easily reducible transition metals. The most widely studied catalysts is Li-MgO which abstracts hydrogen on Li\(^{+}\)-O\(^{-}\) defect sites to create alkyl radicals [15, 16]. High performance can be also achieved using Li/Mg/O catalysts promoted with dysprosium [17]. For the promoted and unpromoted catalysts, the highest ethylene yields have been achieved when the catalyst is doped with chlorine [17, 18]. It has been suggested that halides are beneficial because they help generate singly charged ethyl radicals through heterolytic cleavage of the C-H bond. These radicals are important for achieving high ethylene yields in the high temperature reaction [11, 12]. This ethylene radical reacts with surface oxygen atoms to form an ethoxide species which can decompose to ethylene or desorbs into the gas phase and engage in
free radical chemistry. It should be noted that the work presented in this dissertation will deal with a low temperature ODH catalyst.

2.3 Low Temperature Catalysts

The low temperature ODH catalysts contain easily reducible transition metal oxides (V, Mo, Sb, Nb) and are used in a wide array of selective oxidation reactions including oxidative dehydrogenation of ethane, propane, butane, 1-butene and ethylbenzene [10, 12, 19-30]. These catalysts operate by a Mars-van-Krevelen type redox mechanism. The reaction is strictly heterogeneous and the homogenous gas phase reactions involving ethyl radicals play no part here. The work presented in this dissertation focuses on low temperature ODH catalysts.

A number of bulk, mixed oxides have been reported active in the oxidative dehydrogenation of ethane. One well known catalyst is Mo/V/Nb which has been shown to be effective for ethane ODH [31-33] and can be improved with the incorporation of tellerium. Mo/V/Sb mixed oxides are also active and selective in ethane ODH achieving ethylene selectivities of 80% at ethane conversions of 65% [34]. The catalyst performance of these two systems was correlated to the presence of orthorhombic Te2M20O57 and (SbO)2M20O56, respectively, where M is Mo, V or Nb.

Vanadium and molybdenum are the most studied active metals for ODH of lower alkanes and have been extensively investigated [24, 26, 27, 29, 30, 32, 35-39]. Often times, these metals are deposited on the surface of another metal oxide (the support) such as SiO2, TiO2, Al2O3 or ZrO2 resulting in improved activity, selectivity and mechanical strength. In fact, the choice of support is of fundamental importance in the design of effective oxidation
catalysts. The choice of support can affect the metal oxide dispersion through the number and activity of support hydroxyl groups. Additionally, the choice of support can have major influences on the activity of the catalyst. Tian et al. have demonstrated that the nature of the support can influence the catalytic activity in selective oxidation reactions (including oxidative dehydrogenation) by over an order of magnitude [40-42]. By first constructing TiO\textsubscript{x}, AlO\textsubscript{x} and ZrO\textsubscript{x} monolayers on a SiO\textsubscript{2} support and then anchoring isolated VO\textsubscript{4} species on these, turnover frequencies in methanol selective oxidation to formaldehyde were modified by a factor of 10. They suggest that the electronegativity of the V-O-S bond influences the activity. By using supports with lower electronegativities, it is possible to increase the electron density of the oxygen atom making it more active.

2.4 Structure of Supported Catalysts

Supported oxide catalysts possess a number of oxygen species including: M=O, M-O-M, M-O-S, where M is the active metal, S is the support and O is an oxygen atom. These three functional groups have varying reactivities and their reactivity relative to one another depends on the type of metal. Typically, the M-OH functional groups (the hydroxyls) are the most reactive and the active metals (molybdenum or vanadium) are anchored to these sites [26, 38, 40, 43]. Therefore, higher concentrations of isolated surface hydroxyls and more reactive surface hydroxyls leads to more highly dispersed active metal oxides. At low loadings, the active metal oxides tend to exist as isolated surface species where the metal is bonded to the support through an oxygen atom (see Figure 2-1). As the loading of active metal oxides increases, the isolated species start to interact and bond with one another forming 2-dimensional polymeric surface species.
The presence of isolate monomeric, polymeric and crystalline species on the catalyst surface has an effect on oxidative dehydrogenation activity. At low loadings, there are no M-O-M bonds present. These isolated species are present for both molybdenum and vanadium at low loading levels. Supported vanadium catalysts containing isolated vanadium domains consists of a vanadium atom bonded to the support through three oxygen atoms and a single terminal oxygen-vanadium bond. Differences exist in the literature regarding the structure of supported molybdenum catalysts. Some researchers have suggested a structure where molybdenum possesses one terminal M=O bond and four M-O-S bonds [44, 45]. Recent studies using UV-Raman spectroscopy and isotopic labeling, however, have demonstrated that group IV metals such as molybdenum possess a surface consisting of two terminal M=O bonds when supported on silica [46]. The same research concluded that vanadium possessed one terminal oxygen bond as suggested previously. Figure 2-1 shows the two suggested molybdenum oxide structures. Additionally, Raman spectroscopy on molybdenum supported on silica suggests that at low loading the molybdenum exists as a tetrahedrally coordinated species while at high loadings octahedral polymeric species form [47]. As mentioned above, Wachs et al. have shown that the nature of the support has a significant effect (up to an order of magnitude) on the catalytic activity of the active oxide [48, 49]. This suggests that the M-O-S bonds are somehow involved in the active site in selective oxidation reactions.

As loading levels are increased, polymeric species begin to form and at loading levels above monolayer coverage the active metal begins to form three dimensional crystalline phases [38, 50]. For both molybdenum and vanadium catalysts, research has demonstrated a maximum in turnover frequency at intermediate loading levels where the
presence of non-crystalline polymeric species are detected [23, 36, 51]. The selectivity is also affected by the distribution of active sites suggesting that isolated monomeric structures are most selective in propane ODH. The formation of crystalline vanadium and molybdenum do not improve propane oxidative dehydrogenation turnover frequency due to the inaccessibility of a number of the vanadium-oxygen bonds.

Additionally, the properties of a catalyst can be affected by adding small amounts of an additive. In oxidative dehydrogenation research the additives are usually alkali metals or halides. These additives exert a promoting effect on the activity and selectivity of catalysts through a variety of mechanisms. Promotion of molybdenum on zirconia catalysts with Li, K and Na have demonstrated decreases in conversion but increases in selectivity leading to increases in olefin yield [52]. Studies have shown a suppression of the unselective consecutive oxidation of olefin to CO\textsubscript{x} species. It has been suggested that alkali metals can have many effects on oxidative dehydrogenation catalysts including: geometric effects, reducibility effects and effects on acid-base properties.

The most widely argued effect of alkali promoters on oxidative dehydrogenation catalysts has been the effect on the acid-base properties [53-55]. An additive of electronegativity lower than that of the metal cation in a M-O bond would induce a relatively higher electron density on the active oxygen site. It is suggested that a slightly basic sight is needed for the initial hydrogen abstraction from the alkane molecule. Additionally, the acidity of the active site also effects the desorption of the olefin molecule. A site of higher lewis basicity will lead to easier desorption of the olefin due to the olefin’s electron rich double bond. A balance is required because a catalyst that is strongly basic will be poisoned by CO\textsubscript{2} that will not desorb from the surface [56]. These
effects can be studied in many ways including temperature programmed adsorption/desorption experiments with probe molecules and measurements of heats of adsorption and desorption. Past research in our group has shown that potassium improves adsorption/ desorption behavior and oxygen exchange between bulk MnMoO$_4$ catalysts and gas phase oxygen in the oxidative coupling of methane. Isotopic labeling techniques demonstrated that the rate of lattice oxygen incorporation into the products was found to change with potassium promotion [57].

The active metal reducibility can also be affected by the introduction of an alkali or halide promoter. Temperature programmed reduction profiles on promoted catalysts show that alkali promoters often induce shifts to higher reduction temperatures. For supported vanadium and promoted with potassium, an increase in reduction peak temperature has been reported for alkali promoters [58]. Research on potassium promoted vanadium catalysts has shown a decrease in the rate of catalyst reduction by propane but no decrease in the activation energy suggesting that the promoter may block some active sites [59].

2.5 Mixed Oxide Catalysts

A great deal of literature exists regarding the use of more than one metal oxides, known as mixed oxides, as catalyst [60-62]. Catalyst supports consisting of more than one metal oxides can provide benefits beyond those of single oxide supports. In particular, a silica-titania mixed oxide is able to preserve the catalytic active sites of a VO$_x$/TiO$_2$ or MoO$_x$/TiO$_2$ catalyst while gaining the mechanical and thermal stability of a silica based catalyst. These materials also possess new catalytic active sites. These types of catalysts
often have enhanced acidity due to the creation of unique Si-O-Ti sites not present on the individual oxides. Additionally, it has been demonstrated that the typical octahedral coordination state of anatase TiO₂ can be accompanied by small tetrahedral sites when using a mixed silica-titania oxide [63]. These new catalytic sites can lead to improved chemical properties and active sites useful for catalytic reactions. Other benefits, not obtainable with single metal oxides, are also possible such as higher surface areas and higher active metal dispersions.

Previous research in our group has demonstrated that 10wt% molybdenum dispersed in a silica-titania mixed oxide matrix is quite active for propane and ethane oxidative dehydrogenation [26, 27, 29, 30, 32, 37, 39, 64, 65]. When properly made using a sol-gel technique, the molybdenum is well dispersed throughout the silica/titania matrix. The interactions between these species have a synergistic effect on the olefin yield. X-ray photoelectron spectroscopy has shown that at low molybdenum loadings, MoOₓ is preferentially supported on titania species but as loading is increased MoOₓ increasingly interacts with silica [39].

In addition to using different support materials, the surface characteristics of a catalyst can be tuned by the addition of small quantities of another metal, called a promoter. These promoters affect the surface properties of a catalyst by creating active sites, improving dispersion, modifying lattice oxygen diffusivity, and adjusting the reducibility of the metal cation [37]. Hence, the surface properties of a catalyst can be “tuned” by the addition of promoter metals. Our research group has extensively investigated the influence of promoters on silica-titania supported molybdenum catalysts [24, 26, 27, 29, 30, 32, 57, 64].
The affects of potassium promotion on silica-titania supported molybdenum catalyst have been investigated in the oxidative dehydrogenation of propane [27, 29, 30]. Mo (V) is related to the active site in this reaction but the electronic nature of the coordinated oxygen atoms is likely the underlying cause of its activity [37]. Electron spin resonance experiments showed that the presence of potassium alters the electronic structure of the surface Mo (V) species, lowering molybdenum’s coordination sphere from 6 to 5. This change of coordination creates highly distorted molybdenum species and may be responsible for the observed increase in propane ODH reactivity [37]. Though it is understood how these structural changes affect the oxidation/reduction cycle, their influence on the nature of oxygen species during reaction remains unknown.

Other work has focused on the addition of halide promoters to silica-titania supported molybdenum catalysts [24, 26, 32, 64]. Post-reduction x-ray photoelectron spectroscopy studies demonstrated that the addition of chlorine strongly influenced the reducibility of surface molybdenum oxide species. In the presence of chlorine, propane was only able to reduce molybdenum to Mo (V) whereas in the absence of chlorine, propane reduced some molybdenum to Mo (IV) [26]. Steady state reaction experiments showed improved alkane conversion and olefin yield in oxidative dehydrogenation reactions over chlorine doped catalysts.
Figure 2-1 – Possible structures of monomeric supported molybdenum
2.6 Mars-van-Krevelen Mechanism

Ethane oxidative dehydrogenation is typically considered to occur by a network of consecutive and parallel reactions (see Figure 2-2). The three primary reactions that occur are oxidative dehydrogenation of ethane, the undesired direct combustion of ethane and the undesired secondary combustion of ethylene. Both the latter two reactions can limit the selectivity and yield during ethane oxidative dehydrogenation. In fact, the major challenge of ethane oxidative dehydrogenation is controlling the selectivity of the reaction. The ethylene formed during ODH tends to be combusted in the secondary reaction. Multiple reviews summarize the performance of a number of ODH catalysts from the literature [9, 11, 12]. The trend in reaction data shows that, as the alkane conversion increases, the selectivity towards the desired olefin decreases. That is to say, as higher ethane conversions are obtained, a greater fraction of the products are the result of unselective ethane or ethylene combustion.

Many studies have investigated the reaction mechanism in propane and ethane oxidative dehydrogenation [66-68]. Burch et al demonstrated that the reducibility of the active metal is closely related to catalytic activity [69-71]. It has also been suggested that the ODH reaction rates more closely correlate with UV-Vis adsorption edge energy which indicates the ease that lattice oxygen atoms transfer electron to the metal center [72]. These results suggest that the reduction of the catalyst is involved in the oxidative dehydrogenation mechanism.
Steady State Transient Isotopic Kinetic Analysis (SSITKA) has been used to probe the ODH reaction mechanism. In SSITKA, a reaction is run and allowed to reach steady state. Then the isotopic composition of one of the reactants is abruptly switched while maintaining the concentration of the gas. For instance, a feed containing 5% O$_{16}^2$ would be abruptly changed to 5% O$_{18}^2$. The resulting relaxation and evolution of products containing O$_{18}^8$ atoms provides information about the reaction mechanism and can be monitored with a mass spectrometer.

Bell et al. [73] have explored the oxidative dehydrogenation reaction mechanism on MoO$_x$/ZrO$_2$ catalysts and determined a number of important points. Lattice oxygen is required for oxidative dehydrogenation as evidenced by the slow incorporation of O$_{18}^8$ in the reaction products after an isotopic switch. C-H bond activation is irreversible as evidenced by the lack of C$_3$H$_8$ with mixed deuterium-hydrogen content during ODH with a C$_3$H$_8$/C$_3$D$_8$ mixture. Kinetic isotope effects were observed during propane dehydrogenation and propene combustion suggesting that C-H bond dissociation is a kinetically relevant reaction step. Deuterium exchange occurs readily between propane and water suggesting reversible hydroxyl recombination steps. These data suggest a redox type mechanism where lattice oxygen atoms react with the alkane to produce an olefin. The catalyst is reduced during this process and gas phase oxygen must then reoxidize the catalyst in a separate step. Similar results have been demonstrated for vanadium catalysts as well and it is now widely accepted that the oxidative dehydrogenation of lower alkanes by transition metal catalysts occurs by a Mars-Van Krevelen redox mechanism.
Figure 2-2- Oxidative dehydrogenation reaction scheme
During oxidation, the catalyst surface is reduced as lattice oxygen atoms activate ethane molecules, ultimately forming olefins (see Figure 2-3). Ethane must first adsorb to a surface oxygen atom (O*) and a C-H bond must be cleaved forming an alkyl intermediate (Eqn. 1) and a hydroxyl group on the catalyst surface (Eqn. 2). This initial cleavage of the ethane C-H bond is widely considered the rate limiting step and the literature consistently shows that consumption rates are first order in ethane concentration [55, 66].

The adsorbed alkyl species, which is adsorbed to an oxygen atom, then loses a second hydrogen atom forming ethylene and another hydroxyl group on the catalyst surface (Eqn. 3). Finally, two hydroxyl groups combine to form water and a lattice vacancy (V*) where there was initially an oxygen atom (Eqn. 4). Gas phase oxygen then adsorbs to the surface and undergoes a series of electron transfer processes before being incorporated back into the lattice and restoring the initial oxidation state of the catalyst (Eqn. 5), thus completing the redox cycle (Figure 2-4).

\[
\begin{align*}
\text{C}_2\text{H}_6 + \text{O}^* & \leftrightarrow \text{C}_2\text{H}_6\text{O}^* \quad \text{(Eqn. 1)} \\
\text{C}_2\text{H}_6\text{O}^* + \text{O}^* & \rightarrow \text{C}_2\text{H}_5\text{O}^* + \text{OH}^* \quad \text{(Eqn. 2)} \\
\text{C}_2\text{H}_5\text{O}^* & \rightarrow \text{C}_2\text{H}_4 + \text{OH}^* \quad \text{(Eqn. 3)} \\
2\text{OH}^* & \leftrightarrow \text{H}_2\text{O} + \text{V}^* + \text{O}^* \quad \text{(Eqn. 4)} \\
\text{O}_2 + 2\text{V}^* & \rightarrow 2\text{O}^* \quad \text{(Eqn. 5)}
\end{align*}
\]

When in equilibrium with the gas phase, the surface is populated by short-lived oxygen species \(\text{O}_2^-\) and \(\text{O}^-\) (see Figure 2-4) that can affect catalyst performance. The
Figure 2-3 – Mars van Krevelen redox mechanism.
Left – catalyst reduction by alkane. Right – catalyst re-oxidation with O₂
$O_{2(g)} + e^- \rightarrow O_{2(ads)}^-$

$O_{2(ads)}^- + e^- \rightarrow 2O_{(ads)}^-$

$O_{(ads)}^- + e^- \rightarrow O_{lattice}^{2-}$

Figure 2-4 - Electron Transfer Processes During Catalyst Re-oxidation
strongly electrophilic species, $\text{O}_2^-$ and $\text{O}^-$, are believed to be responsible for the unselective complete oxidation of lower alkanes leading to combustion products, CO and CO$_2$, while nucleophilic lattice $\text{O}_2^-$ is believed to selectively produce olefins, though the lattice oxygen could participate in the combustion of ethylene [74, 75]. The nature of these oxygen species depends on reaction conditions, degree of catalyst surface reduction, the counter metal oxide cation and the structure of surface species but the exact relationship is difficult to characterize [37].

2.7 ODH Using N$_2$O as Oxidant

It’s clear that many properties of the catalyst are responsible for ethane oxidative dehydrogenation performance. Because the rate limiting step in the oxidative dehydrogenation of ethane involves the breaking of a C-H bond and because of the inherent difficulty of detecting $\text{O}^-$ and $\text{O}_2^-$ species, most research has focused on the alkane activation. Understandably, most researchers have emphasized catalyst reducibility and acid/base properties while properties regarding the re-oxidation process have been largely ignored.

In the 1970’s Lunsford et al. studied N$_2$O dissociation on a number of catalysts including MoOx/SiO$_2$ and MgO [76-80]. They suggest that N$_2$O dissociates to predominantly form $\text{O}^-$ species and that these $\text{O}^-$ species are able to undergo exchange with oxide ions in the lattice of MoOx/SiO$_2$ catalysts [81]. They even used N$_2$O during ethane ODH and methane partial oxidation and observed activities and selectivities that differ from those obtained using molecular oxygen over these MoOx/SiO$_2$ catalysts [76].
They conclude that the O- species is formed on molybdenum reduced to the Mo\(^{5+}\) state and that O’ is the active form of oxygen for C\(_2\)H\(_6\) dehydrogenation. This conflicts with the more common (and more recent) view that lattice oxygen is responsible for C\(_2\)H\(_6\) dehydrogenation. Clearly, in some way, the choice of oxidant has a significant effect on performance in ethane oxidative dehydrogenation.

In addition to the catalyst structure, the choice of oxidant can have interesting effects on ODH performance. Lunsford et al. studied N\(_2\)O dissociation on a number of catalysts including MoO\(_x\)/SiO\(_2\) and MgO\([76, 79, 80]\). They suggest that N\(_2\)O dissociates to predominantly form O’ species and that these O’ species are able to undergo exchange with oxide ions in the lattice of MoO\(_x\)/SiO\(_2\) catalysts\([81]\). They have even used N\(_2\)O during ethane ODH and methane partial oxidation and observed activities and selectivities that differ from those obtained using molecular oxygen over these MoO\(_x\)/SiO\(_2\) catalysts\([76]\). They conclude that the O- species is formed on molybdenum reduced to the Mo\(^{5+}\) state and that O’ is the active form of oxygen for C\(_2\)H\(_6\) dehydrogenation. This conflicts with the more common view that lattice oxygen is responsible for C\(_2\)H\(_6\) dehydrogenation.

More recently, propane ODH has been carried out on vanadium catalysts using N\(_2\)O as the oxidant yielding improved propylene selectivities. Using UV-Vis spectroscopy, Kondratenko et al.\([82-84]\) have demonstrated that VO\(_x\)/Al\(_2\)O\(_3\), VO\(_x\)/SiO\(_2\) (including MCM-41 and MCM-48) and bulk vanadates (VO\(_2\), V\(_2\)O\(_3\) and V\(_2\)O\(_5\)) operate in a more reduced state when N\(_2\)O is used as the oxidant. The increase in propylene selectivity is attributed to this decrease in catalyst oxidation state. Based on density functional theory, Rozanska et al.\([85]\) have even proposed that oxygen is able to form a
peroxovanadate species that N\textsubscript{2}O cannot. This peroxovanadate is considered active for the oxidation of propylene and may explain the decreased selectivity when using N\textsubscript{2}O.

While the choice of N\textsubscript{2}O as an oxidizing agent appears unviable from an economic standpoint due to its inhibitive cost, N\textsubscript{2}O may be employed as a research tool. Using N\textsubscript{2}O may reduce the significance of the O\textsuperscript{2−} species during ethane oxidative dehydrogenation. In the ODH literature, the emphasis has been placed mostly on the C-H activation step and on the reducibility of the catalysts employed. As demonstrated by the early research by Lunsford et al., the oxidation step plays some important and often neglected role in the oxidative dehydrogenation of ethane.

The present study aims to determine the effects of using N\textsubscript{2}O and O\textsubscript{2} as oxidant during ethane ODH on a molybdenum based catalyst. Special focus is placed on the effect of oxidant on the structure of the catalyst and on the kinetics of the ethane ODH reaction. With these goals in mind, steady-state ethane ODH using O\textsubscript{2} or N\textsubscript{2}O as oxidant was performed at various contact times and various oxidant concentrations. Catalyst structure was monitored using post-reaction X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction and reoxidation experiments (TPR/TPO) monitored with Raman spectroscopy. Post-reaction TPO and XPS experiments were performed to characterize differences in surface carbon species after ethane ODH using N\textsubscript{2}O or O\textsubscript{2}.
3.1 Catalyst Preparation

A one pot sol-gel/co-precipitation technique was used to prepare a 10wt%Mo/Si:Ti catalyst. Tetraethylorthosilicate (TEOS), from Aldrich, and titanium(IV)isopropoxide (TIP), also from Aldrich, were placed in a 1:1 volume mixture of ethyl and propyl alcohol. TEOS and TIP were added in quantities such that the molar ratio of SiO$_2$ to TiO$_2$ would be 1:1. The solution was continually stirred using a PTFE magnetic stir bar. While stirring, an aqueous solution containing ammonium heptamolybdate (from Malinkrodt) was slowly added dropwise using a syringe pump. A controlled inorganic polymerization reaction occurred, dispersing molybdenum through the silica/titania network. The solution was allowed to stir for 15 minutes after the entirety of the ammonium heptamolybdate solution had been added. The resulting gel was then dried in an oven at 110°C overnight. After drying, the catalyst was ground into a fine powder using a mortar and pestle. The powder was then calcined at 550°C in air for 5 hours to oxidize to sample and remove any remaining organics. Precursors were added in quantities such that the final product contained 10wt% molybdenum and a 1:1 molar ratio of SiO$_2$ to TiO$_2$. 
3.2 BET Surface Area Analysis

The catalyst surface area is an important factor in catalytic reactions. Higher surface areas tend to give increased activity because more active sites will be accessible to the gas phase. The Brunauer, Emmett and Teller method (BET), developed in 1938, is commonly used for the determination of the surface area of solids. The linearized BET equation is written as

\[
\frac{P}{n_a (P_o - P)} = \frac{1}{n_{a,m} C} + \frac{(C - 1)P}{n_{a,m} CP_o}
\]

where \( P \) is the pressure, \( P_o \) is the adsorbate saturation pressure at the temperature of the experiment, \( n_a \) is the number of moles of adsorbate adsorbed at a given relative pressure \( (P/P_o) \) and \( n_{a,m} \) is the amount of adsorbate adsorbed for form a single monolayer on the sample. According to the derivation of the BET equation, \( C \) is related to the enthalpy of adsorption below monolayer coverage. After much research on BET surface areas, this interpretation is widely disregarded, however \( C \) is still constant and can be used to determine BET surface areas.

Samples are dosed with various pressures of gas and allowed to equilibrate. The amount of gas adsorbed \( (n_a) \) is determined by the change in pressure. The unknowns are \( C \) and \( n_{a,m} \) and a plot of

\[
\frac{P}{n_a (P_o - P)} \text{ vs. } \frac{P}{P_o}
\]
yields a straight line with an intercept of \( \frac{1}{n_{a,m}C} \) and a slope of \( \frac{(C - 1)}{n_{a,m}C} \).

The specific BET surface area can then be calculated using

\[
a_s = \frac{n_{a,m}L \alpha_m}{m}
\]

where \( a_s \) is the specific BET surface area, \( a_m \) is the cross-sectional area of an adsorbate molecule (0.162 nm\(^2\) at 77 K for \( \text{N}_2 \)), \( n_{a,m} \) is the number of moles of adsorbate adsorbed and \( L \) is Avogadro’s number.

Static surface area and pore volume measurements were made using a Micromeritics ASAP 2010 accelerated surface area and porosimetry instrument. Nitrogen was the adsorbent at liquid nitrogen temperature (77 K). \( \text{N}_2 \) adsorption and desorption isotherms were collected at relative pressures (\( P/P_o \)) between 0 and 1. BET surface area was calculated using 8 points lying on the adsorption isotherm between 0 and 0.1 \( P/P_o \). BJH pore size distributions (PSD) were determined using the desorption branch of the isotherm. Samples were degassed under vacuum at 200°C overnight before being analyzed.

3.3 Catalyst Activity Testing

Steady-state activity measurements were conducted using either \( \text{O}_2 \) or \( \text{N}_2 \text{O} \) to determine their relative performance in the ethane oxidative dehydrogenation reaction. 50mg of 10%Mo/Si:Ti catalyst was mixed with 250mg of quartz powder and placed into a fixed-bed quartz reactor with quartz frit bed. A type K thermocouple in contact with
the upstream side of the catalyst bed was used to measure temperature. In all experiments, ethane conversion was kept below 5%. The reactor system is shown in Figure 3-1.

Experiments were run at 600°C at differing contact times. Contact times were changed by varying the total gas flow rate (using Brooks 5850E mass flow controllers) while maintaining the relative concentrations of each gas phase component. The gas phase compositions were 5% C₂H₆, 5% O₂ and balance helium or 5% C₂H₆, 10% N₂O and balance helium. A separate set of steady-state experiments was run at 600°C and a constant contact time of 0.625 mg s/cm³. During these experiments, the ratio of oxidant concentration to ethane concentration was varied.

In all experiments, dead volume within the reactor was filled with loosely packed quartz wool to eliminate the possibility of homogeneous gas-phase reactions. Blank runs were conducted without catalyst using a quartz reactor packed with quartz wool. The results showed negligible ethane conversion at the feed conditions studied. Feed and effluent composition analyses were conducted using an Agilent 3000A micro gas chromatograph equipped with 0.32mm PLOT molesieve and 0.32mm PLOT Q columns with backflush and variable volume injectors, respectively. Both columns used TCD detectors. G.C. data points were collected and averaged after 60 minutes on stream and all carbon balances close with +/- 5%.

Conversion, selectivity and yield are all calculated on a carbon atom basis. These definitions ensure that conversion, selectivity and yield have values between 0 and 100%. Ethane conversion is defined as:
Figure 3-1 – ODH steady-state reaction system configuration
\[ X_{\text{ethane}} = \frac{\sum (n_i \times C_i)_{\text{products}}}{2 \times n_{\text{ethane}}} \]

where \( n_i \) and \( C_i \) are the number of moles of and carbon atoms in molecule \( i \), respectively.

It should be noted that the numerator summation contains only the products formed, not ethane. The selectivity of component \( i \) is defined as:

\[ S_i = \frac{n_i \times C_i}{\sum (n_i \times C_i)_{\text{products}}} \]

and the yield of component \( i \) is defined as:

\[ Y_i = \frac{n_i \times C_i}{2 \times n_{\text{ethane}}} \]

Using these definitions, the yield of a given component is simply the selectivity of that component times the conversion of ethane. On a graph of selectivity versus ethane conversion, the product with the higher selectivity at a given conversion will also have the higher yield. These definitions also ensure that conversion, selectivity and yield have values between 0 and 100%.

3.4 Temperature Programmed Oxidative Dehydrogenation

The performance of \( \text{O}_2 \) and \( \text{N}_2\text{O} \) as oxidants were measured during an ethane ODH reaction using a temperature programmed technique. In this technique, 100 mg of 10 wt\% Mo/Si:Ti was loaded into a quartz U-tube reactor. 30 cc/min of 7.5\% ethane, 2.5\% oxidant (either \( \text{O}_2 \) or \( \text{N}_2\text{O} \)) and 90\% helium was introduced to the sample before beginning the temperature ramp. The temperature was ramped from room temperature to
600 °C at a rate of 10°C/min. Online reactor effluent measurements were collected using a Shimadzu QP QP5050 quadrupole mass spectrometer. Mass to charge ratios (m/z) of 18, 28, 32 and 44 were monitored.

3.5 Determination of Post Reaction Chemical State of Molybdenum using XPS

X-ray photoelectron spectroscopy (XPS), also known as ESCA (Electron Spectroscopy for Chemical Analysis) is capable of providing quantitative information regarding the chemical composition and state of a catalyst surface. Each chemical element has a characteristic binding energy associated with the core electrons located near the atomic nucleus. In XPS, a substance is exposed to monochromatic X-ray radiation under ultra high vacuum. Electrons, called photoelectrons, are ejected from their atomic orbitals with a characteristic kinetic energy. The kinetic energy of these electrons can be measured with an electrostatic analyzer and related to a fundamental property called the binding energy.

\[ KE = h\gamma - BE - \phi_{SP} \]

where KE is the kinetic energy, \( h\gamma \) is the energy of the incident monochromatic X-ray photons, BE is the binding energy and \( \phi_{SP} \) is the spectrometer work function (a known function of the instrument). Binding energy can be directly calculated from this equation because all other quantities are known. The electron binding energy is related to the local chemical environment and can also provide information regarding the oxidation of each atom. Additionally, the intensity of each binding energy peak can provide information about the relative abundance of species at the sample surface.

The chemical state of molybdenum and carbon on post-ethane ODH samples was investigated by X-ray photoelectron spectroscopy. Post-reaction samples were prepared
using the reaction system described in section 2.2. The steady-state reaction was carried out for 6 hours at 600°C and the reaction feed was composed of 10% C₂H₆, 5% O₂ (or 10% N₂O), balance helium at 50ml/min. At the end of 6 hours, the reactor was flushed with helium (50ml/min) for 30 minutes at 600°C and, cooled to room temperature under the same atmosphere. The reactor was then sealed under helium and transferred to a glove box. The samples were pressed onto stainless steel sample cups inside the glove box and transferred to the vacuum chamber. X-ray photoelectron spectra were collected using a Kratos Axis Ultra spectrometer operated at 13kV and 10 mA using AlKα radiation. Data analysis with background subtraction and curve fitting was done on XPS Peak 4.1. All spectra were referenced to the silica 2p₃/2 peak at 102.5 eV. Doublet splitting for all deconvoluted Mo 3d peaks was held constant at 3.2 eV and the area ratio between 3d₅/₂ and 3d₃/₂ was held constant at 3:2. For each spectra, the counts per second were divided by the number of sweeps and the transmission value at that binding energy. This allowed peak area ratios to be compared between spectra.

3.6 Laser Raman Spectroscopy

When radiation passes through a sample, the sample scatters a fraction of the incident beam in all directions. A small fraction of this scattered radiation is inelastically scattered. The difference in energy between the incident radiation and the inelastically scattered radiation gives information about the vibrational modes of the sample molecules. Raman spectra are created by plotting the difference in wavenumber between incident and scattered radiation (Raman shift) versus the intensity of the inelastically scattered radiation. The technique gives the same type of information as infrared spectroscopy but it is important to
note that the techniques are complimentary. In order for a vibrational mode to be Raman active, bond polarizability must be a function of bond distance while in infrared spectroscopy the bond dipole moment must vary with bond distance in order to be active.

Laser Raman spectra (LRS) were acquired using a Horiba-Jovin Yvon LabRam HR confocal Raman spectrometer with 800 mm focal length. The spectrometer was equipped with a 50x long working distance microscope objective, 1200 mm grating, He-Ne red laser (633 nm) and a Peltier-cooled CCD camera. Spectra were collected by averaging 50 scans with an acquisition time of 8 seconds and a power of less than 5 mW at the sample. 10%Mo/Si:Ti catalyst was pre-treated in-situ in a Linkam Scientific CCR1000 catalyst cell reactor with quartz window and a alumina/silica sample cup. The sample was treated under 10%O₂/He at 500°C for 30 minutes and then cooled to room temperature under helium before being reduced in 5%H₂/He using a 10°C/min ramp rate to 550°C. The pre-treatment ensures that the catalyst surface is dehydrated and that any other adsorbed species are removed. The sample was then cooled to room temperature under helium before a temperature programmed oxidation experiment was performed in either 5% O₂/He or 10% N₂O/He using a 10°C/min ramp rate to 550°C. Raman spectra were collected at room temperature before the experiment, after the reduction step, and after the reoxidation steps.

Post reaction Raman experiments were also run using the Horiba-Jovin Yvon spectrometer described above. 6 hours of steady-state ethane oxidative dehydrogenation was run in the Linkam Scientific CCR1000 catalyst cell reactor using 10% C₂H₆, 10% N₂O and balance helium at 600°C. After reaction, helium was introduced at 600°C and the cell was cooled to room temperature before spectra were collected.
3.7 Temperature Programmed Reduction/Oxidation

Temperature programmed techniques typically use a small catalyst sample placed in a quartz, fixed bed reactor heated by a programmable furnace. The sample is exposed to a flow of reactive gases while the temperature is increased at a constant rate. The reactor effluent composition is monitored continuously using a thermal conductivity detector (TCD) or a mass spectrometer (MS). Ideally the feed compositions, contact times and temperatures are chosen such that the reactor operates as a differential reactor (i.e. – constant gas phase composition, constant flow rate and no concentration or temperatures profiles down the length of the reactor).

For a temperature programmed oxidation (TPO) experiment, the mole balance around a differential reactor is:

\[-r_o = \frac{dO^*}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(O^*)\]

where \(-r_o\) is the rate of atomic oxygen consumption (experimentally measurable), \(O^*\) is the degree of oxidation (varying from 0 to 1), \(A\) is a constant term including the pre-exponential factor and the concentration of reactant in the gas phase (which is constant), \(E_A\) is the activation energy, \(R\) is the universal gas constant, \(T\) is the temperature and \(f(O^*)\) is some function of the degree of oxidation. Assuming a linear temperature ramp, an equation such as \(\beta = dT/dt\) can be written and substituting we arrive at:

\[\frac{dO^*}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(O^*)\]

which is the equation used to describe the TPO reaction as a function of temperature.
One method for determining kinetic parameters, known as the Kissinger method, involves the taking the second derivative with respect to temperature and setting it to zero at the rate maximum:

$$\frac{d}{dT} \left( \frac{dO^*}{dT} \right)_{T=T_{\text{max}}} = \frac{d}{dT} \left( \frac{A}{\beta} \exp\left( -\frac{E_A}{RT} \right) f(O^*) \right)_{T=T_{\text{max}}} = 0$$

using the product rule gives:

$$0 = \left( \frac{E_A}{RT^2} \right) \frac{A}{\beta} \exp\left( -\frac{E_A}{RT} \right) f(O^*) + \frac{A}{\beta} \exp\left( -\frac{E_A}{RT} \right) \frac{df(O^*)}{dO^*} \frac{dO^*}{dT} \bigg|_{T=T_{\text{max}}}$$

Recalling the definition of \(dO^*/dT\) allows simplification to:

$$0 = \frac{dO^*}{dT} \left( \frac{E_A}{RT^2} + \frac{A}{\beta} \exp\left( -\frac{E_A}{RT} \right) \frac{df(O^*)}{dO^*} \right) \bigg|_{T=T_{\text{max}}}$$

Further simplification leads to:

$$\frac{\beta E_A}{ART_{\text{max}}^2} = \exp\left( -\frac{E_A}{RT_{\text{max}}} \right) \frac{-df(O^*)}{dO^*}$$

Finally, taking the natural logarithm and simplifying gives:

$$\ln\left( \frac{\beta}{T_{\text{max}}^2} \right) + \ln\left( \frac{E_A}{AR} \right) = -\frac{E_A}{RT_{\text{max}}} + \ln\left( -\frac{df(O^*)}{dO^*} \right)$$

This equation relates the heating rate (\(\beta\)), the temperature of maximum reactant consumption (\(T_{\text{max}}\)) and the activation energy (\(E_A\)). Plotting \(\ln(\beta/T_{\text{max}}^2)\) versus \(1/T_{\text{max}}\) gives a linear line with a slope of \(-E_A/R\) allowing the determination of the activation energy.

In oxidative dehydrogenation, the catalyst is reduced by the alkane and subsequently reoxidized by oxygen in a redox type mechanism. Because the rate limiting step is related to the reduction step, there is a dearth of literature regarding the catalyst
reoxidation. In the following experiments, we have attempted to determine kinetic parameters related to the reoxidation of 10%Mo/Si:Ti using O₂ and N₂O as oxidants. Determination of these parameters can help elucidate the differences in reaction kinetics when using O₂ and N₂O as oxidants.

Temperature programmed oxidation of pre-reduced 10%Mo/Si:Ti was carried out using a quartz reactor with a quartz frit bed and a fast response furnace (Carbolite, MTF 10/15/130) for precise temperature control. A micro GC (Agilent 3000A) equipped with molecular sieve and plot Q columns and programmed for fast analysis was utilized for quantitative determination of oxidant consumption. The microGC was used because of its ability to quantitatively measure N₂O and O₂ concentrations and because of its reproducibility and accuracy. The pre-reduced catalyst samples were prepared in-situ by reduction of 150mg of sample in 5%H₂/He (40ml/min) using a temperature ramp rate of 10°C/min and a setpoint and hold time of 550°C and 30 minutes, respectively. The reactor was then flushed with helium (40ml/min) for another 30 minutes at 550°C and cooled to room temperature. The feed, consisting of 4% N₂O or 2% O₂ in helium (40ml/min) was then introduced to the reactor at room temperature. The temperature program was started 30 minutes after the introduction of the oxidizing agent to the reactor. The same experiment was repeated with various heating rates to determine the reoxidation activation energy of 10%Mo/Si:Ti using N₂O and O₂. The temperature program was as follows: holding for 30 minutes at room temperature; heating at 10, 13, 16 or 19°C/min to 630°C, and holding at 630°C for 20 minutes. During both reduction and reoxidation of the catalyst, the line from the reactor to the micro GC inlet was heated to 100°C with a heating cord to prevent condensation. Activation energies of reoxidation
with O₂ and N₂O were estimated using the Kissinger method. In this method, a series of temperature programmed experiments are run at various temperature ramp rates (β). The activation energy of the oxidation process can be estimated using the temperature at which the maximum oxidant conversion occurs (Tₘₐₓ). A plot of 1/Tₘₐₓ vs. ln(β/Tₘₐₓ²) yields a straight line giving a slope of −E_A/R, where -E_A is the activation energy and R is the universal gas constant.

3.8 Post-Reaction Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) of post reaction samples is a commonly used method to determine if carbon deposition has occurred on the sample. Carbon on the surface will be oxidized to CO₂ and evolve from the catalyst. Additionally, it is often possible to determine whether multiple types of carbon surface species exist through the presence of multiple CO₂ peaks. Carbon deposition on 10%Mo/Si:Ti was studied using post-ethane ODH temperature programmed experiments. 100mg of 10%Mo/Si:Ti was packed inside a quartz U-tube reactor between quartz wool plugs and pretreated under 10%O₂/He (50ml/min) at 550°C for 30 minutes. The reaction mixture, containing 10% C₄H₁₀, 5% O₂ (or 10% N₂O) in He, was then introduced at the same temperature and a flow rate of 50ml/min. After letting the reaction run for 6 hours at 550°C, the reactor was flushed with He (50ml/min) for 30 minutes before cooling the reactor. 5% O₂/He (50ml/min) was then introduced to the reactor at room temperature and the temperature program was started once the mass to charge signals had stabilized. The reactor was then heated to 630°C at a rate of 10°C/min and held at 630°C for 15
minutes. Species desorbing from the surface were monitored by a MKS Cirrus quadrupole mass spectrometer. During pretreatment, reaction and temperature programmed oxidation, the lines from the reactor to the mass spectrometer were heated to 100°C to prevent condensation of the species eluted from the reactor.

3.9 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique where an ultra thin sample is imaged using a beam of high energy electrons. In bright field mode, the image is formed directly from occlusion of electrons at thicker regions of the sample. The areas with no sample appear bright. The resulting electron beam is then focused with a series of electromagnetic lenses to give a contrast image analogous to the image formed from an overhead projector. Transmission electron microscopy (TEM) was performed using a Phillips Tecnai F20 instrument with FEG. The instrument was operated at an accelerating voltage of 200 kV and all images were collected in brightfield mode. Samples were dispersed in ethanol before being loaded onto lacey/formvar carbon which was deposited on a 200 mesh copper grid. Post N₂O and post O₂ ODH samples were imaged to determine whether carbon fibers were present after reaction.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Influence of N₂O on Steady State C₂H₆ Oxidative Dehydrogenation

N₂ adsorption/desorption isotherms (see Figure 4-1) were collected for 10% Mo/Si:Ti. The results are clearly identifiable as type IV according to the IUPAC classification indicating strong adsorbent-adsorbate interactions. Monolayer adsorption begins first and occurs up to 0.1 P/Pₒ. Capillary condensation begins to occur at a relative pressure of 0.5 to 0.6 and begins leveling off near 0.9. Capillary evaporation is shifted to substantially lower relative pressures leading to a desorption hysteresis. This hysteresis is indicative of a mesoporous material with pores in the range of 2 to 50 nanometers. BET measurements indicate a surface area of 130m²/g in agreement with previous results on this catalyst [26] and the BJH adsorption calculations indicate a pore size distribution centered at 5nm (see Figure 4-2).

The catalytic activity of 10%Mo/Si:Ti for ethane ODH was determined at 600°C at contact times ranging from 0.46 to 1.0 mg s/cm³ using O₂ or N₂O as oxidant. The feed concentrations for these experiments were C₂H₆/O₂/He = 5/2.5/92.5 and C₂H₆/N₂O/He = 5/5/90. The sole reaction products during ODH reaction testing are C₂H₄, CO and CO₂.
Figure 4-1 – Nitrogen adsorption and desorption isotherms on 10%Mo/Si:Ti.
Figure 4-2 – Pore size distribution of 10%Mo/Si:Ti as determined from nitrogen adsorption isotherm.
Figure 4-3 shows the ethane conversion for each oxidant as a function of contact time. Regardless of the oxidant used, ethane conversion increases monotonically with contact time. Ethane conversion, when using oxygen, varies from 2.8% at 0.46 mg s/cm$^3$ to 4.3% at 1.0 mg s/cm$^3$. When using N$_2$O, the ethane conversion varies from 2.4% mg s/cm$^3$ to 4.1% at 1.0 mg s/cm$^3$. At a given contact time, ODH reactions run using oxygen always show greater ethane conversion than reactions run using nitrous oxide.

Figure 4-4 shows the selectivities for CO, CO$_2$ and C$_2$H$_4$ as a function of ethane conversion when using either O$_2$ or N$_2$O as oxidant. The main product observed when altering contact times was ethylene regardless of the oxidant used. Ethylene selectivities are always 75% and above while the next most abundant product, CO, always has selectivities of 15% and below. Ethylene selectivity is higher when using nitrous oxide than when using oxygen regardless of the ethane conversions achieved in these experiments. When ethane conversion is 4.2% using N$_2$O, ethylene selectivity is 85% while the experiment using O$_2$ achieves a selectivity of 83% at a much lower ethane conversion of 2.8% (the lowest conversion achieved when using O$_2$). At low ethane conversion, ethylene selectivity reaches as high as 88% when using nitrous oxide. Oxygen, on the other hand, starts at an ethylene selectivity of 83% at low ethane conversion and decreases with increasing conversion until reaching 75% at 4.3% ethane conversion. It should be noted that while using oxygen, the ethylene selectivity decreases much more quickly with increasing ethane conversion than when using nitrous oxide.

Carbon monoxide is the second most abundant product and its selectivity is always higher when using oxygen as oxidant during ethane ODH. CO selectivity varies from 12% to 15% at ethane conversions of 2.8% and 4.3%, respectively. When using
nitrous oxide, on the other hand, CO selectivity varies from 10% to 11% at ethane conversions of 2.4% and 4.2%, respectively. CO₂ selectivity is the lowest of all the products and, like carbon monoxide, it is more abundant when using O₂ as oxidant. CO₂ selectivity varies from 4.3% to 9.5% as ethane conversion varies from 2.8% to 4.7% when using oxygen. When using N₂O, CO₂ selectivity varies from 2.5% to 3.8% at 2.4 and 4.2% ethane conversion, respectively.

It is interesting to note that, when using N₂O as the oxidant, the product distribution is relatively invariant to ethane conversion. Though ethylene selectivity does decrease slightly and CO and CO₂ selectivities increase slightly with increasing ethane conversion, the trend is far less pronounced than when O₂ is used as oxidant, such that the change in selectivity is at least twice as high when using O₂ as opposed to N₂O. While changing the contact time has a similar effect on ethane conversion regardless of oxidant, the effect of contact time on selectivity is far more pronounced when using O₂.

The inverse relationship between ethane conversion and ethylene selectivity is well known and widely reported in the literature [9, 11, 26]. This phenomenon is due to the consecutive conversion of ethylene to CO and CO₂. The smaller decrease in C₂H₄ selectivity in the presence of N₂O suggests that the consecutive oxidation of C₂H₄ is suppressed when using nitrous oxide. When using O₂, on the other hand, the consecutive oxidation of C₂H₄ proceeds more quickly. As ethane conversion increases the concentration of ethylene also increases. This leads to a higher rate of ethylene combustion leading to lower ethylene selectivity. The increase in CO and CO₂ selectivities is similar when using the same oxidant.
Figure 4-3 – Ethane conversion at various contact times during steady-state ethane ODH. Reaction conditions: 600°C (●) C₂/N₂O/He = 5/5/90, (■) C₂/O₂/He = 5/2.5/92.5.
Figure 4-4 – Selectivity at various ethane conversions during steady-state ethane ODH at 600°C. (□) C$_2$H$_4$ selectivity C$_2$/N$_2$/O/He=5/5/90, (○) C$_2$H$_4$ selectivity C$_2$/O$_2$/He = 5/2.5/92.5, (♦) CO selectivity C$_2$/O$_2$/He = 5/2.5/92.5, (▲) CO selectivity C$_2$/N$_2$/O/He = 5/5/90, (■) CO$_2$ selectivity C$_2$/O$_2$/He = 5/2.5/92.5, (●) CO$_2$ selectivity C$_2$/N$_2$/O/He = 5/5/90.
Steady-state ethane ODH experiments were run at a constant ethane concentration of 10% and a varying concentration of oxidant. Figure 4-5 shows ethane conversion during ODH as a function of atomic O to C$_2$H$_6$ ratio. When using oxygen as the oxidant, the ethane conversion and ethylene yield change by 2% and 1% relative, respectively, as the O/C$_2$H$_6$ ratio changes from 0.5 to 2.0. When using nitrous oxide as oxidant, the ethane conversion and ethylene yield increase by over 25% and 24% relative, respectively, as the O/C$_2$H$_6$ ratio changes from 0.5 to 2.0.

The results shown in Figure 4-5 for O$_2$ are not surprising considering that numerous studies have shown that varying oxygen concentration during ODH of ethane has no effect on the olefin formation rate [12, 66, 86]. This is due to the vastly different time scales involved in catalyst oxidation by oxygen and catalyst reduction by C$_2$H$_6$. Transient reaction experiments monitored by UV-Vis have suggested that oxygen can oxidize the surface at rates of $10^3$ to $10^5$ times faster than the rate limiting C-H bond abstraction step over an alumina supported vanadium catalyst [67]. Even at relatively low O$_2$ concentrations the catalyst is fully oxidized and increasing O$_2$ concentration does not result in any greater degree of catalyst oxidation. The results shown in Figure 4-5 suggest that when using N$_2$O as oxidant in ethane ODH, the reoxidation step becomes kinetically relevant. It is conceivable that this step is kinetically relevant because of slower catalyst reoxidation when using N$_2$O. This possibility is explored in detail in following sections.

The selectivities of CO, CO$_2$ and C$_2$H$_4$ at various ethane conversions are shown in Figure 4-6 during experiments in which the O/C$_2$H$_6$ ratio was varied. Selectivities are only shown for the reaction run using N$_2$O as the oxidant because C$_2$H$_6$ conversion did.
Figure 4-5 – Ethane conversion at various atomic oxygen/ethane ratios during steady-state ODH. Reaction conditions: 600°C, W/F = 0.625 mg s/cm³, (○) 5% ethane, 2.5, 5, 7.5 and 10% nitrous oxide, balance helium and (■) 5% ethane, 1.25, 2.5, 3.75 and 5% oxygen, balance helium.
Figure 4-6 – Selectivities at various ethane conversions during ethane ODH using N₂O as oxidant, (▲) ethylene selectivity (■) CO₂ selectivity (●) CO selectivity.
not change in the experiments using O\textsubscript{2}. As ethane conversion increases, selectivity to ethylene decreases and selectivity to CO increases. This is consistent with the over-oxidation of C\textsubscript{2}H\textsubscript{4} to CO. This could be accounted for by an increase in the number of active oxygen species, capable of C\textsubscript{2}H\textsubscript{4} oxidation, with increasing N\textsubscript{2}O concentration.

4.2 Influence of N\textsubscript{2}O on Temperature Programmed C\textsubscript{2}H\textsubscript{6} ODH

It should be noted that the CO signal (m/z=28) also contains a contribution from fragments generated by CO\textsubscript{2}. Additionally, in the ODH experiments where N\textsubscript{2}O is oxidant, the CO\textsubscript{2} and N\textsubscript{2}O signals are not shown since both share a common mass to charge ratio of 44. In the experiments where O\textsubscript{2} is the oxidant, there is no overlap and the CO\textsubscript{2} signal is shown.

The temperature programmed ODH experiments show that substantially more ethylene is formed when using N\textsubscript{2}O as the oxidant than when using O\textsubscript{2} as the oxidant (see Figure 4-7 and Figure 4-8). Additionally, the ethylene signal appears to increase above the baseline at a temperature of 400 °C when using N\textsubscript{2}O. When using O\textsubscript{2} the ethylene signal leave the baseline until around 475°C. This is in agreement with steady state reaction results that show higher ethylene yields when using N\textsubscript{2}O. It is also clear that the CO signal (m/z=28) increases more gradually and is lower at 600 °C when N\textsubscript{2}O is the oxidant. This also agrees with the steady state reaction experiments where less CO\textsubscript{2} and CO were formed in the presence of nitrous oxide.

It is also interesting to note that the water signal leaves the baseline below 450 °C when using N\textsubscript{2}O as oxidant while the signal doesn’t leave the baseline until
Figure 4-7 – Temperature programmed reaction– C$_2$H$_6$ to N$_2$O ratio of 2:1 [37]
Figure 4-8– Temperature programmed reaction – \( \text{C}_2\text{H}_6 \) to \( \text{O}_2 \) ratio of 2:1 [37]
approximately 475°C when using O₂. Also the water signal seems to be higher at all temperatures when N₂O is the oxidant. However, once the signal leaves the baseline when using molecular oxygen the signal seems to increase at a more rapid rate. This behavior is somewhat surprising considering the stoichiometry of the selective and non-selective reactions. When using O₂ as the oxidant, more COₓ is formed and consequently we would expect more H₂O to be formed. In the ethane ODH reaction, 1 mole of water is formed for every 1 mole of ethane that is dehydrogenated. In the unselective combustion reactions, however, 3 moles of water is formed for every 1 mole of ethane consumed.

4.3 Post-Reaction Oxidation State

In order to investigate the oxidation state of the 10%Mo/Si:Ti catalysts during ODH, post-reaction X-ray photoelectron spectroscopic analyses were conducted after steady-state ethane ODH using either O₂ or N₂O as oxidant. XPS spectra of fresh 10%Mo/Si:Ti (see Figure 4-9) shows a single doublet at 232.8 and 236.0 eV corresponding to Mo 3d₅/₂ and 3d₃/₂ peaks, respectively [87, 88]. This indicates that the as prepared catalyst has molybdenum fully oxidized to Mo(VI) on the surface. Figure 4-10 4a shows the deconvoluted Mo3d spectrum for post-reaction ethane ODH using oxygen as the oxidant. The spectrum shows one doublet characteristic of Mo(VI) located at 232.8 and 236.0 eV corresponding to the Mo 3d₅/₂ and 3d₃/₂ peaks, respectively. There are no indications of additional peaks. These results show that the 10%Mo/Si:Ti catalyst was operating at a molybdenum oxidation state of 6⁺ and that the catalyst surface is not reduced when exposed to helium before transfer to the XPS chamber.
Figure 4-9 – X-ray photoelectron spectroscopy of Mo3d region collected on pristine 10% Mo/Si:Ti catalyst.
Figure 4-10– X-ray photoelectron spectroscopy of Mo3d region collected after steady-state ethane ODH using C₂/O₂/He = 10/5/85.
The deconvoluted Mo3d spectrum for post-reaction ethane ODH using nitrous oxide as oxidant is shown in Figure 4-11. This spectrum, in contrast to post-oxygen ODH, shows multiple molybdenum doublets. The intense Mo(VI) doublet is still present at 232.8 and 326.0 eV corresponding to Mo 3d$_{5/2}$ and 3d$_{3/2}$ peaks, respectively. Now, however, the Mo(VI) 3d$_{5/2}$ peak has a distinct shoulder on the low binding energy side. The de-convolution shows that there is a doublet at 230.7 and 233.8 eV with the lower binding energy peak component accounting for this shoulder. This doublet at 230.7 and 233.8 eV is associated with Mo(V) 3d$_{5/2}$ and 3d$_{3/2}$ peaks, respectively. A peak due to Mo(IV) 3d$_{5/2}$ is also clearly seen at 229.2 eV and the corresponding 3d$_{3/2}$ peak is located at 232.4 eV [87, 88].

The XPS results indicate that molybdenum is in a lower oxidation state in the post-N$_2$O oxidative dehydrogenation sample. The post-N$_2$O sample contained Mo(VI), Mo(V) and Mo(IV) whereas the post-O$_2$ sample appeared fully oxidized with only Mo(VI) appearing. The post-N$_2$O ODH catalyst has peak areas of Mo(VI)/Mo(V)/Mo(IV) = 84/8.3/7.7 corresponding to an average molybdenum oxidation state of 5.8. Similar XPS results have been reported on vanadium catalyst during propane ODH with N$_2$O [89]. 16% of the molybdenum atoms are reduced after post-N$_2$O ODH. Kondratenko et al. [82, 84] have reported similar results using UV-Vis. Their vanadia catalysts were in a more reduced state when using N$_2$O as the oxidant in propane ODH. This may suggest that N$_2$O is either unable to oxidize certain sites or that the oxidation of the catalyst is slower leaving a greater fraction of sites reduced. It should also be noted that we observed visible changes in color of post-N$_2$O ODH 10%Mo/Si:Ti. Fresh 10%Mo/Si:Ti is white and the color remains unchanged after ODH using O$_2$. After ODH
Figure 4-11 – X-ray photoelectron spectroscopy of Mo3d region collected after steady-state ethane ODH using C_2/N_2O/He = 10/10/80.
using N₂O, however, the catalyst color has become purple and it is well known that MoO₂ is violet in color.

Clearly, the working oxidation state of the catalyst is different when performing ODH with O₂ or N₂O. It is widely accepted that the oxidative dehydrogenation of ethane over easily reducible transition metal oxides proceeds via a Mars-van-Krevelen redox mechanism. During ODH, the catalyst surface is reduced as lattice oxygen atoms activate ethane molecules, ultimately forming olefins. Ethane must first adsorb to a surface or lattice oxygen atom (O*) and a C-H bond must be cleaved forming an alkyl intermediate (reaction 1) and a hydroxyl group on the catalyst surface (reaction 2). This initial cleavage of the ethane C-H bond is considered the rate limiting step and the literature consistently shows that ethylene formation rates are first order in ethane concentration [55, 66]. The alkyl intermediate, which is adsorbed to an oxygen atom, then loses a second hydrogen atom forming ethylene and another hydroxyl group on the catalyst surface. Finally, two hydroxyl groups combine to form water and a lattice vacancy (V*) leaving the active site in a reduced state. Gas phase oxygen must then adsorb to a vacancy and reoxidize the active site (reaction 3).

\[
\begin{align*}
C₂H₆ + O* & \rightleftharpoons C₂H₆O* \quad (1) \\
C₂H₆O* + O* & \rightarrow C₂H₅O* + OH* \quad (2) \\
O₂ + 2V* & \rightarrow 2O* \quad (3)
\end{align*}
\]

Changes in oxidation state could certainly account for the behavior observed in Figure 4-4. A catalyst in a more oxidized state (such as during ODH with O₂) would have a greater number of reactive lattice oxygen atoms. Therefore, when the ethane conversion is increased, the ethylene that is formed would more likely have access to a
lesser number of reactive lattice oxygen atoms. During N$_2$O ODH, the ethylene molecule would be near too few lattice oxygen atoms to oxidize to CO or CO$_2$ which would require 4 and 6 oxygen atoms, respectively. This could account for the relative invariance in product selectivities vs. ethane conversion (Figure 4-4) when using N$_2$O as the oxidant. This is a concept known as site isolation and was originally proposed by Graselli [90, 91] to account for hydrocarbon oxidation and ammoxidation. Grasselli and Callahan [90] stated that oxidation catalysts become selective when the number of active oxygen species on the surface are limited and when these species are spatially isolated from one another. This has been proposed as one possible explanation for the improved selectivities when using N$_2$O in propane ODH over vanadia [62, 82-84].

Another possible explanation that has arisen from DFT studies on propane over supported vanadium catalysts suggests the existence of a peroxovanadate intermediate when using O$_2$ as the oxidant [85]. It has been reported that these peroxovanadate species, which are active for propane oxidation and 10 to 100 times more active for propene oxidation, cannot form in the presence of N$_2$O. Peroxomolybdate species have been observed in solution by Raman spectroscopy and $^{95}$Mo NMR [92-94]. It is possible that O$_2$ is forming active peroxomolybdate species during the reoxidation process. The absence of peroxomolybdate species could account for a higher selectivity when using N$_2$O. However, the increases in ethane consumption and ethylene formation with N$_2$O concentration, shown in Figure 4-5, cannot be explained by the presence of these peroxomolybdate species.
The XPS results are also consistent with the ODH reaction data collected at different oxidant concentrations (Figure 4-5). When using O₂ as the oxidant, increasing the O₂ concentration does not lead to an increase in ethylene formation rate because the molybdenum is already fully oxidized. When using N₂O as the oxidant, however, an increasing concentration of N₂O will increase the rate of catalyst reoxidation. This will lead to a steady-state with a higher proportion of oxidized molybdenum. In a Mars-van Krevelen mechanism, the rate of ethane C-H bond activation is proportional to the number of active oxygen sites on the catalyst.

4.4 Reduction and Oxidation of 10%Mo/Si:Ti

Temperature programmed reduction and reoxidation experiments were performed to determine the redox properties of the 10%Mo/Si:Ti catalyst. Temperature programmed reduction of 10%Mo/Si:Ti in 5% H₂/N₂ gives a single hydrogen consumption peak located at 460°C (see Figure 4-12) suggesting a single reduction step. Integration of peak areas suggests that the catalyst is proceeding from an oxidation state of Mo(VI) to Mo(IV) during the reduction.

\[ \text{Mo}^{6+}O_x + H_2 \rightarrow \text{Mo}^{4+}O_{x-1} + H_2O \]

Figure 4-13 shows the reoxidation of 10%Mo/Si:Ti using 2% O₂/He or 4% N₂O/He. The results for oxygen and nitrous oxide both show a single oxidant consumption peak suggesting a single oxidation step. O₂ is able to oxidize the 10% Mo/Si:Ti at much lower temperatures than N₂O. O₂ consumption reaches a maximum at 265°C while the N₂O peak does not reach a maximum until 481°C suggesting that oxygen is a stronger
Figure 4-12 – Temperature programmed reduction using 5% H₂/He.
oxidizing agent than nitrous oxide. The result supports the conclusions reached from steady-state ethane ODH and post-reaction XPS that the catalyst reoxidation was kinetically relevant when using N₂O and that molybdenum was more reduced after using N₂O as oxidant.

During the nitrous oxide TPO, a total of 0.16 mmol of atomic oxygen was consumed while the O₂ TPO showed a total of 0.15 mmol of atomic oxygen consumed. These values correspond to the oxidation of all the molybdenum in the sample from Mo(IV) to Mo(VI) to within 5% for both oxidants. These results suggest that the peaks observed in both the TPR and TPO experiments are due to the catalyst oxidation state changing from Mo(VI) to Mo(IV) and vice versa.

It is interesting to note that, according to the measured N₂O consumption, nitrous oxide is able to fully oxidize the molybdenum in 10%Mo/Si:Ti from Mo(IV) to Mo(VI) even though it does not occur until a higher temperature.

The structure of molybdenum in the 10%Mo/Si:Ti catalyst was monitored using Raman spectroscopy before and after reduction by 5%H₂/N₂ (see Figure 4-14). The fresh pre-reduced catalyst shows a band at 635 cm⁻¹ corresponding to anatase titania. Previous research on this catalyst using X-ray diffraction has shown a broad anatase titania band indicating its presence in a finely dispersed state [24]. A broad weak band from 750 cm⁻¹ to 950 cm⁻¹ is assigned to the Mo-O-Mo asymmetric stretch and the Si-O-Si symmetric stretch [24]. The band located at 995 cm⁻¹ is due to terminal Mo=O groups.
Figure 4-13– Temperature programmed oxidation of pre-reduced 10% Mo/Si:Ti with 2%O$_2$/He and 4%N$_2$O/He.
Previous work on our catalyst has shown that crystalline molybdenum will not form until loading levels of 20wt% molybdenum [26, 39]. Crystalline MoO$_3$ is a very strong scatterer and would be easily detected by sharp, intense bands at 820cm$^{-1}$ and 995cm$^{-1}$. After reduction in hydrogen, the signal intensity decreases significantly. Therefore, the spectrum of the reduced sample was collected using longer acquisition times and more scans than the other spectra. Though the intensity of all bands has decreased, the same bands as the fresh catalyst are observed. Recent literature has demonstrated that molybdenum on silica supports possess two terminal oxygen bonds [46, 95]. The oxidant consumption from the TPR/TPO results presented above suggest that the catalyst is reduced from Mo(VI) to Mo(IV). With this extent of reduction, and assuming that at least some of the molybdenum is in a dioxo structure, Mo=O terminal bonds would remain. Figure 4-15 shows some of the possible molybdenum structures on the catalyst.

The catalyst structure was also monitored after reoxidation by N$_2$O or O$_2$. The observed bands are identical for the pre-reduced catalyst, the catalyst reoxidized with O$_2$ and the catalyst reoxidized with N$_2$O. Bands are still observed at 635cm$^{-1}$, 820cm$^{-1}$ and 995cm$^{-1}$ but the sharp, intense bands located at 995cm$^{-1}$ and 820cm$^{-1}$ associated with crystalline MoO$_3$ are not present. This suggests that both oxygen and nitrous oxide are able to restore the molybdenum to its pre-reduction state. Apparently molybdenum atoms are bound to the support and not able to aggregate together to form metallic molybdenum at reduction temperatures used in this study. If this occurred, crystalline molybdenum could form during the reoxidation process and would be readily visible in Raman. These results agree with the TPR and TPO results that indicated reduction of Mo(VI) to Mo(IV) and subsequent reoxidation back to the original state regardless of the oxidant used.
Figure 4-14 - spectra of fresh, 5% H₂/N₂ reduced, 4% N₂O/He reoxidized and 2% O₂/He reoxidized 10% Mo/Si:Ti. Bulk MoO₃ included as reference.
Figure 4-15 – Possible molybdenum structures for fully oxidized (6+) and reduced molybdenum (4+).
Additionally, this provides evidence that the structure of the molybdenum species is not changing with reduction and reoxidation regardless of oxidant used.

4.5 10%Mo/Si:Ti Activation Energies of Reoxidation Using O₂ and N₂O

Temperature programmed reoxidation (TPO) studies were performed at varying temperature ramp rates to determine activation energies of reoxidation using N₂O and O₂. 10%Mo/Si:Ti was pre-reduced in 5% H₂/He before being oxidized in 2% O₂/He or 4% N₂O/He at ramp rates of 10, 13, 16 and 19°C/min. Figure 4-16 shows O₂ TPO experiments at varying heating rates while Figure 4-17 shows a Kissinger plot for this experiment. As heating rates increase, Tₘₐₓ shifts higher from 460.5 to 487.5°C. Figure 4-18 shows that during N₂O TPO experiments, Tₘₐₓ shifts from 244°C to 274°C as heating rate increases from 10 to 19°C/min. Figure 4-19 show plots of ln(β/Tₘₐₓ²) vs. 1/Tₘₐₓ used to determine the activation energies of reoxidation using O₂ and N₂O. Figure 4-17 gives a slope of -4.98 which corresponds to an activation energy of 41 kJ/mol for reoxidation using O₂. The values used to calculated this activation energy are presented in Table 4-1. Figure 4-19 gives a slope of -11.76 which corresponds to an activation energy of 98 kJ/mol for reoxidation using N₂O. The values used for this activation energy calculation are presented in Table 4-2. The use of N₂O as oxidant makes the activation energy of reoxidation much closer to the apparent ODH activation energy which suggests that the rates of catalyst reoxidation and reduction will be much closer when using N₂O as oxidant. Heracleous et al. [96] have shown that ethane ODH on titania and alumina supported molybdenum catalysts had apparent
Figure 4-16 - Temperature programmed oxidation of pre-reduced 10% Mo/Si:Ti (in 5% H₂/He) using various temperature ramp rates and 2%O₂/He.
Figure 4-17- Determination of activation energies using Kissinger method for 2% O₂/He temperature programmed oxidation at various heating rates.
Table 4-1 - Determination of activation energies using Kissinger method for 2% O₂/He temperature programmed oxidation at various heating rates.

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>Temp °C</th>
<th>Temp K</th>
<th>$\ln (\beta/T_{max}^2)$</th>
<th>$1000/T_{max}$ (K⁻¹)</th>
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<td>19</td>
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<td>265</td>
<td>538</td>
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<td>10</td>
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<td>517</td>
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<td>1.93</td>
</tr>
</tbody>
</table>
Figure 4-18 - Temperature programmed oxidation of pre-reduced 10% Mo/Si:Ti (in 5% H₂/He) using various temperature ramp rates and 4%N₂O/He.
Figure 4-19 - Determination of activation energies using Kissinger method for 4% N₂O/He temperature programmed oxidation at various heating rates.
<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>Temp °C</th>
<th>Temp K</th>
<th>ln ((\beta/T_{\text{max}}^2))</th>
<th>1000/T_{\text{max}} (K⁻¹)</th>
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<td>760.5</td>
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<td>481</td>
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<td>733.8</td>
<td>-10.89</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Table 4-2 - Determination of activation energies using Kissinger method for 4% N₂O/He temperature programmed oxidation at various heating rates.
activation energies of 104 and 91 kJ/mol, respectively using O₂ as oxidant. Vanadia based catalysts have been shown to have activation energies of 120 +/- 15 kJ/mol during ethane ODH with O₂ [36].

The TPO experiments show that the activation energy of reoxidation using N₂O is 2.4 times higher than that required when using O₂. This difference likely accounts for the ability of O₂ to oxidize the reduced sample at lower temperature than N₂O. At a given extent of conversion and temperature, we can calculate a rough estimate of differences in the TPO reoxidation rates of O₂ and N₂O using the following equation.

\[
r_{O₂}/r_{N₂O} = k_{O₂}/k_{N₂O} \exp[(E_{N₂O}-E_{O₂})/RT]
\]

where \( r \) is the rate of reoxidation, \( k \) is the pre-exponential factor and \( E \) is the activation energy of reoxidation. Argyle et al. [67] suggested that the rate of reoxidation during propane ODH with O₂ was \( 10^3 \) to \( 10^5 \) times faster than the C-H bond breaking step. Based on our TPO activation energies and assuming equal pre-exponential factors, the O₂ reoxidation rate would be approximately 1700 times faster than the N₂O reoxidation rate at 550°C.

N₂O can adsorb to the catalyst surface either through a nitrogen atom or an oxygen atom. DFT calculations on a vanadia based catalyst have suggested that adsorbed N₂O is more stable when adsorbed via a nitrogen atom but only decomposes when adsorbed through an oxygen atom [85]. This limitation in the orientations that lead to reaction would result in a decreased pre-exponential factor relative to oxygen. Additionally, the non-reactive adsorption of N₂O would lead to a decrease in the number of sites available for reoxidation by nitrous oxide and a further decrease in the reoxidation rate. Therefore, we may expect the O₂ pre-exponential factor to be greater
than N₂O so that the difference between reoxidation rates would be even higher. The O₂:N₂O reoxidation rate ratio of 1700, arrived at by assuming equal pre-exponential factors, serves as a lower boundary for the actual value. Based on these results, we can expect that reoxidation with N₂O proceeds so much more slowly than when using O₂ that the reoxidation step, it is no longer kinetically decoupled from the reduction process.

XPS experiments show that molybdenum has an average oxidation state of 5.8 during ethane ODH with N₂O. Looking at the TPO experiment with 10°C/min temperature ramp rate and picking an extent of reduction of 0.12 (which occurs at 520°C) allows an estimation of the rate of N₂O consumption rate at conditions similar to our steady-state ethane ODH experiments when N₂O was the oxidant. The TPO shows an N₂O consumption rate of 6.0x10⁻⁴ mmol N₂O/s g catalyst. At 500°C and a fraction of reduction equal to 0.17, 7.3x10⁻⁴ mmol N₂O/s g catalyst were consumed. As a comparison, the rate of ethane consumption using 50 ccm 5% N₂O, 5% C₂H₆ during steady-state ethane ODH using N₂O at 500°C is 3.0x10⁻⁴ mmol C₂H₆/s g catalyst. Under similar conditions, N₂O consumption is approximately twice as fast as ethane consumption indicating that it would be a kinetically relevant step in the ODH reaction. It is impossible to make a similar estimate using the O₂ TPO because the catalyst is always fully oxidized at temperature well below 500°C.

Considering that N₂O has a higher activation energy and a higher enthalpy of formation than O₂, the transition state that O₂ passes through must be of lower energy than that available to N₂O. The most obvious choice of transition states available to O₂ but not to N₂O would be a peroxomolybdate type species (see Figure 4-20). Peroxomolybdates have been detected spectroscopically in liquid phase reactions [92-94].
Additionally, a peroxomolybdate species has been suggested as an intermediate in the oxidation of reduced molybdenum with O₂ [44]. It is possible that the peroxomolybdate species could provide a low energy transition state not accessible to nitrous oxide but, to the author’s knowledge, there have been no theoretical studies of molybdenum oxidation using O₂ and N₂O that could help to confirm or deny this.

4.6 Surface Carbon Formation

Post-ODH reaction temperature programmed oxidation experiments were conducted on spent 10%Mo/Si:Ti catalyst after 6 hours of time on stream. TPO experiments used 5% O₂ in helium and tested catalysts after ethane ODH where either O₂ or N₂O was oxidant. Figure 4-21 shows the CO₂ profile for ethane ODH spent catalysts. The catalyst that used oxygen as the oxidant during ethane ODH shows no signs of CO₂ evolution during the TPO. The catalyst that used N₂O as the oxidant during ethane ODH, however, shows a single well defined peak with CO₂ evolution beginning near 330°C and reaching a maximum at 440°C.

It is unlikely that these are intermediates because the reactor was flushed with helium for 30 minutes at 600°C directly before conducting the TPO. More likely, the TPO results indicate the presence of some kind of surface carbon species after ODH using N₂O. A peak from m/z=18 (not shown) corresponding to water was also observed with a maximum near 440°C. This indicates that the surface contains carbon and hydrogen indicating a large portion of the carbon must be in non-graphitic. It should be noted that, in separate ODH experiments using N₂O as oxidant conducted at the same conditions, catalyst activity for ODH was monitored and did not change with 15 hours on
Figure 4-20– Possible peroxomolybdate species.
stream indicating that the carbon deposition proceeds very slowly or ceases after a certain time.

Bands corresponding to graphitic carbon and disorders in graphitic carbon, known as the g and d-bands, are often detected using Raman spectroscopy during alkane dehydrogenation in the absence of oxidant [97]. These bands would be located near 1580 and 1360 cm\(^{-1}\), respectively [98]. In-situ ODH Raman experiments failed to show these bands indicating that graphitic carbon is not present. Two sharp, intense bands were present, however, at 1372 and 1401 cm\(^{-1}\) (see Figure 4-22). The sharp band at 1372 cm\(^{-1}\) is attributed to CH\(_3\) deformation modes. The higher wavenumber band is more difficult to assign but it may be due to CH\(_2\) deformation mode which typically occur around 1450 cm\(^{-1}\) or a second CH\(_3\) deformation shifted to higher wavenumbers.

Additionally, ex-situ transmission electron microscopy experiments (Figure 4-23) conducted after ethane ODH using N\(_2\)O failed to show the presence of any carbon fibers. No differences could be seen between post O\(_2\) and post N\(_2\)O ODH samples. All indications are that the catalyst does not have graphitic carbon on its surface after ethane ODH using N\(_2\)O or O\(_2\) as the oxidant.

X-ray photoelectron spectroscopy studies were conducted on fresh 10%Mo/Si:Ti and 10%Mo/Si:Ti exposed to 6 hours of ethane ODH using O\(_2\) or N\(_2\)O. Figure 4-24 compares the C1s spectra for fresh sample, post-O\(_2\) ODH sample and post-N\(_2\)O ODH sample. The fresh 10%Mo/Si:Ti and the post-O\(_2\) ODH samples appear very similar with noisy broad peaks near 284 eV. Considering the similarities between the fresh and post-
Figure 4-21 – CO₂ profiles during temperature programmed oxidation of post-reaction 10% Mo/Si:Ti catalyst. (a) C₂/O₂/He = 10/5/85, (b) C₂/N₂O/He = 10/10/80.
Figure 4-22 – Post-N$_2$O ODH reaction Raman spectroscopy.
Figure 4-23 – Post-N₂O ODH transmission electron microscopy.
O₂ ODH samples, it is likely that the surface carbon has not undergone any changes with ethane ODH using O₂. The carbon is likely atmospheric contamination or may be organic precursors that cannot be decomposed.

The post-N₂O ODH sample, on the other hand, appears quite different. It has a significantly higher C1s signal than either the post-O₂ ODH sample or the fresh sample. The C1s/Mo3d, C1s/Si2p and C1s/Ti2p ratios are 6.6, 5.6 and 6.7 times higher for the post-N₂O sample than for the post-O₂ ethane ODH sample. The results unambiguously demonstrate that the post-N₂O 10%Mo/Si:Ti has a substantially greater proportion of carbon on its surface than the post-O₂ ODH sample. Additionally, the C1s spectra for the post-N₂O ODH sample is well structured and can easily be deconvoluted. Figure 4-25 shows the deconvoluted C1s spectra for post-N₂O ODH 10%Mo/Si:Ti. The two most intense peaks located at 284 and 285.5 eV correspond to sp² and sp³ hybridized C-C respectively [99, 100]. The small peak located at 287.5 eV is assigned to C=O functional groups [101]. The small peak at 289.3 can be assigned either to COO or COOH functional groups [101, 102]. These oxygen containing functional groups could form either during ethane oxidative dehydrogenation. The sp³ carbon peak is by far the most intense peak constituting 63% of the total deconvoluted peak area while sp² hybridized carbon accounts for 24%. This result agrees with Raman spectra and transmission electron microscopy experiments (neither experiment shown) that show no presence of graphitic carbon. XPS results indicate that a small fraction of the carbon is sp² hybridized. Most likely the carbon takes an amorphous polymeric form.
Figure 4-24 – X-ray photoelectron spectroscopy of C1s region collected after steady-state ethane ODH - comparison of fresh, post-O₂ ODH and post-N₂O ODH spectra.
Figure 4-25 – X-ray photoelectron spectroscopy of C1s region collected after steady-state ethane ODH - deconvolution of post-N₂O ODH spectra.
CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

Ethane oxidative dehydrogenation reaction results show that, when using O$_2$ as the oxidant, the conversion of ethane increases more quickly with contact time than when using N$_2$O as oxidant. Selectivity to ethylene decreases more quickly with conversion when using O$_2$ as the oxidant as well. Additionally, when varying the oxidant concentration, an increase in ethane conversion and ethylene formation rate is observed only when using N$_2$O as oxidant. For oxygen, an increase in oxidant concentration has no effect on ethane conversion. Considering these reaction results and the results of post reaction XPS that show the post O$_2$ ODH sample only has Mo (VI) while the post N$_2$O ODH sample has Mo(VI) and Mo(IV), it is concluded that the oxidation state is responsible for the observed behavior.

These results, considered together, can be explained by a concept first proposed by Callahan and Grasselli in 1963 [91]. Site isolation has been invoked a multitude of times to explain the relationship between yield and catalyst oxidation state in selective oxidation reactions [90, 103-105]. Site isolation states that spatially isolated collections of lattice oxygen atoms are required to obtain selectivity in selective oxidation reactions. The number of these active oxygen sites dictates the reaction pathway. For instance, if
ethane were reacted at a site with access to two reactive oxygen atoms, the ultimate product would not be CO or CO₂ because they require more atomic oxygen per ethane molecule to form (see Figure 5-1).

Site isolation can explain the tendency for increasing COₓ selectivity to increase more quickly during O₂ ODH as contact time is increased. When 10% Mo/Si:Ti is in a more oxidized state, increasing the ethane conversion will inevitably lead to more COₓ formation because more surface ethylene is created and there is great amount of oxygen available for reaction. When using N₂O, on the other hand, there are fewer active oxygen species and increasing the ethane conversion will have a lesser effect on COₓ selectivity. This hypothesis can also explain the data in Figure 4-5 and Figure 4-6. The molybdenum is fully oxidized when using O₂ so increasing the O₂ concentration will have no effect on the number of lattice oxygen atoms available for reaction. Increasing the N₂O concentration will increase the rate of reoxidation leading to a steady-state with more Mo(VI), and consequently, higher ethane conversion and ethylene formation rates.

Callahan and Grasseli [91] applied Monte Carlos simulations of their theory of site isolation to the selective oxidation of propylene to acrolein. They concluded that as catalyst oxidation state increased, the conversion of propylene decreased. They also showed that the selectivity towards acrolein increased as catalyst oxidation state decreased. The non-selective products, CO and CO₂, were selectively formed at higher catalyst oxidation state. This relationship between propylene conversion, acrolein selectivity and catalyst oxidation state led to the conclusion that intermediate oxidation states lead to the higher yield of acrolein. Hence, the highest yields are achieved when a balance between activity and selectivity is struck. Considering that during ethane ODH
with O₂, the catalyst is in a fully oxidized state, decreasing the catalyst oxidation state would lead to higher yields. It is likely that the higher yields obtained when using N₂O are due to this effect.

It should be noted that contributions from adsorbed oxygen species cannot be ruled out. Therefore, at this time, we cannot state that the differences in ethane ODH activity and selectivity when using N₂O are due solely to the state of catalyst reduction. There is, however, strong evidence that the catalyst is operating in a lower oxidation state when using N₂O as the oxidant and the site isolation hypothesis can be used to explain the steady-state reaction data obtained.

Temperature programmed reduction and reoxidation experiments demonstrated that the 10%Mo/Si:Ti reoxidation activities when using O₂ and N₂O were 41 and 98 kJ/mol, respectively. The most obvious explanation for the lower activation energy when using O₂ as oxidant is that O₂ can form peroxomolybdate species which would not be accessible to N₂O. This may provide a lower energy transition state during catalyst reoxidation with O₂.

At 550°C, the rate of reoxidation using N₂O is at least 1700 times slower than the rate of reoxidation using O₂. Reported literature values of activation energies for ethane and propane ODH on molybdenum and vanadium catalysts vary from 90 to 120 kJ/mol [36, 106]. These values are similar to the reoxidation activation energy when using N₂O which suggests that the rates of catalyst reduction and oxidation would be close to one another when using N₂O as the oxidant. The rate of reoxidation when using N₂O was 6.0x10⁻⁴ mmol N₂O/s g catalyst at 520°C and an extent of reduction of 0.12. This is approximately twice as fast as the steady-state rate of C₂H₆ consumption during oxidative
dehydrogenation. This means that the reoxidation step is kinetically relevant when N₂O is used as the oxidant which is in stark contrast to the situation when O₂ is oxidant. This helps explain the steady-state reaction data shown in Figure 4-5 and Figure 4-6.

Temperature programmed oxidation experiments demonstrated the presence of surface carbon species on the catalyst surface after ODH using N₂O as oxidant. This suggests that N₂O does not oxidize all the carbon species on the surface like O₂ does. Time on stream ODH experiments demonstrate that the catalyst activity does not decrease with time suggesting that the rate of carbon deposition is very slow or that the carbon deposition stops or reaches a steady state. Post N₂O ODH Raman experiments show bands characteristic of organic CH₃ and possibly CH₂ deformation modes. Additionally, no g or d-bands associated with graphitic carbon were detected on the catalyst surface. Together with post reaction XPS experiments that show the presence of predominantly sp³ and some sp² hybridized carbon, suggest that some sort of polymeric amorphous carbon species are present on the catalyst surface during ODH with N₂O.

Clearer insights into the workings of redox catalyst for oxidative dehydrogenation may be gained through further study of ODH using N₂O as the oxidant. Well controlled preparation of simple supported catalysts could be useful to elucidate the effects of N₂O during ODH. Using inactive, high surface area supports such impregnated with small quantities of molybdenum would lead to simple isolated monomeric molybdenum structures. By gradually increasing the loading, it would be possible to see how the isolation of sites affects the catalyst activity and selectivity. Additionally, reactions could be run with O₂ and N₂O to determine differences with oxidant on catalysts with different molybdenum loadings.
With these catalysts, it is easy to determine the turnover frequency during oxidative dehydrogenation. It may be particularly insightful to determine the oxidation state in-situ using UV-Vis spectroscopy. If the oxidation states of the catalysts can be matched during O₂ and N₂O oxidation, it could be determined whether the oxidation state alone is responsible for the changes in activity and selectivity. Based on the number of oxidized sites during each reaction, a “true” turnover frequency could be determined. This turnover frequency would account for the number molybdenum species that are not active due to being in a more reduced state.

Important mechanistic properties could be determined using O¹⁸ labeled N₂O. Steady-state transient isotopic kinetic analysis experiments could provide detailed information about the reaction mechanism during ODH with N₂O. In these experiments, an ODH reaction would be carried out using O₂¹⁶. After steady-state is reached a quick switch is performed so that a gas of the same composition is now flowing over the catalyst but instead of O₂¹⁶ as the oxidant, O₂¹⁸ would be the oxidant. The results can be measured by mass spectrometry to determine when the different isotopes appear in the products. These types of experiments have been performed in the literature using O₂ to determine the reversibility of elementary steps such as O₂ dissociation and the reaction of hydroxyls to form water. Using labeled N₂O would allow the determination of N₂O dissociations reversibility and whether the reaction mechanism is the same with N₂O and O₂. If a switch from O¹⁶ to O¹⁸ labeled N₂O was conducted, substantial lags in the time required for O¹⁸ containing H₂O to appear would suggest that the reaction is occurring through lattice oxygen not through adsorbed oxygen species.
Figure 5-1 – Simplified representation of effect of catalyst oxidation state
PART 2

PREFERENTIAL OXIDATION OF CARBON MONOXIDE
CHAPTER 6

INTRODUCTION TO PREFERENTIAL CARBON MONOXIDE OXIDATION

Fuel cells directly convert chemical energy into electricity with efficiencies greater than those achieved by heat engines. There are a number of kinds of fuel cells such as solid oxide fuel cells, alkaline fuel cells, molten carbonate fuel cells and proton exchange fuel cells. The cells are constructed of different materials, operate at different temperatures and utilize different kinds of fuels. Proton exchange membrane (PEM) fuel cells have attracted significant interest due to their low temperature of operation (80°C), high power density, and high efficiency. Additionally, PEM fuel cells are environmentally benign. When hydrogen is used as the fuel, a PEM fuel cell only generates water exhaust. A doubling of the world’s energy needs by 2050 and the need for energy sources that do not emit carbon dioxide and other pollutants has prompted an intense effort to promote a “hydrogen economy” as a long term solution for energy security. Proton exchange membrane (PEM) fuel cells promise to be clean and efficient alternatives to combustion of fuels for power generation in stationary and mobile applications [107, 108].
Hydrogen can be produced from a diverse collection of domestic resources including biomass, coal, natural gas or from any source of electricity through the electrolysis of water. Current production of hydrogen for the refining industry is performed mainly through the reforming of natural gas

\[ CH_4 + H_2O \rightarrow 3H_2 + CO \]

During this process, a substantial amount of CO is formed. This process is typically followed by a water gas shift reactor. The water gas shift reaction is thermodynamically limited at the high temperatures necessary to obtain sufficient reaction rates.

\[ CO + H_2O \rightarrow H_2 + CO_2 \]

Therefore, there are typically two water gas shift reactors used to treat the effluent from a reforming process: a high temperature reactor and a low temperature reactor. Even at low temperatures, however, the water gas shift reactor is unable to reduce the CO concentrations to less than 0.2-2 vol% [109-111].

Unfortunately, the platinum anode materials used in PEM fuel cells are easily poisoned by trace amounts of carbon monoxide. It is estimated that CO concentrations must be reduced to less than 10 ppm for a Pt anode and less than 100 ppm for CO tolerant alloy anodes [109-111]. The United States Department of Energy (DOE) Hydrogen Analysis Group (H2A) has devised standards to estimate the cost of hydrogen production and the DOE set a goal of 2 to 3 dollars per gallon of gasoline equivalent (gge) delivered at the pump.

There are a number of available methods for purification of H2 stream such as pressure-swing adsorption, Pd membrane separation and catalytic methanation. One
particularly attractive method of CO removal is the preferential oxidation (PROX) of carbon monoxide in hydrogen rich streams. This technique offers the benefits of low cost and ease of implementation. The challenge in the PROX reaction is to find catalysts that are active and selective in the appropriate temperature window. The loss of hydrogen due to an undesired side reaction can reduce the value of the PEM feed stream. The catalyst should operate at a temperature between that of the low-temperature water gas shift reactor (250°C) and the PEM fuel cell (80°C). In this temperature window, catalysts must be active for the desired CO oxidation reaction and inactive for the undesired H₂ combustion reaction.

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \quad (\Delta H_{\text{rxn}}^0 = -283 \text{ kJ/mol}) \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} \quad (\Delta H_{\text{rxn}}^0 = -242 \text{ kJ/mol})
\end{align*}
\]
7.1 Early Work

Figure 7-1 shows the network of possible reactions during preferential oxidation of carbon monoxide (PROX). The desired reaction is the oxidation of CO to form CO₂. In the presence of hydrogen, however, other undesired reactions become possible. Hydrogen combustion can occur, consuming H₂ and O₂ to form H₂O. Also, CO can react with H₂ in the methanation reaction to form CH₄. While this reaction would eliminate the undesired CO, it would also consume hydrogen resulting in a fuel penalty.

Early work on the preferential oxidation of carbon monoxide (PROX) reaction was performed to purify hydrogen feed streams for the production of ammonia. Supported platinum, rhenium and ruthenium catalysts were shown to be effective for the PROX reaction [112]. Some of the first PROX research to be published specifically in regard to purifying PEM feed streams was conducted by Oh and Sinkevitch [113]. They reported high activity for Ru/Al₂O₃ catalysts and high selectivities for both Ru/Al₂O₃ and Rh/Al₂O₃.
Figure 7-1 – PROX reaction scheme

$\text{CH}_4 + \text{H}_2\text{O}$

$\rightarrow$ $\text{O}_2 \rightarrow \text{CO} \rightarrow \text{CO}_2$

$\rightarrow \text{H}_2 \rightarrow \text{H}_2\text{O}$

[Methanation] [CO oxidation] [H$_2$ combustion]
7.2 Gold and Platinum Catalysts

Despite their high costs, noble metal catalysts are by far the most studied catalysts in the CO oxidation literature [114-121]. In particular, supported platinum and gold catalysts have been among the most frequently studied catalysts for the PROX reaction. Early work consisted of supporting platinum on zeolites and showed good activity and selectivity [121, 122]. A number of promoted platinum containing catalysts have been tested in the PROX reaction. The inclusion of nickel, cobalt and sodium in platinum based samples has resulted in highly performing PROX catalyst.[123-125]. At low temperatures, supported gold catalysts have been shown to be quite active, however the selectivity rapidly decrease as temperature is increased [126]. For both platinum and gold catalysts, it has been proposed that H\textsubscript{2} and CO compete for adsorption sites on the metal atoms [127, 128]. In general, platinum is considered more active than gold but gold tends to have higher O\textsubscript{2} selectivity to CO\textsubscript{2} at low temperatures. Additionally, the cost associated with the use of platinum or gold in the catalysts is of great concern. The development of a low cost transition metal catalyst could offer significant cost benefits over the use of precious metal catalysts.

7.3 Non-Precious Metal Catalysts

One recent trend in the literature has been the investigation of ceria supported catalysts. Ceria is able to easily store, release and transport large quantities of oxygen. Typically, platinum or gold are supported on the ceria [116, 129-132] but, more recently, copper on ceria has been used with good results [133-137]. The interface between the
active metal and CeO$_2$ can be important because ceria can provide oxygen to CO species adsorbed on the active metal. This interaction can result in a synergistic effect on reaction activity and is particularly important on Cu on CeO$_2$ catalysts [136, 138]. The copper on ceria catalysts are particularly interesting because of the synergistic effect and because copper is an inexpensive non-precious metal.

Other studies using non-precious metals have also been successful. Cobalt in particular has shown good CO oxidation activity when incorporated with other metals [139, 140]. Bulk cobalt (Co$_3$O$_4$) has also been tested and shows excellent carbon monoxide oxidation activity. Research suggests that Co$^{3+}$ is the active site and provides its oxygen to the carbon monoxide ultimately forming a Co$^{2+}$ site that is re-oxidized with oxygen [141, 142]. Unfortunately, Co$_3$O$_4$ catalysts deactivate with time forming Co$^{2+}$ sites that do not re-oxidize. [141]. The active Co$^{3+}$ sites can only be recovered by high temperature treatments, usually in oxygen.

In preferential CO oxidation, where a hydrogen atmosphere is present, the tendency for Co$_3$O$_4$ to reduce would likely be even greater. Metallic cobalt is not active for CO oxidation and has the tendency to catalyze the methanation and hydrogen combustion reactions. It’s possible, that if supported on another metal, a cobalt catalyst could be stable in a hydrogen atmosphere and retain the benefit of high activity. Surprisingly little research has been conducted on supported cobalt catalysts.
7.4 Cobalt-Based Catalysts

A number of bulk 3d transition metal oxides have been tested and, of them, cobalt oxide shows the greatest activity [143]. Studies using bulk Co$_3$O$_4$ indicate that cobalt oxide is quite active for CO oxidation but that bulk cobalt oxide can reduce to metallic cobalt under the excess of hydrogen present under PROX reaction conditions [144, 145]. This could lead to an increase in the rate of the undesired hydrogen combustion reaction or to an increase in the rate of the undesired methanation reaction. It has also been suggested that Co$^{3+}$ in an octahedrally coordinated state is the active site during CO oxidation in the absence of hydrogen [146].

Previously, our research group has created a series of cobalt supported catalysts and tested them for activity in the PROX reaction [147]. The activity trend was as follows: Co/ZrO$_2$ > Co/SiO$_2$ > Co/CeO$_2$ > Co/TiO$_2$ > Co/Al$_2$O$_3$. While Co/ZrO$_2$ was most active, it is interesting to note that activity on Co/CeO$_2$ was good despite a relatively low surface area (~7 m$^2$/g). Co/ZrO$_2$ was very active and, in the desired temperature window, was able to achieve sufficient conversion to decrease the concentration of CO from 1% to 10 ppm in the presence of H$_2$. It should be noted that the reaction temperature used to obtain 10 ppm was 175°C which is within the desired temperature window (250 to 80°C).

Temperature programmed reaction experiments over our 10wt% Co/ZrO$_2$ (not shown) demonstrated that the catalyst exhibited three distinct regions of activity depending on the temperature. At temperatures below 175°C, the oxidation of CO to CO$_2$ is the only reaction that occurs. As temperature is increased beyond 175°C, the undesired hydrogen combustion reaction becomes significant and the conversion of CO decreases. Once temperature is increased past 240°C, however, the methanation reaction becomes
dominant. Methanation removes CO but only occurs after all oxygen has been consumed leading to a decrease in O₂ to CO₂ selectivity. Additionally, methanation consumes hydrogen and only occurs at high temperatures.

The zirconia interacts strongly enough with the cobalt to prevent agglomeration and loss of surface area. Both X-ray diffraction and Raman spectroscopy showed that the cobalt existed as highly oxidized, crystalline Co₃O₄. Since bulk cobalt reduces easily under H₂, very few cobalt based catalysts have been research for the PROX reaction. When supported on ZrO₂, however, cobalt oxide does not reduce as easily. It is likely that supports which are able to finely disperse crystalline cobalt into small, stable particles will show high activity in the preferential oxidation of carbon monoxide.
8.1 Catalyst synthesis

Nanoparticle CeO$_2$ support was prepared in the following way. Ce(NO$_3$)$_3$·6H$_2$O was dissolved in an equal volume ethylene glycol and water mixture to form solution $A$. Tert-butylamine ((CH$_3$)$_3$CNH$_2$) was dissolved in an equal volume mixture of ethylene glycol and water to form solution $B$. Solution $B$ was added to solution $A$ dropwise and the resulting solution was stirred for 15 minutes using a magnetic stir bar. The solution was then transferred to a Pyrex glass bottle, sealed and placed in a drying oven set at 100°C for 30 hours. CeO$_2$ precipitates were washed three times with de-ionized water and collected by vacuum filtration between each wash. The resulting precipitate was then dried in air at 100°C overnight. The sample was then calcined in air at 400°C for 4 hours with a heating rate of 10°C per minute. The resulting CeO$_2$ support had a BET surface area of 95m$^2$/g and a BJH pore volume of 0.21cm$^3$/g.

Incipient wetness impregnation was used to synthesize a 10wt% cobalt on CeO$_2$ catalyst. An aqueous solution of the cobalt nitrate precursor, Co(NO$_3$)$_2$·6H$_2$O (Aldrich), was used to impregnate the previously prepared CeO$_2$ nanoparticle support. Two impregnation steps were performed on the catalyst, with a 4 hour, 110°C drying period.
between the two impregnations. After the second impregnation, the catalyst was dried at 110°C overnight. The sample was then transferred to a calcination furnace and heated at a rate of 10°C/min to 400°C in air and held here for three hours.

8.2 Surface Area Analysis

The catalyst surface area is an important factor in catalytic reactions. Higher surface areas tend to give increased activity because more active sites will be accessible to the gas phase. The Brunauer, Emmett and Teller method (BET), developed in 1938, is commonly used for the determination of the surface area of solids. The linearized BET equation is written as

\[
\frac{P}{n_a (P_o - P)} = \frac{1}{n_{a,m} C} + \frac{(C - 1)P}{n_{a,m} C P_o}
\]

where \(P\) is the pressure, \(P_o\) is the adsorbate saturation pressure at the temperature of the experiment, \(n_a\) is the number of moles of adsorbate adsorbed at a given relative pressure \((P/P_o)\) and \(n_{a,m}\) is the amount of adsorbate adsorbed for form a single monolayer on the sample. According to the derivation of the BET equation, \(C\) is related to the enthalpy of adsorption below monolayer coverage. After much research on BET surface areas, this interpretation has been widely disregarded, however \(C\) is still constant and can be used to determine BET surface areas.

Samples are dosed with various pressures of gas and allowed to equilibrate. The amount of gas adsorbed \((n_a)\) is determined by the change in pressure. The unknowns are \(C\) and \(n_{a,m}\) and a plot of
\[
\frac{P}{n_a (P_o - P)} \text{ vs. } \frac{P}{P_o}
\]

yields a straight line with an intercept of \( \frac{1}{n_{a,m} C} \) and a slope of \( \frac{(C - 1)}{n_{a,m} C} \).

The specific BET surface area can then be calculated using

\[
a_s = \frac{n_{a,m} L a_m}{m}
\]

where \( a_s \) is the specific BET surface area, \( a_m \) is the cross sectional area of an adsorbate molecule (0.162 nm\(^2\) at 77 K for N\(_2\)), \( n_{a,m} \) is the number of moles of adsorbate adsorbed and \( L \) is Avogadro’s number.

Static surface area and pore volume measurements were made with a Micromeritics ASAP 2010 accelerated surface area and porosimetry instrument using nitrogen as the adsorbent at liquid nitrogen temperature (77 K). N\(_2\) adsorption and desorption isotherms were collected at relative pressures (\( P/P_o \)) between 0 and 1. BET surface areas were calculated using points 10 points lying on the adsorption isotherm between 0 and 0.1 \( P/P_o \). Samples were degassed under vacuum at 200 °C overnight before being analyzed.
8.3 Cobalt Metal Dispersion

Active metal dispersion is an important parameter in heterogeneous catalysis. Highly dispersed active metals provide more surface active sites than large crystalline domains. Cobalt metal dispersion was measured using hydrogen chemisorption performed at liquid nitrogen temperatures (77K) using a Micromeritics ASAP 2010 instrument. Catalyst pre-reduction was carried out in 100% H₂ at 500°C for 60 minutes. Samples were then flushed with helium at 500°C for 30 minutes before being evacuated at 510°C. After evacuation, samples were cooled to liquid nitrogen temperature under vacuum before chemisorption analysis was performed using an atmosphere of 100% H₂.

8.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique where an ultra thin sample is imaged using a beam of high energy electrons. In bright field mode, the image is formed directly from occlusion of electrons at thicker regions of the sample. The areas with no sample appear bright. The resulting electron beam is then focused with a series of electromagnetic lenses to give a contrast image analogous to the image formed from an overhead projector. Transmission electron microscopy (TEM) was performed using a Phillips Tecnai F20 instrument with FEG. The instrument was operated at an accelerating voltage of 200 kV and all images were collected in brightfield mode. Samples were dispersed in ethanol before being loaded onto lacey/formvar carbon which was deposited on a 200 mesh copper grid.
8.5 Laser Raman Spectroscopy

When radiation passes through a sample, the sample scatters a fraction of the incident beam in all directions. A small fraction of this scattered radiation is inelastically scattered. The difference in energy between the incident radiation and the inelastically scattered radiation gives information about the vibrational modes of the sample molecules. Raman spectra are created by plotting the difference in wavenumber between incident and scattered radiation (Raman shift) versus the intensity of the inelastically scattered radiation. The technique gives the same type of information as infrared spectroscopy but it is important to note that the techniques are complimentary. In order for a vibrational mode to be Raman active, bond polarizability must be a function of bond distance while in infrared spectroscopy the bond dipole moment must vary with bond distance in order to be active.

Laser Raman spectra (LRS) were acquired using a Horiba-Jovin Yvon LabRam HR confocal Raman spectrometer with an 800 mm focal length. The spectrometer was equipped with a 100x microscope objective, 1200 mm grating, He-Ne red laser (633 nm) and a Peltier-cooled CCD camera. Spectra were collected under atmospheric conditions on post calcinations Co$_3$O$_4$, CeO$_2$ and 10%Co/CeO$_2$ by averaging 60 scans with a power of less than 5 mW at the sample.

8.6 X-ray Diffraction

X-ray diffraction (XRD) is a technique that is widely used for identification and quantification of crystalline phases in samples. XRD can be particularly useful in catalysis because specific crystalline phases may be active for specific types of reactions.
If crystalline phases are undesired, XRD can determine the maximum metal loading before crystalline phases begin to form. In XRD, a monochromatic X-ray beam is directed toward the sample. Crystalline samples possess a periodic array of atoms located at distinct distances and direction from one another. X-rays photons interact with the sample and are scattered in all directions. There are certain discrete directions that result in strong constructive interference and they are given by Bragg’s law

\[ n\lambda = 2d \sin \theta \]

where \( n \) is an integer, \( \lambda \) is the wavelength of the incident X-ray, \( d \) is the distance between lattice planes and \( \theta \) is the angle between the diffracted X-ray beam and the lattice plane. In practice, XRD spectra are often compared to reference spectra available in database or in the literature.

X-ray diffraction (XRD) experiments were performed using a Bruker D8 Advanced X-Ray Power Diffractometer with a monochromatically isolated Cu K\(_{\alpha1}\) radiation source and a Braun position sensitive detector (operated at 50mA and 40kV) that measures 8° 2\( \theta \) simultaneously. Diffraction patterns were collected in air at ambient conditions in reflection mode using a rotating 9 sample holder with polyethylene sample holders. Patterns were collected from 20 to 90° 2\( \theta \) using a step size of 0.01445° and a dwell time of 1 second.

8.7 Diffuse Reflectance Infrared Spectroscopy

Intermediate species on the catalyst surface can be investigated using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). DRIFTS allows the
identification of small amounts of chemical species adsorbed to the catalyst surface under various gas phase conditions and temperatures. This technique allows effective analysis of powdered samples with a minimum of sample preparation because no pellet pressing is necessary. Diffuse reflection occurs when a beam of radiation strikes the sample surface. Because the particles at the surface of a powder are randomly oriented, radiation is reflected in all direction. Some of the radiation is reflected deeper into the sample before being randomly reflected back out. During each reflection process, absorption occurs at wavelengths corresponding to differences in vibrational energies of surface species. Typically, the intensity of the reflected radiation is roughly independent of the viewing angle.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed using a Thermo Nicolet 6700 spectrometer equipped with a KBr beamsplitter and liquid nitrogen cooled MCT detector. Background and spectra were collected by averaging 500 scans and a spectral resolution of 4 cm⁻¹. In the temperature programmed desorption (TPD) experiments, the sample was pretreated in 25 ml/min helium at 300 °C for 30 minutes and backgrounds were collected while cooling under helium flow. Carbon monoxide was adsorbed using 30 ml/min of 0.7% CO/He for 10 minutes at 50 °C. The sample was heated from 50 °C to 300 °C and held for 10 minutes before spectra were collected. The in-situ PROX experiments use the same pretreatment and background collection procedure as the TPD experiments. Spectra were collected under 30 ml/min of 1% CO, 1% O₂ and 60% H₂ in He at 50 °C intervals from 50 °C to 300 °C.
8.8 Steady State Preferential CO Oxidation Experiments

Steady-state activity measurements were performed using a stainless steel tube (1/4” O.D.) fixed bed reactor with catalyst loaded between two quartz wool plugs. The reaction temperature was measured using a K-type thermocouple in contact with the quartz wool upstream of the catalyst bed. Gas flow rates were controlled using Brooks 5850E mass flow controllers and experiments consisted of varying the weight hourly space velocity (WHSV), the H₂ concentration and the CO/O₂ concentrations ratio. Weight hourly space velocities were altered by changing the catalyst weight loaded into the reactor from 100mg to 200mg and by changing the total reactant gas flow rate from 50ccm to 25ccm. Weight hourly space velocities of 7500, 15000 and 30000 cc g(cat)⁻¹ h⁻¹ were tested in the PROX reaction using 1% CO, 1% O₂, 10% H₂ and balance helium. For experiments testing the CO/O₂ concentration ratios, 1% CO and either 1% or 0.5% O₂ were tested at a WHSV of 15000 cc g(cat)⁻¹ h⁻¹. The effects of H₂ concentration were investigated using 1% CO, 2% O₂, various H₂ concentrations and balance helium at a WHSV of 30000 cc g(cat)⁻¹ h⁻¹.

Samples were pre-treated in a 30 ml/min flow of 10% O₂/He for 30 minutes at 300°C before being cooled to room temperature under helium flow. Feed and effluent composition analyses were conducted using an Agilent 3000A micro gas chromatograph equipped with 0.32mm PLOT molesieve and 0.32mm PLOT Q columns with backflush and variable volume injectors, respectively. Both columns have TCD detectors and the detector on the mole sieve column is capable of detecting less than 5 ppm carbon monoxide. G.C. data points were collected and averaged after 60 minutes on stream and all carbon balances close with +/- 5%.
The conversions of CO ($X_{CO}$) and O$_2$ ($X_{O2}$) as well as the O$_2$ selectivity to CO$_2$ ($S_{CO2}$) are defined as follows:

\[
X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}}
\]

\[
X_{O2} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}}
\]

\[
S_{CO2} = \frac{[CO_2]_{out} - [CO_2]_{in}}{2 \times (O_2)_{in} - (O_2)_{out}}
\]

8.9 Temperature Programmed Reduction Studies

Temperature programmed reduction (TPR) is a widely used technique in heterogeneous catalysis. TPR reveals the number of reducible sites present on the catalyst and the temperature at which the sites reduce. Reducibility is an extremely important aspect of catalysis, particularly in systems with redox type mechanisms. In TPR, a reducing gas is flowed over the catalyst (typically at room temperature). The temperature of the catalyst is increased at a constant rate with time. The consumption of the reducing gas is monitored by measuring the gas phase concentration of reducing agent downstream of the catalyst bed.

A hydrogen TPR of CoO$_x$/CeO$_2$ was performed using an in lab gas flow system equipped with thermal conductivity detector. 30 mg of catalyst was placed in a quartz U-tube reactor and pre-treated in helium at 500°C for 30 min, and then allowed to cool to
room temperature under helium flow. The reduction was performed with 30 ccm of 5% hydrogen in nitrogen with a temperature ramp from room temperature to 800°C at a rate of 10°C/min. The reactor effluent was passed through a column of silica gel to remove moisture before reaching the TCD.

A carbon monoxide TPR of CoO_x/CeO_2 was performed and monitored using a mass spectrometer. 50 mg of catalyst was placed in a quartz U-tube reactor and pretreated in 10% O_2 in helium at 300°C for 30 min, and then allowed to cool to room temperature under helium flow. The reduction was performed with 40 ccm of 5% CO in helium from room temperature to 400°C at a temperature ramp rate of 10°C/min.

8.10 CO Oxidation and H_2 Oxidation Experiments

Insight into the preferential CO oxidation network can be gained by studying oxidation reactions separately for CO and H_2. By running separate reactions, the kinetic parameters of each can be determined and compared to the reaction results where both reactants are co-fed over the catalyst. CO oxidation and H_2 oxidation reactions were run using 50mg of 10%CoO_x/CeO_2 catalyst. During CO oxidation, 3.3% CO, 3.3% O_2 and balance helium were fed over the catalyst at a flow rate of 150ccm at various temperatures. During H_2 oxidation, 3.3% H_2, 3.3% O_2 and balance argon were fed over the catalyst at 75ccm at various temperatures. CO, H_2 and O_2 conversions were maintained below 15% to ensure differential reactor operation allowing easy determination of activation energies and pre-exponential factors. Activation energies
were determined using Arrhenius plots and assuming the rate of reaction can be expressed as:

\[ r_i = A \exp(-E_A/RT) \]

where \( r_i \) is the rate of reaction \( i \), \( A \) is the preexponential factor and includes gas phase concentrations, some function of the number of active sites and the temperature independent rate constant, \( E_A \) is the activation energy, \( R \) is the universal gas constant and \( T \) is the absolute temperature.

Feed and effluent compositions were analyzed using an Agilent 3000A micro gas chromatograph equipped with 0.32mm PLOT molesieve and 0.32mm PLOT Q columns with backflush and variable volume injectors, respectively. Helium was used as microGC carrier gas during the CO oxidation experiments and argon was used as microGC carrier gas during the H\(_2\) oxidation experiments to ensure optimum TCD sensitivity for the measured components. G.C. data points were collected and averaged after 60 minutes on stream and all carbon and hydrogen balances close with +/- 5%.

8.11 Temperature Programmed Preferential CO Oxidation

Temperature programmed reaction (TP-Rxn) experiments were conducted to determine the activity and selectivity of the catalyst over large temperature ranges. These experiments are useful for covering a large temperature range and observing where different reaction pathways light off. 100 mg of sample was loaded between two quartz wool plugs in a quartz U-tube reactor. The sample was pretreated in 40 ml/min 10% O\(_2\)/He for 30 minutes at 300 °C before being cooled to room temperature under helium. The reactant gases consisting of 1% CO, 1% O\(_2\), 60% H\(_2\) and balance helium were then
introduced at a flow rate of 30 ml/min. The temperature was increased at 5 °C/min from room temperature to 350 °C and held for 30 minutes. The reactor effluent was monitored using a quadrupole mass spectrometer (Cirrus residual gas analyzer from MKS instruments). O₂, CO, CO₂, CH₄ and H₂O signals were monitored using mass to charge ratios of 32, 28, 44, 15 and 18, respectively. The CO signal was corrected to account for fragmentation from CO₂.

8.12 Time on Stream Reaction Experiments

Catalyst stability is an important parameter when evaluating the effectiveness of a preferential CO oxidation catalyst. Stability has been a concern on other cobalt based catalysts and activity losses have been attributed to the reduction of CoOₓ to lower valency states [143]. To test catalyst stability, time on stream reaction experiments were performed using a stainless steel tube (1/4” O.D.) fixed bed reactor with catalyst loaded between two quartz wool plugs. The reaction temperature was measured using a K-type thermocouple in contact with the quartz wool upstream of the catalyst bed. Gas flow rates were controlled using Brooks 5850E mass flow. Experiments were run using 200mg of 10%CoOₓ/CeO₂ catalyst under a 50ccm flow rate of 1% CO, 1% O₂, 60% H₂ in balance helium at 175°C.

Samples were pre-treated in a 30ccm flow of 10% O₂/He for 30 minutes at 300°C before being cooled to room temperature under helium flow. Feed and effluent composition analyses were conducted using an Agilent 3000A micro gas chromatograph.
equipped with 0.32mm PLOT molesieve and 0.32mm PLOT Q columns with backflush and variable volume injectors, respectively. Both columns have TCD detectors and the detector on the mole sieve column is capable of detecting less than 5 ppm carbon monoxide. G.C. data points were collected and averaged after 60 minutes on stream and all carbon balances close with +/- 5%.
CHAPTER 9
RESULTS AND DISCUSSION

9.1 Characterization of Catalyst Textural Properties

Nitrogen adsorption/desorption isotherms were collected on the 10% CoOx/CeO2 catalyst. The isotherm (Figure 9-1) is identified as a type IV isotherm according to the IUPAC classification indicating a mesoporous material with pores in the range of 2 to 50 nanometers. Capillary condensation begins to occur above at a relative pressure of 0.7 and above and appears to be leveling off near the saturation pressure. Capillary evaporation is shifted to relative pressures of over 0.05 lower than capillary condensation creating a hysteresis between the two branches and indicating the presence of mesopores. This isotherm is easily identifiable as a type IV isotherm according to the IUPAC classification indicating a mesoporous material with pores in the range of 2 to 50 nanometers. The Brunauer-Emmet-Teller (BET) surface area of the 10%Co/CeO2 sample is 78m²/g.

Figure 9-2 shows the pore size distributions (PSD) for the 10%CoOx/CeO2 catalyst as determined from the adsorption branch of the N2 isotherm. The pore size distribution is centered around 9 nm for the 10%CoOx/CeO2 catalyst. The pore count decreases to very small numbers at pore size values below 36nm indicating that very few
of pores lie outside of the mesoporous range of 2 to 50nm. The BJH cumulative pore volume of the 10%Co/CeO$_2$ catalyst as determined from the adsorption isotherm is 0.15cm$^3$/g.

Nitrogen adsorption/desorption isotherms were also collected on the CeO$_2$ nanoparticle support. The BJH cumulative adsorption pore volume of the CeO$_2$ support is 0.21cm$^3$/g and this value was used to prepare 10wt% CoO$_x$/CeO$_2$ using the incipient wetness impregnation technique. The BET surface area of the CeO$_2$ support was 95m$^2$/g which is substantially higher than the commercial support surface area reported previously [147].

Transmission electron microscopy of the CeO$_2$ support reveals bundles of agglomerated nanoparticles (see Figure 9-3). These particles are regularly shaped polyhedron with diameters near 4 nanometers. Nanopolyhedra are a common shape when synthesizing cerium oxide using hydrothermal methods.

These very small particles are responsible for the high surface area observed during BET analysis of the support. The pore volumes measured by nitrogen adsorption/desorption are due to the arrangement of the nanoparticles into bundles. The agglomeration of the nanoparticles creates small voids between the particles leading the adsorbate condensation and the measured pore volumes. TEM images were also taken on the 10%Co/CeO$_2$ sample (not shown). The images did not appear different from those of the support. Small nanoparticles were observed but cobalt oxide could not be discerned.
Figure 9-1 – Nitrogen adsorption and desorption isotherms on 10%Co/CeO$_2$. 
Figure 9-2 – Pore size distribution of 10%Co/CeO$_2$ as determined from nitrogen adsorption isotherm.
Figure 9-3 – TEM micrograph of CeO$_2$ support nanoparticles.
from cerium oxide. It is likely that the cobalt oxide is well dispersed into small particles on the CeO₂ support. Hydrogen chemisorption experiments conducted on the 10%Co/CeO₂ catalyst support this observation showing a cobalt dispersion of 12%. This dispersion is far higher than the previously reported cobalt dispersion on CoOₓ/CeO₂ prepared on commercial CeO₂ and considering the high activity per surface area of that catalyst it is expected that this 10%Co/CeO₂ catalyst will perform far better during preferential CO oxidation [147].

9.2 Catalyst Activity at Various Weight Hourly Space Velocities

The steady state activity of our CoOₓ/CeO₂ catalyst was studied at three different weight hourly space velocities: 7500, 15000 and 30000 cc g(cat)⁻¹ h⁻¹ using 1% CO, 1% O₂, 10% H₂ and balance helium. Figure 9-4 shows the CO conversion for these three weight hourly space velocities. At a given temperature, increasing the weight hourly space velocity decreases the CO conversion. At 7500 cc g(cat)⁻¹ h⁻¹ the catalyst reaches near 100% CO conversion at 150°C and remains at 100% conversion as temperature is further increased. Upon increasing the WHSV to 15000 cc g(cat)⁻¹ h⁻¹, however, the temperature at which 100% CO conversion occurs increases to 175°C and remains at 100% as temperature is further increased to 200°C. As WHSV is further increased to 30000 cc g(cat)⁻¹ h⁻¹, the CO conversion decreases again reaching a maximum of over 99% at 200°C. The O₂ conversion (not shown) follows a similar trend, as expected, with higher conversions occurring at lower WHSV. These results demonstrate that the CoOₓ/CeO₂ catalyst is highly active for the preferential CO oxidation reaction and is able
to achieve 100% conversion over a wide range of temperature depending on the weight hourly space velocity.

Figure 9-5 shows the O₂ selectivity to CO₂ for the 10% CoOₓ/CeO₂ catalyst using 1% CO, 1% O₂, 10% H₂ and balance helium. This data corresponds to the CO conversion data given in Figure 9-4. For all weight hourly space velocities, the selectivity drops monotonically as the temperature increases. For all weight hourly space velocities, the O₂ selectivity to CO₂ remains at 95% or above at temperatures below 150°C. In fact, all catalysts show near 100% selectivity at temperature of 125°C and below. As temperatures are increased above 150°C, selectivity further drops for all weight hourly space velocities tested. At 30000 and 15000 cc g(cat)⁻¹ h⁻¹, selectivity at 200°C drops to 83% and 70%, respectively. At 7500 cc g(cat)⁻¹ h⁻¹, selectivity drops more rapidly reaching 55% at 200°C. These results show that the 10% CoOₓ/CeO₂ catalyst is able to achieve high O₂ to CO₂ selectivities while at the same time achieving high carbon monoxide conversion. The decreases in selectivity observed at higher temperatures are due to the unselective combustion of hydrogen to form water. It is apparent from the data shown in Figure 9-4 and Figure 9-5 that the conditions favoring high CO conversion, namely high temperatures and low weight hourly space velocities, also favor unselective H₂ combustion. The unselective combustion of hydrogen will be discussed in more detail in some of the following experiments presented below.
Figure 9-4 – CO conversion at WHSV of (▲) 7500, (●) 15000 and (■) 30000 cc g(cat)$^{-1}$ h$^{-1}$ over 10%CoO$_x$/CeO$_2$. Feed composition: 1% CO, 1% O$_2$, 10% H$_2$, balance He.
Figure 9-5 – O₂ selectivity to CO₂ at WHSV of (▲) 7500, (●) 15000 and (■) 30000 cc g(cat)⁻¹ h⁻¹ on 10%CoOₓ/CeO₂. Feed composition: 1% CO, 1% O₂, 10% H₂, balance He.
9.3 Crystallographic Properties of 10% CoOₓ/CeO₂

Figure 9-6 shows Raman spectra for Co₃O₄, CoOₓ/CeO₂ and CeO₂ nanoparticles. The Co₃O₄ spectra shows five Raman active modes typical of the spinel structure located at 193, 475, 516, 615 and 680 cm⁻¹. The peaks at 193, 516 and 615 cm⁻¹ have been attributed to the F₂g phonon mode while the peaks at 475 and 680 cm⁻¹ have been assigned to the E₉ and A₁g phonon modes, respectively [148, 149]. The Raman spectrum of CeO₂ shows a single broad and intense peak located at 462 cm⁻¹. This peak is assigned to the F₂g phonon mode of cubic fluorite CeO₂ [150-152]. The Raman spectrum of CoOₓ/CeO₂ clearly shows peaks characteristic of Co₃O₄ located at 193, and 615 cm⁻¹. Additionally, there are two overlapping peaks located at 459 and 472 cm⁻¹. The peak at 459 cm⁻¹ is assigned to the F₂g phonon mode of CeO₂ while the peak at 472 cm⁻¹ is assigned to the E₉ phonon mode of Co₃O₄. The presence peaks at 193, 472 and 615 cm⁻¹ indicate that cobalt is present near the catalyst surface as Co₃O₄.

X-ray diffraction patterns were collected for Co₃O₄ precipitates, CeO₂ and CoOₓ/CeO₂ samples and are shown in Figure 9-7. The Co₃O₄ precipitates, used as a reference, show diffraction peaks characteristic of the spinel structure with the (220), (311), (400), (511) and (440) reflections occurring at 31.3°, 36.8°, 44.9°, 59.4° and 65.3° 2θ, respectively [153]. The XRD pattern for the CeO₂ nanoparticles is typical of the cubic fluorite structure with peaks at 28.2°, 33.0°, 47.5°, 56.5°, 59.3° 69.3° and 76.8° 2θ representing the (111), (200), (220), (311), (222), (400) and (331) reflections, respectively.
The CoOx/CeO2 diffraction pattern shows strong peaks due to CeO2 and weaker peaks due to Co3O4. The (111), (200), (220), (311), (400) and (311) peaks of CeO2 are all present. There is also a small peak present at 59.3° which is assigned to the (222) reflection of CeO2 though it should be noted that Co3O4 gives a peak at 59.4° 2θ. Regardless of the identity of this peak, there are two peaks that can be unambiguously attributed to the presence of Co3O4 on the CoOx/CeO2 sample. These peaks, present due to the (311) and (440) reflections of Co3O4, are located at 36.8° and 65.3° 2θ, respectively.

It should be noted that no evidence of CoO was observed in the Raman spectrum or the XRD pattern of the CoOx/CeO2 catalyst. CoO peaks, which are not observed, would be located at 143, 221 and 296 cm⁻¹ [154] in Raman spectroscopy and 36.9°, 42.9°, 62.0°, 73.3° and 77.4° 2θ [155] in X-ray diffraction experiments. These results show that crystalline Co3O4 is formed on the CeO2 support during calcinations at 400 °C in air. It is not surprising that Co3O4 is found rather than CoO due to the higher thermodynamic stability of Co3O4 [156] both under ambient conditions and at higher temperatures.

9.4 Activity of 10% CoOx/CeO2 Under High H2 Concentrations

Steady-state reaction experiments were conducted to determine the performance of 10% CoOx/CeO2 and the effect of the CO:O2 concentration ratio in high concentrations of hydrogen. In these experiments, the reactant concentrations were 1% CO, 1%O2 or 0.5% O2, 60% H2 and balance helium. Additionally, the CeO2 nanoparticle support
Figure 9-6 – Raman spectra of CeO$_2$, Co$_3$O$_4$ and CoO$_x$/CeO$_2$. 
Figure 9-7 – X-ray diffraction patterns of CeO$_2$, Co$_3$O$_4$ and CoO$_x$/CeO$_2$. 
(without any cobalt loaded) was tested for preferential CO oxidation activity under conditions with excess oxygen present.

Figure 9-8 shows the effect of oxygen concentration on CO conversion during the steady-state PROX reaction. Over the 10% CoOx/CeO2 catalyst, changing from stoichiometric to excess oxygen increases the CO conversion substantially. This suggests that the rate of rate of The CO oxidation is dependent on oxygen concentration and can be increased by introducing higher amounts of O2. Under both excess and stoichiometric conditions, the CO conversion rate increases with temperature until reaching a maximum at 175°C. When using stoichiometric and excess concentrations of oxygen, the maximum CO conversions are 78% and 99.9%, respectively. At temperatures above 175°C, the CO conversion begins to decrease due to the competitive combustion of hydrogen. When using stoichiometric oxygen (0.5% O2), as temperature increases above 200°C the CO conversion drops dramatically. This is due to complete consumption of all the oxygen. CO conversion over the bare CeO2 nanoparticles follows a similar trend, though the carbon monoxide conversion is substantially lower than on the 10% CoOx/CeO2 catalyst. The CeO2 reaches a maximum CO conversion of 34% at 175°C before the activity begins to decrease due to hydrogen combustion.

Figure 9-9 shows the O2 to CO2 selectivity during the steady-state PROX reaction. The reaction using a stoichiometric amount of oxygen has a higher selectivity at all temperatures except for 225°C. This shows that, although the activity of the catalyst is improved under increased oxygen concentrations, the O2 selectivity to CO2 actually decreases with higher oxygen concentrations. For both excess and
Figure 9-8 – Influence of CO/O₂ ratio on CO conversion: (●) 1% CO, 1% O₂, 60% H₂ balance He over 10% CoOₓ/CeO₂ (■) 1% CO, 0.5% O₂, 60% H₂, balance He over 10% CoOₓ/CeO₂ (▲) 1% CO, 1% O₂, 60% H₂, balance He over CeO₂ nanoparticle support.
Figure 9-9 – Influence of CO/O₂ ratio on O₂: (●) 1% CO, 1% O₂, 60% H₂ balance He over 10% CoOₓ/CeO₂ (■) 1% CO, 0.5% O₂, 60% H₂, balance He over 10% CoOₓ/CeO₂.
stoichiometric amounts of oxygen, the selectivity begins at its maximum and decreases with temperature. Quite high selectivities can be obtained with the 10% CoOx/CeO2 catalyst when operating under certain conditions. At 150°C under excess oxygen, we are able to obtain 85% O2 selectivity to CO2 at over 90% CO conversion. At 175°C under excess oxygen, O2 selectivity to CO2 is still 56% while CO conversion is 99.9%. Above 225°C the O2 selectivity to CO2 under stoichiometric oxygen conditions drops below that obtained under excess oxygen conditions. This is due to the complete consumption of oxygen under the stoichiometric conditions. At the temperatures used in these steady state reactions, the loss in selectivity is due entirely to the combustion of hydrogen.

9.5 Reducibility and Stability Studies on 10% CoOx/CeO2

It has been suggested that on CuO-CeO2 catalysts, a redox couple between copper and ceria at their interface is largely responsible for CO oxidation activity [157, 158]. It has also been demonstrated using spinel oxides containing cobalt that octahedral cobalt (III) sites are active in the oxidation of carbon monoxide [146]. Therefore, the reduction properties of the catalyst may be quite important for both CO and H2 oxidation activity. These two molecules are in competition for active catalyst sites. Additionally, the stability of the catalyst under the reducing conditions of the PROX reaction is important for long term performance. The reducibility of 10% CoOx/CeO2 was investigated using temperature programmed reduction experiments with either hydrogen or carbon monoxide as the reducing agent.
Figure 9-10 shows the H₂ consumption and CO consumption rates versus temperature for the temperature programmed reduction experiments. The hydrogen profile shows very little consumption until 225°C when consumption begins to increase. H₂ consumption increases for the remainder of the experiment. Previous research on supported cobalt catalyst and on Co₃O₄ has shown that bulk cobalt reduction takes place in two steps [159-161]. A peak near 300°C is assigned to the bulk reduction of Co³⁺ to Co²⁺ while a second peak at higher temperatures is generally considered to occur due to the bulk reduction of Co²⁺ to metallic cobalt [159-161]. The results shown in Figure 9-10 suggest that oxidation of hydrogen due to catalyst lattice oxygen atoms does not occur until temperatures above the range used for the preferential CO oxidation reaction. It is also likely that catalyst stability on stream should be good because bulk catalyst reduction by hydrogen does not appear to occur until temperatures above those used in the PROX reaction.

Figure 9-10 also shows the reduction profile of 10% CoOₓ/CeO₂ when using carbon monoxide as the reducing agent. This profile shows a reduction peak occurring at 220°C which is well below the onset of catalyst reduction when using hydrogen as the reducing agent. This suggests that the catalyst is more likely to oxidize CO to CO₂ at lower temperatures while H₂ oxidation tends to occur to a lesser extent at these temperatures. As temperature is increased beyond 220°C, however, lattice oxygen begins to oxidize hydrogen resulting in bulk catalyst reduction. This result is important for two reasons. It suggests that there is a temperature window where catalyst active sites are able to react with CO but not H₂ and it demonstrates an upper temperature limit for
Figure 9-10 – Hydrogen and carbon monoxide temperature programmed reduction profiles over 10% CoO$_x$/CeO$_2$.
the catalyst when operating under PROX reaction conditions. Operating well above 225°C could result in bulk catalyst reduction due to the excess hydrogen present during the PROX reaction. As shown in Figure 9-10, a second higher temperature peak also begins near the end of the CO TPR experiment. This peak is likely due to the bulk reduction of cobalt under CO.

It should be noted that in both the H2 and CO TPR experiments, the thermocouple is placed in the reactor furnace and is not in direct contact with the catalyst bed. This is in contrast to the PROX reaction experiments where the thermocouple is in contact with the quartz wool directly above the catalyst bed. This thermocouple placement likely shifts the reduction profiles to higher temperature during the TPR experiments because both CO oxidation and H2 combustion are highly exothermic reactions.

In order to further characterize the stability of 10% CoOx/CeO2 under the reducing conditions of the PROX reaction, time-on-stream studies were performed. These experiments were conducted using a feed composition of 1% CO, 1% O2 and 60% H2 at a weight hourly space velocity of 15000 cc g(cat)-1 h-1 and a temperature of 175°C. Figure 9-11 shows the time-on-stream CO conversion of 10% CoOx/CeO2. No discernible decrease in activity occurs during the course of the reaction. This result is in contrast to results presented on other catalysts based on cobalt which show decreased activity with time-on-stream likely due to the reduction of active CoOx species to lower valencies as has been reported previously [143]. Additionally, the O2 selectivity to CO2 (see Figure 9-12) quickly reaches 58% and remains stable over the course of the time-on-stream experiment. These results suggest that, on this particular catalyst, reduction of Co3O4 to lower valency states is either not occurring or is occurring on a time scale far
Figure 9-11 – Time on stream conversion over 10%Co/CeO$_2$. Reaction conditions: 175°C and 1% CO, 1% O$_2$, balance helium.
Figure 9-12 – Time on stream O$_2$ to CO$_2$ selectivity over 10%Co/CeO$_2$. Reaction conditions: 175°C and 1% CO, 1% O$_2$, balance helium.
longer than detectable here. This agree with the H₂-TPR results showing that bulk cobalt reduction does not occur until temperatures higher than the 175°C used in this experiment. It should also be noted that 175°C is the optimum temperature to run the reaction. At 175°C, maximum CO conversion is obtained while further increasing the temperature leads to a decrease in CO conversion due to the competitive hydrogen combustion reaction.

9.6 CO and H₂ Oxidation on 10% CoOₓ/CeO₂

Steady-state PROX experiments were conducted to determine the performance of 10%CoOₓ/CeO₂ under various concentrations of hydrogen. CO conversion and O₂ selectivity to CO₂ versus the H₂ concentration of the feed is shown in Figure 9-13. As expected, as hydrogen is introduced into the feed, the O₂ selectivity to CO₂ decreases. When 15% H₂ is introduced, the selectivity drops from 100% to 96%. As shown in Figure 9-13, the CO conversion decreases when from 82% to 66% when hydrogen is introduced into the feed at a concentration of 15%. Ultimately a CO conversion of 58% is reached when the feed concentration of hydrogen is 60%. If the CO and H₂ oxidation reactions occurred on different sites as has been reported for the CuO-CeO₂ [162, 163] catalytic system, the rate of CO oxidation would be independent of the hydrogen concentration in the feed. In this scenario, introducing hydrogen would lead to a decrease in O₂ to CO₂ selectivity as hydrogen reacts with oxygen but would not lead to a decrease in the rate of CO oxidation. The kinetic data shown in Figure 9-13 suggests that H₂ competitively adsorbs on the sites responsible for CO oxidation.
Figure 9-13 – (●) CO conversion and (■) O₂ selectivity to CO₂ during steady-state PROX at 150°C over 10%Co/CeO₂ at various hydrogen concentrations.
CO and H₂ oxidation experiments were independently performed over 10% CoOₓ/CeO₂ catalyst to investigate the two reaction pathways. CO oxidation was carried out using 3.3% CO, 3.3% O₂ and balance helium. Figure 9-14 shows the CO conversion as a function of temperature. CO conversion increases monotonically with temperature until reaching 21% at 150°C. The activation energy for CO oxidation was calculated using the four points collected at the four lowest temperatures. These points were selected to maintain the differential reactor condition by keeping CO conversions below 15%. Figure 9-15 shows the Arrhenius plot for CO oxidation. The resulting slope is -6.23 which corresponds to a CO oxidation activation energy of 52 kJ/mol over our 10% CoOₓ/CeO₂ catalyst. Similar results have been reported previously over a cobalt on zirconia catalyst [164]. The intercept is located at 20.2 and this number will be compared to the results of the H₂ oxidation experiments presented below.

H₂ oxidation was carried out using 3.3% H₂, 3.3% O₂ and balance argon. The H₂ conversion as a function of temperature is presented in Figure 9-16. Measurable H₂ conversions are only obtainable at temperatures higher than those used in the CO oxidation experiments. An H₂ conversion of 1.6% is obtained at 150°C and increases monotonically until reaching 22% at 210°C. The activation energy for H₂ oxidation was calculated using the four points collected at the four lowest temperatures. Figure 9-17 shows the Arrhenius plot for H₂ oxidation. The resulting slope is -8.85 which corresponds to an H₂ oxidation activation energy of 74 kJ/mol on 10% CoOₓ/CeO₂. The intercept is located at 23.4. This shows that the preexponential factor during H₂ oxidation
Figure 9-14 - CO conversion over 10%CoOx/CeO2 during steady-state carbon monoxide oxidation experiments. Reaction conditions: 3.3% CO, 3.3% O2, balance helium.
Figure 9-15 – CO oxidation activation energy as calculated from steady-state carbon monoxide oxidation experiments. Reaction conditions: 3.3% CO, 3.3% O₂, balance helium.
is 25 times higher than the preexponential factor during CO oxidation. Bear in mind that this holds true when during experiments using CO and H\textsubscript{2} concentrations of 3.3%. In the PROX experiments using more realistic feed conditions (see Figure 9-8 and Figure 9-9), the hydrogen concentration is 60% and the CO concentration is 1%. This would magnify the ratio of preexponential factors and increasing the relative magnitude of the H\textsubscript{2} preexponential factor. The high preexponential factor could represent a relatively greater number of sites available for H\textsubscript{2} oxidation as opposed to CO oxidation or a greater turnover frequency per site. The fact that H\textsubscript{2} oxidation is not dominant at lower temperatures is due to the higher activation energy of the reaction (75 kJ/mol versus 52 kJ/mol). This difference results in the requirement for high temperatures before H\textsubscript{2} oxidation reaction is able to occur at appreciable rates.

To further understand the PROX reaction network over our CoO\textsubscript{x}/CeO\textsubscript{2} catalyst, a temperature programmed reaction experiment was conducted. As shown in Figure 9-18, only three products were observed during the course of the TP-Rxn experiment: CO\textsubscript{2}, H\textsubscript{2}O and CH\textsubscript{4}. By following the CO signal, three distinct temperatures where different reactions begin can be observed. As temperature is increased from 50 to 100°C, the CO and O\textsubscript{2} signals slowly decrease while the CO\textsubscript{2} signal slowly increases. At 100°C, the decrease in the CO signal becomes more substantial as does the decrease in O\textsubscript{2} signal and increase in CO\textsubscript{2} signal. At these temperatures, very little water formation is observed. The fact that the O\textsubscript{2} and CO\textsubscript{2} signals decrease in an identical manner while the CO\textsubscript{2} signal appears as the mirror image of the two suggest that the predominant reaction is the selective oxidation of CO to form CO\textsubscript{2}, though there appears to be some water formation. This trend continues until 175°C is reached. As temperature is increased above 175°C,
Figure 9-16 – H$_2$ conversion over 10%CoO$_x$/CeO$_2$ during steady-state hydrogen oxidation experiments. Reaction conditions: 3.3% H$_2$, 3.3% O$_2$, balance argon.
Figure 9-17 – H₂ oxidation activation energy as calculated from steady-state hydrogen oxidation experiments. Reaction conditions: 3.3% H₂, 3.3% O₂, balance argon.
formation of water begins to quicken and the intensity of the O$_2$ signal reaches zero. After the O$_2$ signal reaches zero at 175°C, the CO signal starts to increase while the intensity of the CO$_2$ signal begins to decrease. Apparently, as temperature is increased, hydrogen combustion consumes more oxygen and there is not enough left to react with all of the CO. This suggests that increasing the amount of oxygen in the reaction may give a larger temperature window of 100% CO conversion, albeit at the expense of O$_2$ selectivity to CO$_2$. This trend continues until 275°C and it should be noted that despite the competition from H$_2$ combustion, CO$_2$ is always being formed and the CO signal never reaches its initial intensity suggesting that significant CO oxidation is still occurring. Above 275°C, however, the situation changes and the CO and CO$_2$ signals quickly decrease to zero. Concurrently, the methane signal increases before leveling out around 300°C and the water signal begins to increase again. These signals, taken together, suggest that the CO is reacting with hydrogen to form methane. It is unlikely that, in this experiment, CO$_2$ is reacting with hydrogen in any substantial quantity because the CO$_2$ signal seems to follow the CO signal very closely.

9.7 Determination of Surface Species on 10% CoO$_x$/CeO$_2$

Surface species important for the preferential CO oxidation reaction were investigated using diffuse reflectance spectroscopy. Figure 9-19 shows the high wavenumber region during the CO TPD experiment. There is a broad band located between 3700 and 3000 cm$^{-1}$ corresponding to physically adsorbed water. As temperature is increased, this broad
Figure 9-18 – Temperature programmed PROX reaction over CoOₓ/CeO₂. Reaction conditions: 30 ml/min 1% CO, 1% O₂, 60% H₂, balance He.
band weakens and by 350°C is essentially flat indicating the loss of adsorbed water from the surface. Absorption bands due to bi-bridged and tri-bridged hydroxyl species are present at 3739 and 3660 cm⁻¹ respectively. Both hydroxyl species are stable at high temperatures and do not evolve from the surface until 350°C. As temperature is increased to 200°C, a band centered at 3539 cm⁻¹ appears and remains until 350°C. The band cannot be assigned at this time though we know that it is present in CeO₂ IR experiments with KBr backgrounds (with no adsorbed species). Therefore, it is likely that this band is due to the ceria structure itself or to hydroxyl species on the ceria. Also of interest are two weak bands located at 2967 and 2858 cm⁻¹ corresponding to a formate combination band and a formate C-H stretch, respectively. It is known that bridging hydroxyl groups can interact with CO to yield surface formate groups. These formate bands are stable with temperature and do not decrease in intensity until 350°C.

Figure 9-20 shows the low wavenumber region during the CO TPD experiment. A peak at 1225 cm⁻¹ is present and could be indicative of either bidentate carbonate species or bicarbonate species. If, however, bicarbonate species were present, we would expect to see absorption bands near 1650 and 1480 cm⁻¹ due to asymmetric and symmetric COO stretches, respectively. These bands are not observed so we conclude that the band at 1225 cm⁻¹ is due to the bidentate bicarbonate asymmetric COO stretch. This band decreases rapidly with increasing temperature disappearing by 150°C. The intense band at 1305 cm⁻¹ is assigned to a bidentate carbonate species. This band is also not stable with temperature and is completely gone by 150°C. A weak band at 1372 cm⁻¹ (not labeled) is present due to the C-H bending mode of a bidentate formate species.
Like the other formate bands, it remains present until 350°C. The band at 1395 cm\(^{-1}\) has been assigned in the literature to a monodentate carbonate species and it is completely desorbed from the surface at the relatively low temperature of 150°C. The bands at 1419 and 1445 cm\(^{-1}\) are due to free and ionic carbonate species, respectively. Both of these carbonate species desorb from the catalyst surface by 200°C. Bands at 1569 and 1601 cm\(^{-1}\) are due to formate asymmetric COO stretch and bidentate carbonate C=O stretch species but their individual identity is difficult to ascertain. The shoulder at 1569 cm\(^{-1}\) decreases in intensity as temperature is increased to 150°C. Above this temperature, the band stops decreasing in intensity and begins to shift to lower. The strong band at 1601 cm\(^{-1}\) significantly decreases in intensity as the temperature is raised. By 250°C, the once intense band is almost completely gone. Due to the seeming thermal stability of the band at 1569 cm\(^{-1}\), we tentatively assign this band to the bidentate formate species. The formate bands at 2858, 2967 and 1372 cm\(^{-1}\) are all stable at high temperature. Therefore, the less thermally stable band at 1601 cm\(^{-1}\) is assigned to bidentate carbonate species.
Figure 9-19 – DRIFTS spectra of hydroxyl region during CO temperature programmed desorption on CoOx/CeO2.
Figure 9-20 – DRIFTS spectra of carbonate region during CO temperature programmed desorption on CoOx/CeO2.
CHAPTER 10
CONCLUSIONS AND RECOMMENDATIONS

This work demonstrates the preparation of a 10%CoO\textsubscript{x}/CeO\textsubscript{2} catalyst that is highly effective for the preferential oxidation of carbon monoxide in a hydrogen rich feed. The results indicate that the prepared catalyst has a type IV isotherm with a high surface area of 78m\textsuperscript{2}/g and a pore size distribution centered at 9 nm. The 10%CoO\textsubscript{x}/CeO\textsubscript{2} catalyst possesses a very high cobalt dispersion of 12% which is far superior to the dispersion of a lower surface shown to have high activity per surface area [147]. Transmission electron microscopy of the support shows clusters of small ceria nanoparticles in the shape of polyhedrons. The large surface area of the catalyst can be attributed to this small particle size.

Raman spectroscopy and X-ray diffraction experiments have demonstrated that the cobalt takes the form of Co\textsubscript{3}O\textsubscript{4} and no CoO was detected under any experimental conditions. It is likely that the octahedral Co\textsuperscript{3+} sites are the active sites for oxidation of carbon monoxide [146]. It seems that the ceria provides a high surface area support that interacts strongly enough with cobalt to prevent the aggregation of large Co\textsubscript{3}O\textsubscript{4} particles during preparation. This is important to maintain a high surface area and a high number of exposed active sites. It is also important to point out that the interaction between the
ceria and cobalt is not so strong as to prevent the formation of cobalt oxide species which would likely contain the actives sites for preferential oxidation of carbon monoxide [147, 161, 165].

PROX steady-state reaction experiments show that the 10%CoOx/CeO2 catalyst is able to achieve near 100% CO conversion under a wide range of conditions. CO conversions of near 100% are obtainable from 125°C to 200°C depending on the weight hourly space velocity. Additionally, increasing the concentration of O2 can increase the conversion of carbon monoxide. An O2 to CO2 selectivity of 58% is obtained even under high concentrations of hydrogen (60% H2) at 100% carbon monoxide conversion. The O2 to CO2 selectivity varies with hydrogen concentration and the rate of CO oxidation decreases with the introduction of hydrogen in the feed. This shows that the hydrogen and carbon monoxide rates are not independent and that hydrogen likely competitively adsorbs to sites responsible for CO oxidation. It is possible that H2 and CO oxidation reactions take place on the same actives sites but to the author’s knowledge, there are no reports attributing H2 oxidation activity to octahedrally coordinated Co3+ sites. CO oxidation and H2 oxidation activation energies were 52 and 74 kJ/mol, respectively over our 10%Co/CeO2 catalyst. A very similar CO oxidation activation energy was calculated previously on a cobalt on zirconia catalyst suggesting that the active sites for both catalysts are may be the same [161]. The presence of crystalline Co3O4 was also detected on that catalyst. The preexponential factor for H2 oxidation was determined to be 25
times higher than that of CO oxidation under the reaction conditions used. The high hydrogen concentrations used in the reaction experiments would serve to increase this difference between H₂ and CO oxidation preexponential factors. It is possible that there are more sites available for H₂ oxidation but this reaction requires high temperatures to occur at appreciable rates.

Temperature programmed reaction experiments support the conclusions drawn from the separate CO and H₂ oxidation experiments. Only CO₂, H₂O and CH₄ are observed during the course of the experiment. The concentration profiles of these species, taken together with the concentration profiles of the reactants clearly show three distinct areas of catalyst activity. At temperatures of 175°C and below, CO oxidation is the main reaction as evidenced by the decrease in CO signal and the increase in the CO₂ signal. At temperature from 175°C to 275°C, hydrogen combustion begins to occur compete with the CO oxidation reaction. Above 275°C, methanation takes off but these temperatures are higher than those used during preferential CO oxidation reaction experiments.

Temperature programmed reduction experiments using either CO or H₂ as reducing agent provide some insight into the reactivity and stability of the 10%CoOₓ/CeO₂ catalyst. CO-TPR experiments show a CO consumption peak at temperatures near 220°C. H₂-TPR experiments, on the other hand, show no hydrogen consumption until higher temperatures suggesting that the catalyst surface is more reactive towards CO at
the temperatures used in PROX reactions. The fact that bulk catalyst reduction does not appear to occur until temperatures above 220°C also suggests that the catalyst will be stable under the reducing conditions present in the preferential CO oxidation reaction. Steady-state time-on-stream experiments confirm the stability of the catalyst. No decrease in CO oxidation activity or O₂ to CO₂ selectivity was observed during the course of the experiment.

Further work should be conducted investigating hydrogen oxidation on controlled structures such as Co₃O₄ and perovskite substituted Co to further elucidate the nature of the H₂ oxidation active sites. Though, there is considerable literature studying the CO oxidation sites, the nature of sites responsible for H₂ oxidation remains a question of considerable interest. Fundamental studies on the nature of this site could allow the preparation of catalysts more highly selective catalysts. The study of bulk Co₃O₄ presents a unique opportunity in preferential oxidation of carbon monoxide research. Due to the regular crystalline structure of Co₃O₄, it could provide a model structure where the effects of specific sites could be investigated independently for H₂ and CO oxidation.
APPENDIX A

LIST OF ACRONYMS

DRIFTS – diffuse reflectance infrared Fourier transform spectroscopy

BET – Brunauer-Emmett-Teller surface area method

BJH - Barret-Joyner-Halenda pore size calculation method

GC – gas chromatography

IWI – incipient wetness impregnation

LRS – laser Raman spectroscopy

MS – mass spectrometry

ODH – oxidative dehydrogenation

PEM – proton exchange membrane

PROX – preferential oxidation of carbon monoxide in the presence of hydrogen

PSD – pore size distribution

RF – response factor
SSITKA – steady state isotopic transient kinetic analysis

TCD – thermal conductivity detector

TEM – transmission electron microscopy

TPO – temperature-programmed oxidation

TPR – temperature-programmed reduction

TP-Rxn – temperature programmed reaction

UV-Vis – ultraviolet/visible

XPS – X-ray photoelectron microscopy

XRD – X-ray diffraction

WHSV – weight hourly space velocity
Steady-state reaction experiments utilized an Agilent 3000A microGC with a thermal conductivity detector (TCD) to determine gas stream compositions. The concentrations of O$_2$, N$_2$O, CO, CO$_2$, H$_2$, C$_2$H$_4$ and C$_2$H$_6$ were all determined by the integrated peak area of the TCD signal. For a TCD detector, all response factors are linear and linearity was confirmed for each species. Response factor (RF) is defined as:

$$RF_i = \frac{C_i}{A_i}$$

where $RF_i$ is the response factor for species $i$, $C_i$ is the concentration of component $i$ and $A_i$ is the integrated TCD area for the peak corresponding to component $i$. Once a response factor is known, the concentration of a component can be obtained by multiplying its the integrated TCD area obtained in the experiment by the component’s response factor. The numbers of moles of each species can then be determined using the total gas flow rate and concentrations of each species. Conversion and selectivity definitions are presented in Chapters 3 and 8 for ODH and PROX reactions, respectively.
LIST OF REFERENCES


